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Fishwick, A. H. (1967) *Alkoxyberyllium alkyls and related compounds*, Durham theses, Durham University. Available at Durham E-Theses Online: http://etheses.dur.ac.uk/8530/

ALKOXYBERYLLIUM ALKYLS AND RELATED COMPOUNDS.

- by -

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A thesis submitted for the degree of Doctor of Philosophy.

University of Durham.

July, 1967.

ACKNOWLEDGMENTS.

The author wishes to express his sincere gratitude to his supervisor, Professor G.E. Coates, for his constant help and encouragement throughout the time in which this work was carried out. Thanks are also due to Dr. N.A. Bell and Dr. K. Wade for many helpful discussions, and to Mr. P.D. Roberts for the loan of a typewriter. The author is also indebted to Ethyl Corporation for a Research Studentship.

MEMORANDUM.

The work described in this thesis was carried out in the Department of Chemistry of the University of Durham between October, 1964 and June, 1967. It is, except where acknowledged by reference, the original work of the author, and it has not been submitted for any other degree.

Part of this work is the subject of a paper submitted to the Journal of the Chemical Society, [J. Chem. Soc(A), 6/1473, in press].

SUMMARY.

Some reactions of dialkylberyllium compounds with 'weak acids', yielding 'internal' coordination complexes, have been examined.

With secondary amines, in equimolar amounts, a series of aminoberyllium alkyls, $(RBeNR'_2)_n$, is formed. Their degree of association, n, depends upon the size of the groups R and R'. When R' is methyl, trimers, exemplified by $(EtBeNMe_2)_3$, are formed, and $(MeBeNEt_2)_3$ is also trimeric, but for larger R and R', dimers, such as $(MeBeNPh_2)_2$ and $(EtBeNPh_2)_2$, occur. These compounds must all be formulated with three-coordinate metal, and some of their reactions with pyridine and 2,2'-bipyridyl were investigated. Crystalline complexes, $[R(NR'_2)Be.py]_2$, $R(NR'_2)Be.py_2$ and $R(NR'_2)Be.bipy$, can be formed, but the reactions are sometimes complicated by disproportionation processes. The adduct, $Bu^t_2Be.NHMe_2$, is described.

Alcohols, with dimethylberyllium, yield tetramers, $(MeBeOR)_4$, but lower degrees of association result from the use of bulkier organic groups, as illustrated by $(EtBeOCEt_3)_3$, $(MeBeOCPh_3)_2$ and $(Bu^tBeOBu^t)_2$. When prepared in diethyl ether, some of the products, e.g., $MeBeOPh.OEt_2$, retain ether as coordination complexes. The pyridine adducts, $Me(OMe)Be.py_2$, and $Me(OBu^t)Be.py$ are discussed. Reaction with two molar proportions of alcohol gives the alkoxides $[Be(OMe)_2]_x$, $[Be(OBu^t)_2]_3$ and $[Be(OCEt_3)_2]_2$. The proton magnetic resonance spectra of some of these compounds show some unexpected splittings of signals and, in the cases of $(MeBeOBu^t)_4$ and $[Be(OBu^t)_2]_3$, pronounced solvent effects.

Thiols yield tetramers, $(RBeSR')_4$, presumably

containing four-coordinate beryllium, but, in contrast to the alkoxy- derivatives, no compounds containing three-coordinate metal were isolated. Many of the reactions resulted in disproportionation to R_2Be and $(R'S)_2Be$, but a series of adducts of some of these products, $(RBeSR')_n$, which are unstable to disproportionation, and of the tetramer, $(EtBeSBu^t)_4$, with the bases ether, tetrahydrofuran, pyridine and 2,2'-bipyridyl, was obtained. The alkyl sulphides, $[Be(EtS)_2]_x$ and $[Be(Bu^tS)_2]_x$ are described.

Diethylberyllium and selenophenol give $(EtBeSePh.OEt_2)_2$ or $(PhSe)_2Be.0.65\ OEt_2$, depending on the reactant ratios.

Methylberyllium- 2-dimethylaminoethoxide oligomer, 2-dimethylaminoethylsulphide trimer, ethylberyllium 2-methoxyethoxide tetramer, and the pyridine adducts, $Pr^i_2Be.py_2$ and $Bu^t_2Be.py_2$ were prepared.

CONTENTS.

INTRODUCTION.

INTRODUCTION.

The work described in this thesis is concerned with the preparation of amino-, alkoxy-, and thio- derivatives of alkylberyllium, their coordination chemistry, and their molecular complexity in solution.

In this introduction, the following topics, each of which has a particular relevance to the work investigated, are discussed:

a) the electron donor-acceptor complexes of organoberyllium compounds.

b) the 'internal' coordination complexes of beryllium and other Group II elements,

and, more briefly,

c) the 'internal' coordination complexes of the elements of Group III.

Beryllium has the electronic configuration $1s^2 2s^2$ and due to the small size and consequent high polarising power of the dipositive cation, Be^{2+}, forms covalent compounds almost exclusively. Even beryllium fluoride, which might be expected to be the most ionic compound of beryllium, conducts electricity only poorly in the fused state. The fact that the ionisation potentials of beryllium are high, the first being 215 and the second 420 k.cal.mole^{-1}, is in keeping with these observations, and suggests that free, dipositive beryllium ions do not exist in its compounds.

Beryllium compounds have covalencies of two, three or four for the metal atom. Coordination numbers greater than four have not yet been observed, but may well be found in beryllium analogues of carboranes, should these be prepared. The coordination number of two arises from the use of sp hybrid orbitals by the beryllium atom, giving a linear molecule, as in the case of beryllium chloride at high, temperature, when it is a monomer.[1] Di-t-butylberyllium was also presumed to be monomeric on grounds of its vapour pressure at 25° (35 mm.) [2,22] and it has recently been shown to be a monomer in solution and as vapour.[3] The less common coordination number of three is found in dimethylberyllium -trimethylamine [4], in which the beryllium atom must make use of sp^2 hybrid orbitals, and further examples of this degree of coordination will be described in this thesis. Beryllium, however, has a strong tendency to form covalent compounds using sp^3 hybrid orbitals with a tetrahedral disposition about the metal atom and there are many examples of this type of compound, one of the most common being solid beryllium chloride, which is polymeric. In fact, the coordination of the beryllium atom here is only approximately tetrahedral, as the Cl-Be-Cl angle is only 98°.

The phthalocyanine complex of beryllium constitutes an example of a'forced configuration! It has a square-planar configuration due to the shape and steric requirements of the phthalocyanine molecule.[6]

Electron donor-acceptor complexes of organo-beryllium compounds.

The various methods of preparation, and the physical properties of dimethyl-, diethyl-, di-isopropyl-, di-t-butyl, and diphenylberyllium have been reviewed at some length on several occasions.[5,22,34,58]

Dialkylberyllium compounds react with phenyl isocyanate to give the corresponding anilide,[13] and certain alkylberyllium compounds react with olefins to produce polymerization catalysts,[23] e.g.,

$$Et_2Be + MePr^nC{=}CH_2 \longrightarrow Pr^nMeEtCCH_2BeEt$$

This reaction is carried out at 100° for 82 hours, and a review of similar reactions of aluminium and lithium alkyls has been published.[24]

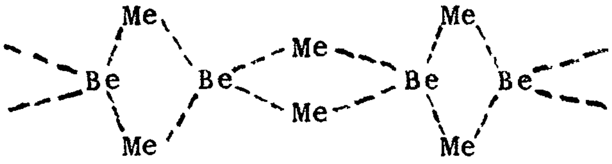
All organo-beryllium compounds react rapidly, and often violently, with water and oxygen, so they must be prepared and handled in atmospheres of nitrogen or other inert gases.

<u>Dimethylberyllium.</u>

An X-ray diffraction study on solid dimethylberyllium has shown that it has a polymeric structure, and is isomorphous with silicon disulphide. The methyl groups are distributed in an approximately tetrahedral fashion about the beryllium atoms (1), and the molecule has the following dimensions:

Bond lengths: Be-C, 1.92 Å: Be-Be, 2.09 Å.

Bond angles: Be-C-Be, 66°: C-Be-C, 114°.



(1)

Both beryllium and carbon use sp^3 hybrid orbitals and it is probable that three-centre molecular orbitals are formed from these.[28,29]

Dimethylberyllium, therefore, only dissolves in substances, e.g. diethyl ether, which coordinate strongly enough to break down its polymeric structure, although it must be remembered that the vapour of dimethylberyllium between 160 and 200° consists of monomers, dimers and trimers except at near-saturation conditions, when polymers are present.[30] Its highly associated nature accounts for the fact that it is only very slightly soluble in benzene, Very stable 1:1 chelate complexes are formed by the bidentate ligands N,N,N',N'-tetramethylethylenediamine, 1,2-dimethoxyethane [36] and N,N,N',N'-tetramethyl-o-phenylenediamine.[35] Cryoscopic molecular weight determinations in benzene, show that the first of these complexes is about ten per cent associated, whilst the other two are monomeric.

Beryllium-methyl symmetric deformation absorptions, in the range 1186-1206 cm.$^{-1}$, have been identified by comparison of the infrared spectra of trimethylamine and N,N,N',N'-tetramethylethylenediamine complexes of Me_2Be and $(CD_3)_2Be$.[53] This assignment is supported by reference to the trimethylaluminium dimer,[54] in which absorptions due to terminal Al-Me symmetric deformation, and bridging methyl, are identified at 1206 and 1255 cm.$^{-1}$ respectively. The symmetric methyl deformation in one of these complexes, which contain terminal methyl groups, would be expected to lie some 50 cm.$^{-1}$ below values obtained for bridging methyls. That this is so is illustrated by the fact that in the infrared spectrum of solid dimethylberyllium, there are two very intense absorptions, at 1243 and 1255 cm.$^{-1}$, due to deformation of the bridging methyl groups.[31] Beryllium-methyl stretching vibrations appeared to be in the range 700-900 cm.$^{-1}$ in the complexes.

The proton magnetic resonance spectra of the diethyl ether, and the above two, complexes of dimethylberyllium were examined. The chemical shifts of the methylberyllium protons were compared with similar values obtained for compounds with methyl groups bound to other electropositive elements.

Colourless, crystalline needles of dimethyldipyridineberyllium, m.p., 91-92°, were isolated from the reaction of pyridine with dimethylberyllium in ether.[36]

Diethylberyllium.

When prepared in ether solution,[13,18] diethylberyllium cannot be completely separated from the ether, but is obtained after prolonged pumping and vacuum distillation, as a colourless, liquid product, containing about two per cent ether, and boiling at 63°/ 0.3 mm. Hg (m.p., -12 to -13°).[18] A few years ago, however, a series of ether-free salts, of general formula $MX(BeEt_2)_n$ were reported.[46-48] M represents an alkali metal, X halide or cyanide, and n = 1,2 or 4. The salts prepared [48] are summarised in Table I, and the tendency for complex formation is CsF > RbF > KF > NaF.

Table I

MX	Product	Remarks
KF	$KF.BeEt_2$	See above
	$KF.(BeEt_2)_2$	See above
RbF	$RbF.(BeEt_2)_2$	Crystalline
CsF	$CsF.(BeEt_2)_2$	Crystalline
KCN	$KCN.(BeEt_2)_4$	Loses pure Et_2Be at 100-150° *in vacuo.*
Et_4NCl	$Et_4NCl.(BeEt_2)_2$	Viscous liquid
NaCN		
NaF		
LiF		No pure compound isolated
CsCl		
KCl		

The crystalline salt, $KF.(BeEt_2)_2$, decomposes at 70° in benzene, forming the insoluble material, $KF.BeEt_2$, and pure, ether-free diethylberyllium, which can be distilled out. Heating $KF.(BeEt_2)_2$ at 100-130° also yields the ether-free dialkyl.[46]

The molecular weight of this material varies with even when the latter is at its boiling point. Some of its coordination complexes have been investigated by Coates and Huck,[4] who found that it coordinates with trimethylamine, trimethylphosphine and dimethyl and diethyl ethers, but not with trimethylarsine or dimethylsulphide. The order of decreasing strength of coordination is $N > P > O > As, S$, which is the same as has been observed for trimethylaluminium [32] and trimethylgallium.[33]

Trimethylamine forms a 1:1 compound, ($Me_3N \rightarrow BeMe_2$), which melts at 36°, is stable thermally up to 180°, and is monomeric in the vapour phase, but slightly associated in benzene solution.[34] A compound $(Me_2Be)_2(NMe_3)_3$, which dissociates on warming, was observed below 9-10°, but this has since been shown, by a tensimetric method, to be incorrect. This method is entirely consistent with the formation of two solid complexes, $Me_3N \rightarrow BeMe_2$, as above, and $(Me_3N)_2.BeMe_2$, which melts at 20° under 1 atm. pressure of trimethylamine, and has dissociation pressures of 9.7 and 16.0 mm. at -9 and -4.5° respectively.[35]

Trimethylphosphine forms a range of compounds $(Me_3P)_x(Me_2Be)_y$; where x = 2,3,1,2,2,2 and y = 1,2,1,3,4,5 respectively. These are a consequence of the complex equilibria set up in the reaction, owing to the similar affinities of dimethylberyllium molecules for trimethylphosphine and for each other. Each compound is stable over a certain range of temperature and pressure of trimethylphosphine.

With dimethyl ether, the compounds $Me_2Be.OMe_2$, $(Me_2Be)_2(OMe_2)_3$, $(Me_2Be)_3(OMe_2)_2$ and $(Me_2Be)_2OMe_2$ were observed, but all are less stable than the phosphine complexes. With diethyl ether, no compound of definite composition was formed.[4]

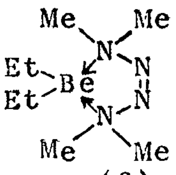
choice of solvent. It is monomeric in the coordinating solvent dioxan, but associated in cyclohexane and benzene, the degree of association apparently being time-dependent.[40]

Like its methyl analogue, diethylberyllium forms complexes with donor molecules. An orange, crystalline complex, $Et_2Be.py_2$, is isolated from the reaction with pyridine.[36]

With trimethylamine, 1:1 and 2:1 compounds, $Me_3N.BeEt_2$ and $(Me_3N)_2.BeEt_2$ are formed. The 2:1 complex exists as a solid below -15.5 to -14°, and the fact that it has a low vapour pressure of trimethylamine at -35°, suggests the existence of an equilibrium between it and the 1:1 adduct. The latter is somewhat associated in cyclohexane.[44]

The reactions of the methyl hydrazines with diethylberyllium and its trimethylamine complex have been investigated. In general, elimination of ethane was not quantitative, and polymeric products were formed, e.g., $(EtBe.MeNNMeH)_x$ from diethylberyllium and N,N'-dimethylhydrazine. However, the adducts $(Me_2NNMeH.BeEt_2)$ and and $Me_2NNMe_2(BeEt_2)_2$ were formed.[43]

Diethylberyllium reacts with tetramethyltetrazene (TMT) to give $Et_2Be.TMT$ at 25°, and $(Et_2Be)_2.TMT$ at 75° [(2) and (3) respectively]. On the basis of their proton magnetic resonance spectra, these complexes are assigned the structures shown.



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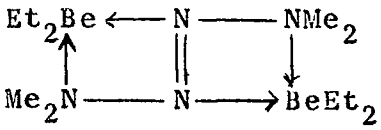
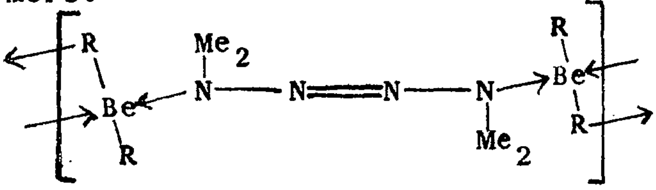


(3)

The pyrolysis of (3) in a sealed vessel was accompanied by evolution of ethane and ethylene, the former possibly by reduction of Et-Be groups, or the evolved ethylene, by Be-H groups. When the pyrolysis was carried out in a vacuum apparatus at low pressure, however, only ethylene was evolved. In both cases, polymeric products, containing ethyl groups in the first case, and ethyl and hydride groups in the second, were formed. From these results, the structure shown (4) is suggested for the polymers.[45]



(4) R = Et orH.

Di-*iso*propylberyllium.

The pure material, which can be obtained from ethereal solutions by refluxing, with continuous pumping, for 16 hours, is a colourless, slightly viscous liquid, freezing at -9.5°. It is dimeric in benzene.

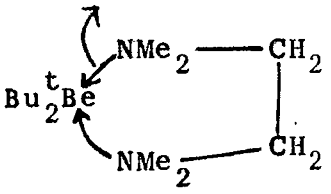
The liquid adduct, $(Pr^{i}_{2}Be\leftarrow NMe_{3})$, is formed with trimethylamine, and is monomeric in benzene. At 200°, it loses a mole of propene, forming feathery needles of $(Pr^{i}BeH.NMe_{3})_{n}$, which has not been further investigated.[52]

Tetramethyltetrazene complexes, $Pr^{i}_{2}Be.TMT$ and $(Pr^{i}_{2}Be)_{2}.TMT$, similar to their ethylberyllium analogues, can be formed, and the pyrolysis, under similar conditions, of the 2:1 adduct yields polymers of structure similar to those described above.[45]

Di-t-butylberyllium.

Di-t-butylberyllium, purified by removing the coordinated ether with beryllium chloride, which has a higher affinity for ether,[2] is monomeric in benzene solution and as vapour.[3] Infrared and Raman spectroscopic data on it, its completely deuterated analogue and di-t-butylzinc, are essentially consistent with a monomeric compound with a linear C-Be-C skeleton, containing 2-coordinate beryllium.[3]

It was shown to react with trimethylamine several years ago,[55] but the product was not well characterized. Recently, however, a stable 1:1 adduct, $Bu^t_2Be \leftarrow NMe_3$, has been prepared from the ether-free material and the amine. It melts reversibly at 45-46° and is monomeric in benzene. Similarly, trimethylphosphine forms $Bu^t_2Be \leftarrow PMe_3$, m.p., 44-46°, which is also a monomer. N,N,N',N'-tetramethylethylenediamine forms a crystalline, monomeric chelate complex, $Bu^t_2Be.TMED$. Its proton magnetic resonance spectrum, in d_8-toluene, has been examined at various temperatures, and shows splitting of the N-Me signal, which is a singlet at room temperature, into a doublet below -25°. This is believed to be due to the fact that one nitrogen atom is coordinated, whilst the other is not. (5) At room temperature, exchange between the two possible forms is so rapid, that the time-average position of all the methyl groups is the same, whereas at lower temperatures, this exchange is slowed to such an extent that the Me_2N groups are no longer equivalent, and, therefore, give rise to a doublet.[56]



(5)

With tetramethyltetrazene, the complexes $Bu^t_2Be.TMT$, at 25°, and $Bu^t_2Be.TMT.Bu^tBeH$, at 90°, are formed. No complex of composition $(Bu^t_2Be)_2$.TMT could be isolated. The pyrolysis of Bu^t_2Be.TMT.Bu^tBeH yields a polymer of structure similar to those described in the section concerning diethylberyllium.[45]

Diphenylberyllium.

Diphenylberyllium is a white, crystalline solid, melting with decomposition at 244-248°.[41,42] It does not dissolve appreciably in benzene at room temperature, but is readily soluble in donor solvents.

The complex salt, $Li(BePh_3)$, can be isolated from the reaction of phenyllithium and diphenylberyllium in ether at room temperature, followed by recrystallization from xylene. Crystallization from dioxan yields $LiBePh_3.(dioxan)_4$. Diphenylmagnesium, -cadmium, and -zinc yield similar compounds.[9]

Diphenylberyllium, with two electron-withdrawing phenyl groups attached to beryllium, may be expected to be more susceptible to the formation of coordination complexes than are dialkylberyllium compounds. Thus it is that coordination complexes with sulphur-containing ligands can be isolated in this case. In fact, the coordination chemistry of diphenylberyllium has been the subject of a recent study.[62] Tensimetric experiments with dimethyl and diethyl ethers, dimethyl and diethyl sulphides, trimethylamine and trimethylphosphine have been carried out, and the reaction products are summarised in Table II.

The heat of dissociation for the process

$$Ph_2Be.L_2 \longrightarrow Ph_2Be.L + L$$

has been measured, and is 17.9, 12.0, 16.7, and 8.68 $kcal.mole^{-1}$ for Me_2O, Me_2S, Me_3N and Me_3P respectively.[58] The order of heat of coordination is $O > N > S > P$, which is not what is normally observed for 'A' type acceptors. This order, however, is probably influenced greatly by steric considerations as well as donor strength.

Table II

Ligand	Compound stable at 0°	Dissociation pressure of 2:1 complex at 0°
Me_2O	$Ph_2Be.(Me_2O)_2$	-
Me_2S	$Ph_2Be.(Me_2S)_2$	-
Et_2O	$Ph_2Be.(Et_2O)$	17.0 mm.
Et_2S	$(Ph_2Be)_2.(Et_2S)_3$	-
Me_3N	$Ph_2Be.NMe_3$	0.8 mm.
Me_3P	$Ph_2Be.(PMe_3)_2$	-

The vapour pressure of $Ph_2Be.(OEt_2)_2$ at 0° indicates that the original claim, that this compound does not lose ether until heated *in vacuo* up to 130°,[59] is false.

The compound $(Ph_2Be)_2.(Et_2S)_3$ is very unusual, and it is suggested that this system may resemble the Me_2Be/Me_3P system,[4] in which several compounds are stable, each at a certain temperature and pressure of trimethylphosphine.

The 2:1 trimethylphosphine and dimethylsulphide complexes were prepared on a larger scale, and shown to be dissociated into the respective 1:1 complex, and free ligand, in benzene solution.

The bidentate ligands, N,N,N′,N′-tetramethylethylenediamine, N,N,N′,N′-tetramethyl-o-phenylenediamine, 1,2-dimethoxyethane and 2,5-dithiahexane all form crystalline, monomeric coordination complexes with diphenylberyllium.

Bipyridyl complexes.[36]

An interesting series of coloured 2,2′-bipyridyl complexes of the organo-, and halide compounds of beryllium has been prepared. Some spectroscopic properties of these are listed in Table III.

The bipyridyl complexes of di-*iso*propylberyllium *iso*propylberyllium hydride and di-n-butylberyllium decomposed to brown tars.

Table III

X in X_2bipyBe	Colour	λmax.(mμ)	Molar extinction coefficient x 10^{-3}
Cl	White	352 infl.	1.2
Br	Pale cream	364	2.4
I	Yellow	368	7.0
Ph	Yellow	353 infl.	0.5
Me	Yellow	395	2.7
Et	Red	461	3.7

The increase in molar extinction coefficient as the electronegativity of the group attached to beryllium decreases, is explained by electron-transfer, into the lowest unoccupied molecular orbital of the bipyridyl, from the Be-C bond in the case of the organo-, and the non-bonding orbital of the halogen in the case of the halide-, complexes.

A similar series of bipyridyl complexes of organozinc compounds is now known.[7]

Two black, crystalline complexes of beryllium have also been prepared, bisbipyridylberyllium, ($bipy_2Be$), from the dilithium adduct of bipyridyl and dichloro(bipyridyl)-beryllium, in 1,2-dimethoxyethane, and crystallized from benzene, and lithium bisbipyridylberyllate, from excess lithium and bisbipyridylberyllium, in ether. This latter product reacts with bromine to form dibromo(bipyridyl)-beryllium.

The magnetic properties of ($bipy_2Be$), and its deep colour, are consistent with its formulation as a coordination complex of the bipyridyl anion, $[(bipy^-)_2Be^{2+}]$.

'Internal' coordination complexes.

The term 'internal' coordination complex applies to the compound produced when the adduct between, usually, an organometallic compound and a ligand containing 'acidic hydrogen' undergoes irreversible decomposition with elimination of one or more moles of alkane, e.g.

$$Me_3Ga.NPh_2H \longrightarrow CH_4 + (Me_2Ga.NPh_2)_n$$

The product, if monomeric, would contain coordinatively unsaturated metal, whose acceptor character was enhanced, bonded to nitrogen with increased donor properties. Thus, in general, these compounds associate to form oligomers, where $n = 2,3$ or 4, or polymers, which are associated by relatively strong coordination. The hydrido-, and organo-, derivatives of the Group III elements have received most attention in this respect, but in recent years, their Group II analogues have been studied in greater detail. The most interesting feature of these compounds is the fact that even the associated products can contain coordinatively unsaturated metal, for example, in $(MeZnNPh_2)_2$. Tetramers, e.g. $(MeZnOMe)_4$, however, probably contain coordinatively saturated metal, as will be shown.

The most important aspect of this type of complex is its degree of association, which appears to be affected by four factors - steric interference, entropy, valency angle strain, and the nature of the intermediates involved in the formation of the complex.[94] The entropy effect will always favour dimers over trimers, as the number of molecules per unit mass will be greater, and steric interaction between large groups will favour dimers, and even monomers, over more associated species. In a dimer, however, there must be valency angle strain, which is more readily tolerated by heavier elements than those of the first period.[95] These three factors alone, however, cannot account for all the observed degrees of association; consider, in this connection, $(MeZnOBu^t)_4$ and $(MeCdOBu^t)_2$. On steric grounds, these degrees of association should be the other way round, as any interaction between methyl and t-butoxy groups would be expected to be greater around the smaller zinc atom. It may be, therefore, that the nature of the intermediate is the most important factor. For example, the bulky phenyl groups in $(Me_2Ga.PPh_2)_2$ may stabilize a monomeric intermediate, formed by intramolecular condensation, which would favour a dimeric product. On the other hand, a polymeric intermediate, formed by intermolecular condensation, would favour trimeric, tetrameric or polymeric products, such as $(Me_2Al.PMe_2)_3$.

Group II elements.

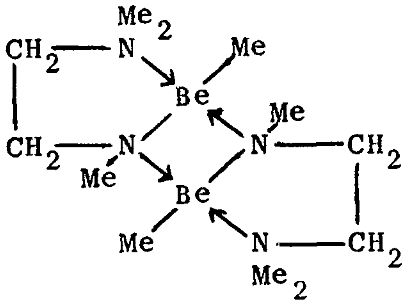
Beryllium.

Reference to the literature will show that the earliest examples of this type of compound, $EtBeNEt_2$,[18] presumed to have been formed from diethylberyllium and diethylamine, and $(Bu^nO)_2Be$,[15] from the reaction of di-n-butylberyllium with air, were not characterized completely. Similarly, Pr^iBeOMe and Pr^iBeNMe_2,[52] formed when di-*iso*propylberyllium reacted with methanol and dimethylamine respectively, although characterized, did not have their degrees of association measured.

Dimethylberyllium, however, was shown to react with dimethylamine to form, firstly, the adduct $Me_2Be\leftarrow NHMe_2$, which melts at 44°, with evolution of methane, leaving the trimeric compound $(MeBeNMe_2)_3$, m.p. 55-6°, to which a cyclic structure (6) is assigned.

be described in this thesis.

N,N,N′-trimethylethylenediamine reacts with dimethylberyllium at room temperature, forming the dimer (7), m.p., 116-118°. The reaction of dimethylberyllium with N,N′-dimethylethylenediamine proceeds, as soon as the mixture melts, to yield a mole of methane and, it is believed, the product (8). This sublimes slowly (in vacuum) at 90°, and at 145°, about 80 per cent of the remaining methyl bound to beryllium is evolved as methane. When it is heated in tetralin solution, methane is evolved quantitatively at 140-150°, and an insoluble polymer (9) is formed.



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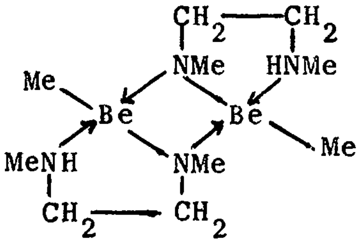

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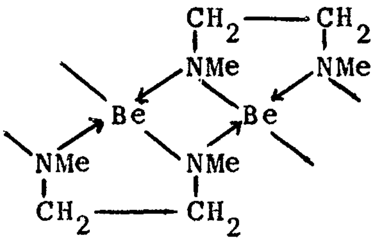


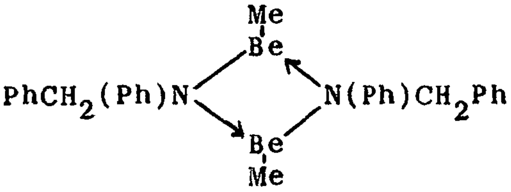
(9)

Unsymmetrical N,N-dimethylethylenediamine reacts just below room temperature to give a product analogous to (8), which sublimes at 115° and melts with evolution of methane at 170° to give, on cooling, a hard glass.

Ethylenediamine liberates about eighty per cent of the methyl from dimethylberyllium at room temperature, with the formation of a white, amorphous, evidently polymeric material. Even after heating to 45°, about six per cent of the methyl groups is retained.[36]

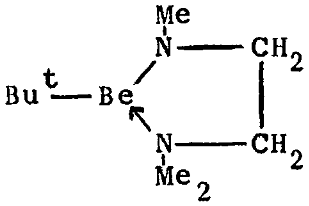
Diphenylberyllium and N,N,N′-trimethylethylenediamine form the product $(PhBeNMeCH_2CH_2NMe_2)_2$, which is dimeric in benzene, and, beyond reasonable doubt, has a structure analogous to (7). The compound melts with decomposition at 255-6°, and is decomposed only slowly by water.[62]

The exothermic reaction between methylberyllium hydride and benzylideneaniline produces the dimeric, liquid product (10), which forms an orange adduct with 2,2′ - bipyridyl.[70]



(10)

N,N,N′-trimethylethylenediamine reacts with di-t-butylberyllium (diethyl ether complex) eliminating isobutane slowly at room temperature to give (11), which is the only known instance of a monomeric (in benzene) aminoberyllium alkyl.



(11) b.p. 45°/1 mm.

Steric inhibition of dimerisation must occur here, and the possibility of beryllium-nitrogen $p_\pi - p_\pi$ bonding has to be considered,[71] although there are, at present, no known examples of this type of bonding in beryllium compounds. Using the Be-N force constant (2.96 m.dyn./Å) found for monomeric $Be[N(SiMe_3)_2]_2$, below,[69] Goubeau has calculated [148] that, even in this compound, the Be-N bond order is only 0.95.

Refluxing of beryllium chloride and sodium bis(trimethylsilyl)amide in ether results in the formation of monomeric beryllium tetrakis(trimethylsilyl)diamide, $Be[N(SiMe_3)_2]_2$, b.p., $110^\circ/0.3$ mm., containing two-coordinate beryllium. The vibrational (infrared and Raman) spectra support a N-Be-N angle of 180°.[69]

Methylberyllium benzyl oxide, $(MeBeOCH_2Ph)_4$, can be prepared either by the reaction of dimethylberyllium and benzyl alcohol, or by the addition of methylberyllium hydride across the carbonyl bond of benzaldehyde. The tetramer is likely to have a nearly cubic Be_4O_4 framework analogous to that found in the alkylzinc alkoxides which will be discussed below. It reacts with 2,2'-bipyridyl, forming a disproportionation product, $Me_2Be.bipy$.[70]

Phenylberyllium methoxide, formed by the exothermic reaction, at room temperature, of diphenylberyllium and methanol, melts at $177\text{-}8^\circ$ and, like methylberyllium benzyl oxide, is tetrameric in benzene. It forms an ether complex, $PhBeOMe.OEt_2$, which is monomeric in benzene.[62]

Dimethylberyllium and benzhydrol, or methylberyllium hydride and benzophenone, produce monomeric (in benzene) $Me(Et_2O)BeOCHPh_2$, which reacts with tetrahydrofuran forming $Me(THF)BeOCHPh_2$, also a monomer in benzene. These compounds, containing three-coordinate beryllium, are of particular interest since alkylzinc and alkylcadmium alkoxides interact only weakly with strong bases, and the formation of the three coordinate beryllium complexes is attributed to steric interference set up by the large diphenylmethoxy group.[70]

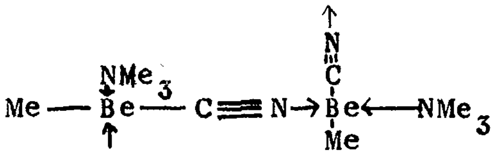
2-Methoxyethanol reacts with dimethylberyllium to give the tetrameric product, $(MeBe.O.CH_2.CH_2.OMe)_4$, in which the alkoxy-oxygen atoms are believed to be coordinated to beryllium in preference to the ether oxygens, by analogy with $(Et_2Al.O.CH_2.CH_2.OEt)_2$, discussed below. In either event, the metal would be four-coordinate in this and other tetrameric alkoxides, a suggestion which will be referred to at some length in connection with the analogous zinc compounds.[73]

Methanol and dimethylberyllium react immediately, below 0°, forming methylberyllium methoxide, which was reported to be dimeric in boiling benzene, though this result may not be correct in view of evidence obtained in the present work. It disproportionates to dimethylberyllium and beryllium methoxide, $Be(OMe)_2$, above 120°.[53]

The displacement of both alkyl groups of a dialkylberyllium compound often yields insoluble, presumably polymeric products. For example, diethylberyllium and diphenylamine give the insoluble, polymeric compound, $[Be(NPh_2)_2]_x$.[65]

A series of insoluble, presumably polymeric, compounds, $[(RO)_2Be]_x$, formed by reaction of phenol, and methoxy-, chloro-, and nitro-, substituted phenols, with dimethylberyllium, is known. Thiophenol reacts to form $[Be(SPh)_2]_x$. $[Be(OPh)_2]_x$ dissolves in boiling pyridine, and other related solvents, to give crystalline adducts, but these are not characterized.[78]

The reaction between hydrogen cyanide and dimethylberyllium also produces polymeric products.[76,77] Beryllium dicyanide is precipitated when ethereal dimethylberyllium is added slowly to excess hydrogen cyanide in benzene. This product does not react with trimethylamine, nor does it dissolve in solvents with which it does not react, since it no doubt has a cross-linked, polymeric structure. Equimolar amounts of the above reactants form soluble methylberyllium cyanide, from which the ether can be removed by pumping at 70°. The residue, however, does not redissolve, and is probably polymeric. This compound cannot be purified, but its coordination complex with trimethylamine was isolated as an involatile, amorphous product (12) from the reaction of dimethylberyllium-trimethylamine and hydrogen cyanide.

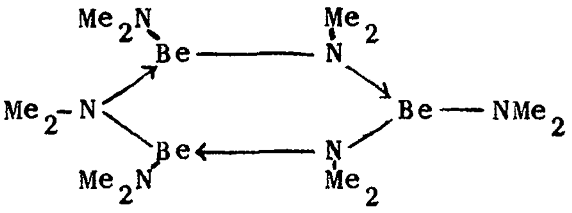


$$\mathrm{Me{-}\underset{\uparrow}{\overset{\overset{NMe_3}{\downarrow}}{Be}}{-}C{\equiv}N{\rightarrow}\underset{Me}{\overset{\overset{\overset{\uparrow}{N}}{\overset{|||}{C}}}{Be}}{\leftarrow}NMe_3}$$

(12)

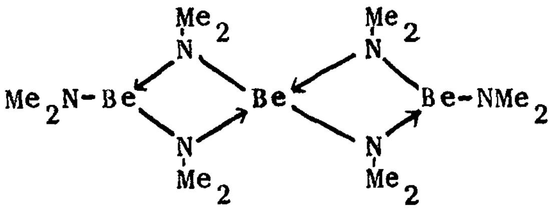
Compounds obtained by displacement of both alkyl groups from dimethylberyllium by piperidine and morpholine are known, but nothing was reported concerning their molecular complexity.[74]

In contrast to the above, the reactions of diethylberyllium and excess dimethylamine at 25°,[64] and di-*iso*propylberyllium and excess dimethylamine [52] at just above room temperature, give bis(dimethylamino)beryllium, $[Be(NMe_2)_2]$, which is trimeric in both benzene solution and the vapour phase, and was originally assigned the cyclic structure (13).



(13)

However, more recent investigations [64] do not agree with this. Differential thermal analysis indicates several different forms of the compound, and these observations, together with proton magnetic resonance spectral data, indicate a bridged, trimeric structure, (14)



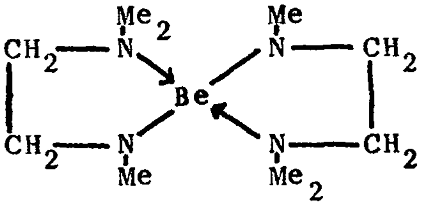
(14)

It is suggested that the other forms of $[Be(NMe_2)_2]_3$ may contain the terminal dimethylamino groups in <u>cis-trans</u> positions.

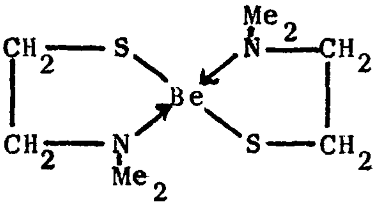
The reactions of N,N,N'-trimethylethylenediamine, 2-methoxyethanol, 2-dimethylaminoethanol and 2-dimethylaminoethanethiol with diethylberyllium, eliminating both alkyl groups, have been investigated.[72] N,N,N'-Trimethylethylenediamine reacts in refluxing benzene to give, after three days, the volatile compound, bis-[2-dimethylaminoethyl(methyl)amino]beryllium, $(Me_2N.CH_2.CH_2.NMe)_2Be$, (15), which is monomeric in benzene. On the basis of the fact that the infrared spectra of the compound in cyclohexane, and as a Nujol mull, are very different, it is suggested that, in solution, some of the dimethylamino becomes detached from beryllium, leaving the latter three-coordinate. With methyl iodide, a di-methiodide, $[Be(NMe.CH_2.CH_2.NMe_3I)_2]_x$, is formed at room temperature. This is formulated as a coordination polymer with bridging nitrogen atoms.

Bis-(2-dimethylaminoethylthio)beryllium, $(Me_2N.CH_2.CH_2.S)_2Be$, was formed by the reaction between excess 2-dimethylaminoethanethiol and diethylberyllium in boiling benzene. It is slightly associated ($n = 1.1$ to 1.3 in 0.09 to 0.2 wt.-% solutions) in benzene, but probably has the chelate structure, (16).

Since a sulphur atom occupies less space than a methylamino group, there would be less tendency, on steric grounds, for the dimethylamino groups to dissociate, as in the above case. Thus it is found that there is no difference between the infrared spectra of the compound as a Nujol mull or a cyclohexane solution.



(15)

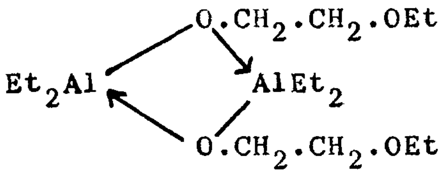


(16)

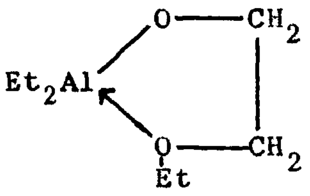
2-Dimethylaminoethanol reacts to form crystalline, bis-(2-dimethylaminoethoxy)beryllium, $(Me_2N.CH_2.CH_2.O)_2Be$, which is oligomeric ($n = 8$ to 11 in 1 to 2 wt.-% solutions) in benzene.

In contrast, diethylberyllium and 2-methoxyethanol react to form a polymeric product, bis-(2-methoxyethoxy)-beryllium, $[(MeO.CH_2.CH_2.O)_2Be]$. When formed in diethyl ether at -78°, this compound was relatively dense, but when the reaction was carried out in benzene at room temperature, it was isolated as a light, porous, rubbery mass. Both products were insoluble in all solvents with which they did not react, observations which suggest a polymeric structure.

The extensive association of the above alkoxy-derivatives may be contrasted with the monomeric amino- and thio- complexes. The donor strength of oxygen bound to an electropositive element is considerably greater than that of ether oxygen, as is shown by the fact that $(Et_2Al.O.CH_2CH_2OEt)_2$ is dimeric,[8] containing uncoordinated ether-oxygen atoms, (17a), whereas coordinated ether-oxygen would lead to a monomeric, chelate structure, (17b).



(17a)



(17b)

In alkoxyberyllium compounds, therefore, association is also likely to be propagated by means of the alkoxy-oxygen atoms, and the ether-oxygen is unlikely to compete successfully for coordination positions about the metal, though the more basic dimethylamino groups in $(Me_2N.CH_2.CH_2.O)_2Be$ may do so.

Methylamine and dimethylberyllium react with elimination of methane, but the other product has not been characterized.[63] Similarly, ammonia liberates methane and ethane from dimethyl-, and diethyl- beryllium respectively, at 0-20°. Even at 50°, however, elimination of alkane was not quantitative. The polymeric products, of type $R\text{-}(Be\text{-}NH\text{-}Be)_n\text{-}NH_2$, were not characterized further. At low temperature (-80°), 1:1 adducts, $R_2Be \leftarrow NH_3$ were observed, but not isolated.[67]

Di-isopropylamine and dimethylberyllium form a fairly stable, monomeric adduct, $Me_2Be \leftarrow NHPr^i_2$, which starts to lose methane slowly at about 100° in the presence of excess amine.[34] Loss of methane was not quantitative, even after refluxing for several days, and this is probably due to steric hindrance by the isopropyl groups.

Methanethiol liberates methane from dimethylberyllium but the other product was not characterized. However, dimethylberyllium, identified by the formation of its trimethylamine complex, could be sublimed from the reaction mixture.[63]

The reaction of dimethylberyllium with oxygen, in ether solution, has recently been studied.[10] The product is a white precipitate, consisting mainly of beryllium methoxide, $Be(OMe)_2$, but containing between 2.6 and 6.9 per cent of peroxidic oxygen.

Magnesium.

The 'internal' coordination complexes of magnesium have received only little attention until very recently, although alkylmagnesium alkoxides have been proposed as intermediates in the reactions of Grignard reagents with ketones,[38,39,49] partial alcoholysis of dialkylmagnesium compounds,[38,39] and the reaction of oxygen with organomagnesium compounds.[37] The earliest authenticated example of this type of compound was n-butylmagnesium isopropoxide, Bu^nMgOPr^i, formed by the reaction of n-butyl chloride, magnesium, and isopropanol in refluxing methylcyclohexane.[25] This compound can also be prepared from n-butylmagnesium chloride and isopropanol or n-butyl chloride, magnesium and sodium isopropoxide. It has recently been shown to be trimeric in benzene,[19] and its lack of acceptor properties have been attributed to Mg-O π bonding, which renders the magnesium four-coordinate. Its reaction with isopropanol, at room temperature, yields bis-(isopropoxy)magnesium, $Mg(OPr^i)_2$, a light, rubbery substance, which loses its rubbery character when stored under nitrogen.[21] Other alkoxy magnesium alkyls have been prepared by the method of mixing an alkyl chloride and an alcohol, in 2:1 molar proportions, with magnesium powder, in refluxing methylcyclohexane, but nothing is reported concerning their molecular complexity.[19]

Ethylmagnesium ethoxide, EtMgOEt, is formed when diethylmagnesium interacts with ether molecules during its pyrolysis at 200°.[26] This compound, produced when a deficiency of oxygen was introduced into an ethereal solution of diethylmagnesium, was found, by vapour pressure measurements on the solution, to be trimeric.[37] It is, however, too insoluble in benzene to permit measurement of its molecular-weight, and is suspected of being polymeric in the crystalline state.[17]

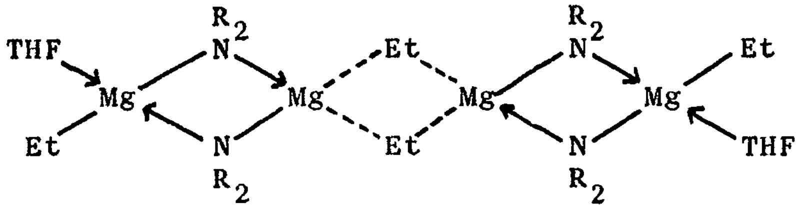
The reactions of diethylmagnesium with diphenylamine and some phosphines have been studied.[12] With diphenylamine, diphenylamino(ethyl)magnesium, $EtMgNPh_2$, is formed, and diphenylphosphine yields diphenylphosphino-(ethyl)magnesium, $EtMgPPh_2$, or bis-(diphenylphosphino)-magnesium, $(Ph_2P)_2Mg$, depending on the reactant ratios. The latter compound gives an adduct, $(Ph_2P)_2Mg.4THF$, with tetrahydrofuran. In similar fashion, phenylphosphine forms phenylphosphino(ethyl)magnesium, EtMgPHPh, or bis-(phenylphosphino)magnesium, $(PhHP)_2Mg$. No molecular-weights were reported for any of these compounds, but $[(Ph)P(CH_2)_3P(Ph)]Mg$, formed by the reaction of P,P$'$-diphenyl-1,3-phosphinopropane and diethylmagnesium, with elimination of two moles of ethane, is monomeric in tetrahydrofuran.

N,N,N$'$-Trimethylethylenediamine reacts with dimethylmagnesium below room temperature, to yield [2-dimethylaminoethyl(methyl)amino]methylmagnesium, m.p., 116-118°, which is dimeric in benzene and is therefore, believed to have a structure [14] analogous to that of the beryllium compound (7), discussed above. Di-isopropylmagnesium and di-t-butylberyllium give analogous products, with elimination of propane and isobutane respectively. The isopropyl derivative is dimeric, and the t-butyl derivative has a mean degree of association of 1.8 at ca. 1.0 wt.-% concentration, both in benzene.[16]

A series of alkylmagnesium alkoxides, prepared by the reaction of a dialkylmagnesium compound with an alcohol, in equimolar proportions, has been reported.[17] With alcohols in which there is chain-branching at the carbon α to oxygen, tetramers (cryoscopically in benzene) are formed, e.g. $(EtMgOPr^i)_4$, $(EtMgOBu^t)_4$ and $(Pr^iMgOPr^i)_4$ but with methanol, ethanol and n-propanol, oligomeric products, $EtMgOPr^n$, Pr^iMgOMe and Pr^iMgOEt, having degrees of association in the range 7-8.4, are formed. These last three alkoxides, like EtMgOEt,[26] could well be polymeric in the crystalline state.

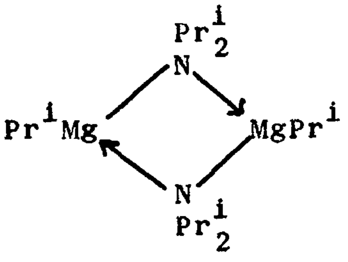
Addition of diethylmagnesium to diethyl ketone yields crystalline $Et(Et_2O)MgOCEt_3$, m.p., 63-64°, which is only slightly associated in benzene. Its formation is attributed to steric interference set up by the alkoxy group, as in the case of $Me(OEt_2)BeCHPh_2$.

The reactions of some secondary amines with magnesium dialkyls have recently been investigated.[11] Dimethylamine and diethylmagnesium, in 1:1 molar proportions, give insoluble, doubtless polymeric, bis(dimethylamino)magnesium, $[(Me_2N)_2Mg]_x$. This is probably formed by disproportionation of dimethylamino-(ethyl)magnesium, which might be expected to be formed initially. In contrast, both diethylamine and di-isopropylamine yield products with one metal-ethyl group per magnesium atom. Ether could not readily be separated from these products, but was displaced by tetrahydrofuran to give viscous liquids, $(EtMgNEt_2)_2 \cdot THF$ and $(EtMgNPr^i_2)_2 \cdot THF$. Their apparent molecular-weights (cryoscopically) indicated some association in benzene, and dimeric structures, (18), containing four-coordinate metal can be formulated.

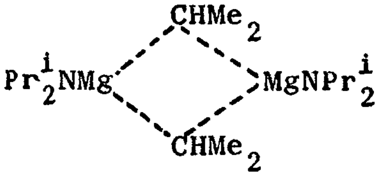


(18)

Diphenylamine forms diphenylamino(ethyl)magnesium, $(EtMgNPh_2)_x$, which is insoluble in hot toluene, and probably polymeric. A monomeric tetrahydrofuran complex, $EtMgNPh_2 \cdot (THF)_2$, can be prepared. With di-isopropylmagnesium, a bis-ether complex, $Pr^iMgNPh_2 \cdot (OEt_2)_2$, is formed at first, but loses ether on heating to about 50° in toluene, giving polymeric $(Pr^iMgNPh_2)_x$. In contrast, di-isopropylamine yields an ether-free product, $(Pr^iMgNPr^i_2)_2$ dimeric in benzene, and, therefore, formulated with three-coordinate magnesium. The displacement of one ethyl group from diethylmagnesium by 2,2,6,6-tetramethylpiperidine also yields a crystalline dimer, 2,2,6,6-tetramethylpiperidino(ethyl)magnesium, and, although in both these cases, it is likely that the structure involves nitrogen bridges, as in (19a), the possibility of carbon bridges, as in (19b), cannot be entirely eliminated.



(19a)

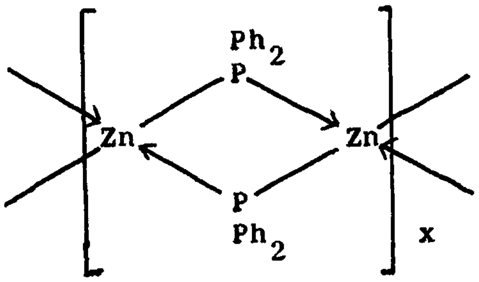


(19b)

Reaction of diethylmagnesium with phenyl cyanide gives a product $(EtMgN{:}CPhEt)_n$, which is extensively associated in benzene (n = 13 and 21 at 1.1 and 4.3 wt.-% concentration). With benzylideneaniline, a dimeric product $[EtMgN(Ph)CHEtPh]_2$, is formed.

Zinc.

Dimethylzinc reacts with a deficiency of oxygen to yield methylzinc methoxide, MeZnOMe,[84,88] which is said to be unchanged even in the presence of excess oxygen.[84] In contrast, diethylzinc gives zinc ethoxide, $Zn(OEt)_2$, Zinc methoxide, $Zn(OMe)_2$, can be prepared, however, from dimethylzinc and excess methanol.[89] Ethylzinc isopropoxide, $EtZnOPr^i$, has been described as a colourless solid, soluble in heptane.[81] The reactions of diethylzinc with acetoxime have been described.[60] In 1:1 molar ratios, ethylzinc acetoximate, $EtZnON{=}CMe_2$, can be crystallized from concentrated ether solutions, but with an excess of acetoxime, insoluble, presumably polymeric, zinc acetoximate, $Zn(ON{=}CMe_2)_2$, is formed. Diethylzinc reacts with an excess of diphenylphosphine at 110-120°, to give bis-(diphenylphosphino)zinc.[80] This compound is insoluble in ether, dioxan, tetrahydrofuran, and hydrocarbons, and is probably polymeric, with the structure shown in (20).



(20)

The zinc amides, $Zn(NH_2)_2$, $Zn(NEt_2)_2$,[90] and $Zn(NH.Et)_2$[91] obtained from diethylzinc and the corresponding amine, all probably have similar, polymeric structures.

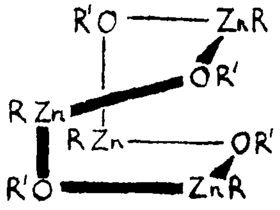
Some infrared studies on diethylzinc-alcohol systems have shown that reaction to give the alkylzinc alkoxide is rapid, but further alcoholysis, to form the zinc alkoxides, is slow, particularly in the case of alcohols in which there is chain-branching at the carbon atom α to the oxygen.[79] Thus, with methanol, zinc methoxide is formed at 30°, but with _iso_propanol, zinc _iso_propoxide is only formed at 80°. t-Butanol does not form zinc t-butoxide even at 80°, but this compound has now been prepared,[56] as an insoluble powder, by treating diethylzinc with t-butanol, in refluxing toluene, for 90 hours. It is probably polymeric. With oxygen, diethylzinc yields zinc ethylperoxide, $Zn(OOEt)_2$, if the oxidation is rapid, but mainly zinc ethoxide, with a little peroxide, and ethylzinc ethoxide, if it is slow. These zinc alkoxides, $Zn(OR)_2$, are useful polymerization catalysts for propylene oxide.[79]

Though the zinc dialkoxides can reasonably be assumed to have polymeric structures, there are no molecular-weight or structural data available for any of the above compounds.

The acidolysis of zinc alkyls by p-toluidine has been studied kinetically. It was found that the relative rates of reaction are $Et_2Zn > Pr^i_2Zn > Pr^n_2Zn > Me_2Zn$, but the intermediates, $RZn.NHC_6H_4.CH_3$, were not isolated.[87]

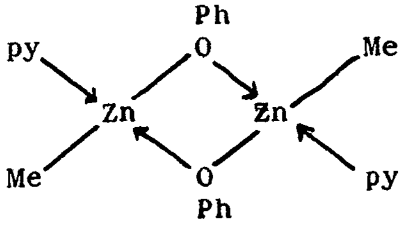
In recent years, some of the above, and many new, 'internal' coordination complexes of zinc have been described, and their preparation has been accompanied by molecular-weight determinations, usually by cryoscopic methods.

Alkylzinc alkoxides, RZnOR' (R = Me; R' = Me, Bu^t, Ph and R = Et; R' = Pr^i, Bu^t), all tetramers in benzene, have been prepared by reaction of the alkylzinc compound with the appropriate alcohol in equimolar proportions. These were presumed to have a nearly cubic structure, in which interaction between adjacent zinc and oxygen atoms, shown as non-bonded in (21), would have the effect of increasing the coordination number of both oxygen and zinc.



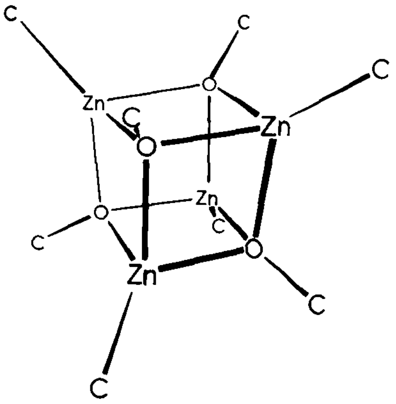
(21)

Thus, the alkoxides do not behave as though they were coordinatively unsaturated, as they can be recovered unchanged from solutions to which pyridine has been added except in the case of methylzinc phenoxide, which forms a dimeric pyridine adduct (22). The oxygen of the phenoxy-group would be expected to have a weaker donor character than that of an alkoxy-group.[83]



(22)

An X-ray crystallographic study of methylzinc methoxide has confirmed that this molecule has, in fact, got a distorted cubic structure, consisting of two interpenetrating tetrahedra, one of zinc, the other of oxygen, atoms, as shown below, (23).[50] By similar means, ethylzinc t-butoxide has also been shown to have a form resembling a cube.[61]



$(MeZnOMe)_4$

Zn-C, 1·94; O-C, 1·46; Zn-O, 2·07 Å
Average angles in 'cube': 96° at oxygen, 84° at zinc

(23)

Although unaffected by pyridine,[83] methylzinc methoxide does form a crystalline (1:1) adduct,

$Me_2N.C_5H_4N.Zn(Me)OMe$, with the more basic 4-dimethylaminopyridine. It is apparently monomeric in benzene. The infrared spectrum of methylzinc methoxide in cyclohexane is almost identical with that of the crystalline solid as a Nujol mull. It is concluded, therefore, that the nearly cubic structure persists in cyclohexane solution.[82]

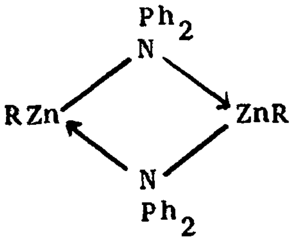
Subsequent to these studies, dimethylzinc has been shown to react with trimethylsilanol to yield a further tetrameric derivative, $(MeZnOSiMe_3)_4$.[145] Recently, however, a dimeric alkoxide, $(Bu^tZnOBu^t)_2$, has been prepared, showing that large groups can cause a reduction in molecular complexity due to steric interaction. A pyridine adduct, presumably analogous to (22), but dissociating into alkoxide and free base in benzene solution, was formed.[56]

The fact that methylzinc 2-methoxyethoxide, $MeZn.O.CH_2.CH_2.OMe$, is also a tetramer, provides further support for the suggestion that the zinc is already four-coordinate, as, presumably, the alkoxy-oxygens are coordinated to metal in preference to the ether oxygens,[83] as in $(Et_2Al.O.CH_2.CH_2.OEt)_2$,[8] discussed above.

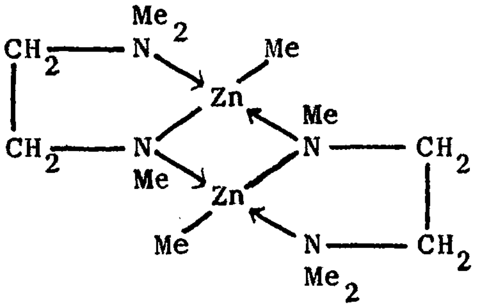
Dimethylamine reacts with dimethylzinc to give bis-(dimethylamino)zinc and unreacted dimethylzinc. The product, $[Zn(Me_2N)_2]_x$, is involatile and insoluble even in pyridine and solutions of 2,2′-bipyridyl. It is evidently polymeric.

Diphenylamine, in contrast, yields dimeric products $(RZnNPh_2)2$, (R = Me, Et), which are crystalline solids. As they are dimeric, they must be formulated with three-coordinate zinc, (24), and this explains the ease of formation of the yellow, crystalline complex, diphenylamino(methyl)bispyridinezinc, $Mepy_2ZnNPh_2$, which is a monomer. An equimolar amount of pyridine, however, does not yield an analogue of (22), but instead, dimethylzinc and bisdiphenylaminobispyridinezinc, $py_2Zn(NPh_2)_2$, by disproportionation.

N,N,N'-Trimethylethylenediamine reacts with dimethylzinc giving colourless crystals of the dimer, $(MeZn.NMe.CH_2.CH_2.NMe_2)_2$, (25).



(24)



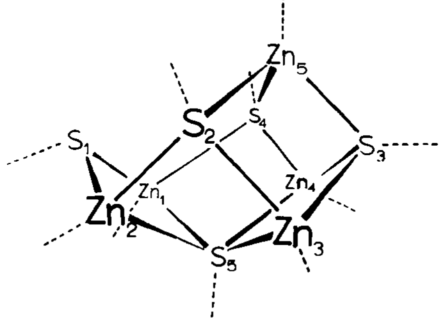
(25)

A further series of organozinc amides, analogous to those discussed above, are known.[57] Molecular-weight measurements in benzene have shown that $PhZnNPh_2$, $EtZnNPh_2$, Pr^iZnNPh_2, Bu^nZnNPh_2, all solids, and $EtZnNEt_2$, a liquid, are dimers.[51] Organozinc phosphides, on the other hand, are more associated, $EtZnPPh_2$ being insoluble in benzene, and probably polymeric, and $(PhZnPPh_2)_n$ having n = 7.2.

Dimethylphosphine and dimethylzinc, in equimolar proportions, react at 95° to form bis-(dimethylphosphino)-zinc, $[Zn(PMe_2)_2]_x$, and dimethylzinc.[93] This phosphide is involatile and insoluble even in pyridine; it probably has a polymeric structure analogous to (20).

Reactions of dialkylzinc with thiols, R'SH, result in an interesting sequence of compounds of general formula RZnSR', which differ markedly from their oxygen analogues in the matter of their degree of association. For R = Me, and R' = Me, Pr^n and Ph, RZnSR' is insoluble in hydrocarbons and, evidently, polymeric. For R = Me, and R' = Pr^i, however, RZnSR' is hexameric, and for R = Me or Et and R' = Bu^t, the products are pentamers, all cryoscopically in benzene. $(MeZnSBu^t)_5$ yields a crystalline pyridine complex, $(MepyZnSBu^t)_2$, analogous to (22). X-ray analysis of $(MeZnSBu^t)_5$ has shown that its structure consists of a square-base pyramid of zinc atoms with each zinc atom, and three sulphur atoms, four-coordinate. It can be seen from the figure (26) that the remaining two sulphur atoms are, respectively, three-, and five-coordinate, the latter being particularly unusual. The directions in which carbon atoms lie are indicated by the dotted lines.[92]

$(Me\,Zn\,SBu^t)_5$



Zn_1-S_1	2·28Å	Zn_2-S_1	2·32Å
Zn_1-S_5	2·98	Zn_2-S_5	2·71
Zn_3-S_5	2·51	Zn_4-S_5	2·51

All other Zn-S 2·41 - 2·47

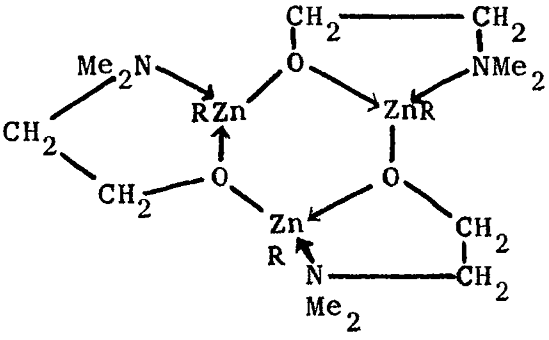
Mean values:

Zn-C 2·01, S-C 1·88, C-C 1·55

(26)

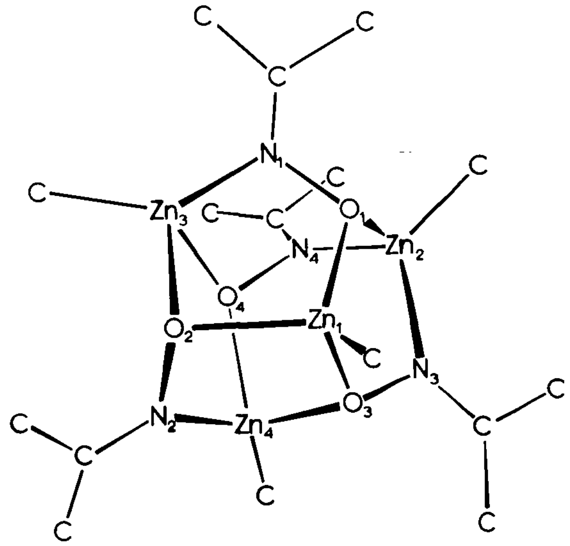
These compounds provide a further illustration of the way in which substitution of a bulky (t-butylsulphide) group for a smaller (methylsulphide) one, can bring about a considerable reduction in the degree of association.[83]

Several 'internal' coordination complexes, in which the donor atom is part of a chelate group, are now known. Dimethyl-, and diethyl- zinc form trimeric products, $(RZn.O.CH_2.CH_2.NMe_2)_3$, (R = Me, Et), with 2-dimethylaminoethanol. As they have relatively high melting points, and do not form methiodides, they are believed to have structures in which the nitrogen is coordinated to zinc, (27).



(27)

Acetoxime and dimethylzinc, in equal amounts, yield methylzinc dimethylketoximate, $(MeZnON{=}CMe_2)_4$, which is a tetramer in benzene solution.[82] It has a cage-like structure, [(28), below], consisting of fused five-, and six-membered zinc-oxygen-nitrogen rings, all zinc atoms being four-coordinate.[75]



$(MeZnON{:}CMe_2)_4$

(28)

Methylzinc acetate, $(MeZnOAc)_x$, and methylzinc dimethylphosphinate, $(MeZnO_2PMe_2)_x$, are polymeric,[83] and contain bridging acetate and phosphinate groups by comparison of their infrared spectra with that of, e.g., $(Me_2GaOAc)_2$, discussed below.

Organozinc compounds can sometimes undergo organometallation reactions with organic functional groups. Phenylisocyanate adds to diethyl-, or diphenylzinc, in boiling benzene, to yield tetramers, $[RZn(NPh)COR]_4$, (R = Et, Ph).

Dimethylzinc can be recovered quantitatively from its reaction with benzophenone, but diethylzinc loses a mole of ethylene to form trimeric $(EtZnOCHPh_2)_3$. Diphenylzinc adds across the C=O bond to give the dimer, $(PhZnOCPh_3)_2$, which, like t-butylzinc t-butoxide, must contain three-coordinate zinc.[82]

Some of the organozinc amides discussed above[51,57] have been shown to undergo aminozincation reactions with carbon dioxide and carbon disulphide, and also to add across the -N=C= bond of phenylisocyanate and phenylisothiocyanate.

Infrared and proton magnetic resonance spectra.

The infrared characteristics of the zinc-methyl group of some of these complexes have been discussed. Symmetric deformation frequencies, $\delta\,(\mathrm{Zn{-}Me})_{\mathrm{sym.}}$, in the range 1145-1178 $\mathrm{cm.}^{-1}$, have been identified, as well as zinc-methyl rocking and stretching vibrations.[83]

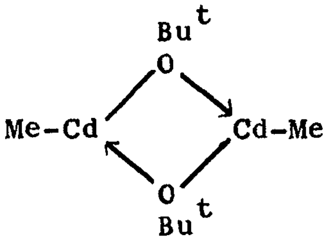
The proton magnetic resonance (p.m.r.) spectra of methylzinc methoxide were first commented upon by Coates and Ridley. The signals due to both the methoxy and methylzinc protons are split into doublets; the Zn-Me doublet collapses to a sharp singlet from 35-45°, but the methoxy doublet remains as such even up to 100°. The spectrum of methylzinc t-butoxide, however, consists, as expected, of two sharp peaks. This was explained in terms of the existence of isomeric forms of the methoxy-compound, denied to the t-butoxy derivative on steric grounds.[83]

Since then, however, a more comprehensive (p.m.r.) study on dimethylzinc/methanol systems in several proportions, and at various temperatures, has led to the conclusion that, in benzene, cyclohexane or ethylene oxide, the monomethanolysis product exists as an equilibrium mixture of dimethylzinc, an aggregate containing equal proportions of methoxy and zinc-methyl groups, and one containing these groups in the ratio 4:3. The latter is formulated empirically as $\mathrm{Me_6Zn_7(OMe)_8}$, but measurements of the vapour pressure of its solutions in benzene showed that its molecular-weight was about half the required value, suggesting that it is a mixture. The aggregates probably involve contributions from complexes of the form $[Me_2Zn]_n[Zn(OMe)_2]_m$, e.g., $[Me_2Zn.Zn(OMe)_2]_3.Zn(OMe)_2$, and, where n = m, units of (MeZnOMe). Analogous conclusions were drawn in respect of diphenylzinc/methanol, diphenylzinc/ethanol and dimethylzinc/ethanol systems, but monoalcoholysis with <u>iso</u>propanol or t-butanol gives products which are best formulated as genuine organozinc alkoxides, $(RZnOR')_n$. Treatment of the appropriate zinc alkoxide with dimethylzinc in benzene gave products identical with the monoalcoholysis product, except in the cases of the t-butoxide and the n-dodecoxide, in which the larger groups may partially prevent the rearrangement to the monoalcoholysis product. Vapour pressure measurements on benzene solutions of $MeZnOBu^t$ showed that its degree of association varied from four in concentrated, to 2.7 in dilute, solutions. Similarly,[85,86] $PhZnOBu^t$ and $PhZn.O.CH_2.CH_2.OMe$ were found to be tetrameric.

Cadmium.

As in the cases of zinc and magnesium, the reactions of organocadmium compounds with molecules containing acidic hydrogen had, until recently, received negligible attention. The products of some reactions with alcohols and thiols, however, have now been examined in some detail.[96]

Methylcadmium methoxide was too insoluble in benzene for molecular-weight measurements, but is said to have a cubic structure on the grounds that its X-ray powder pattern is similar to that of methylzinc methoxide. The cubic structure is also proposed for methylcadmium ethoxide, isopropoxide and phenoxide, all found to be tetramers in benzene. Methylcadmium t-butoxide, however, was anomalous in that it was dimeric. Steric interference, with consequent reduction in the degree of association, would be expected to have more influence around the smaller zinc atom than the larger cadmium atom, so this factor cannot explain the observed molecular-weight. It is also surprising that no pyridine derivative, analogous to (22) can be prepared, since the t-butoxide must be formulated with three-coordinate cadmium, (29).



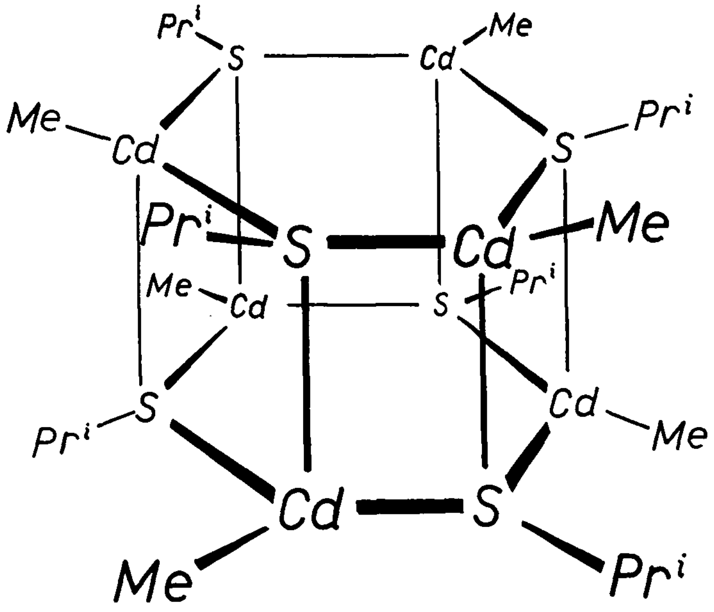
(29)

The phenoxide, however, did yield a pyridine complex similar to (22), above.

The reactions of dimethylcadmium with methane thiol or thiophenol gave insoluble products $(MeCdSMe)_x$ and $(MeCdSPh)_x$, which are presumed to be polymeric. They dissolve in pyridine, presumably as adducts, but pyridine is lost again at reduced pressure.

As in the zinc case, branched-chain thiols gave benzene-soluble derivatives, $(MeCdSPr^i)_6$, similar to the zinc compound, and $(MeCdSBu^t)_4$, which, like other tetramers is assumed to have a cubic structure. The zinc analogue, of course, is pentameric.[83]

A novel structure, involving two six-membered rings, (30), is postulated for methylcadmium isopropyl sulphide. This arrangement would, again, have the effect of increasing the coordination number of the cadmium and sulphur atoms, opposing the formation of pyridine adducts. No such adducts were isolated.



(30)

Methylcadmium trimethylsiloxide, $[MeCdOSiMe_3]_4$, is tetrameric in solvents which do not contain acidic protons, and is presumed to have a cubane structure.[145]

The reactions of diethylcadmium with diethyl ketone yield, on hydrolysis, triethylcarbinol, but no intermediate was isolated.[146]

Other Group II elements.

The organo-derivatives of calcium, strontium and barium are highly reactive, and no compounds analogous to those discussed above are known.

The dialkyls of mercury are not hydrolysed even by dilute acids, so the general reaction of a dialkyl derivative, R_2M, with a weak acid, to yield an 'internal' coordination complex, is of no use in this case. Analogues can be prepared, however, by other methods. For example, phenyl mercury chloride reacts with sodium methoxide to form trimeric phenylmercury methoxide,[68] and the reaction of sodium trimethylsiloxide with methylmercury chloride yields monomeric methylmercury trimethylsiloxide.[145]

Group III elements.

There are numerous examples of this type of compound in the chemistry of the Group III elements, particularly that of boron, so a few, representative, compounds will be mentioned.

Trimethylboron forms an adduct with ammonia, which can be thermally decomposed under pressure to yield aminodimethylborane, Me_2BNH_2, and methane.[97] Coordination saturation can be achieved by dimerization, to give a crystalline solid, with a planar $(B\text{-}N)_2$ ring structure,[101] or formation of a monomeric gas; there is a reversible monomer-dimer equilibrium in the gas phase at room temperature. Apart from the examples discussed above, boron is the only element with the ability to form authentic monomeric species. Several such compounds are known, e.g., $Me_2B.NMe_2$,[98-101] Me_2BNHMe,[101,102] Me_2BOMe,[98,103] Me_2BSMe,[104,105] Me_2BPH_2,[103] $MeB(SMe)_2$,[105] $Bu^nB(NEt_2)_2$ and Bu^tHBNEt_2.[106] Similarly, $(Me_2N)_3B$,[98] $(MeO)_3B$ and $(MeS)_3B$ [104] are all monomers. The existence of some of these compounds has been ascribed to $p_\pi\text{-}p_\pi$ bonding in the B-N or B-O bonds, and the B-N force constant in, for example, Me_2BNMe_2 indicates a double B=N bond.[101] When boron is attached to an element from the second, or later, rows of the periodic table, however, orbital overlap is not favoured, so oligomers or polymers result, e.g., $(Me_2BPMe_2)_3$, $(Me_2PBH_2)_{3,4\ \mathrm{or}\ x}$[103] and $(Me_2AsBH_2)_{3,4\ \mathrm{or}\ x}$[107]. Thus, the monomeric sulphur and phosphorus derivatives appear to be anomalous, but the lack of association in Me_2BSMe has been attributed to weak σ bonding of sulphur to boron being insufficient to hold a polymer together.[108] The tetrameric and polymeric forms of Me_2AsBH_2 and Me_2PBH_2 may arise from steric effects similar to those causing association of H_2BNHMe[109,110] and H_2BNH_2[111,112] to cyclic trimers, the latter also being known as a polymer.[113,114]

Aminodiarylboranes can be dimeric, e.g., $(Ph_2BNH_2)_2$, but tetra-substituted derivatives, exemplified by Ph_2BNMe_2 are monomeric except in very concentrated benzene solutions, when they are more associated. Phosphinodiarylboranes are all monomeric, and the B-P bond has pronounced double bond character, arising from electron flow from the aryl groups into the vacant boron 2p-orbital, making the phosphino-group the negative end of the dipole, (31). In their arsino- analogues, which are again monomers except in very concentrated solutions, the arsino-group is also the negative end of the dipole.[115]

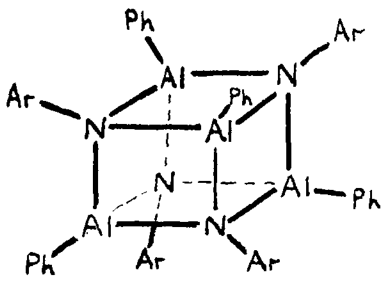
$$\overset{+\!\!\longrightarrow}{Ar_2B{=}PR_2}$$

(31)

The 'internal' coordination complexes of aluminium, gallium, indium and thallium are considered together, as, in many cases, the degrees of association of analogous compounds are the same.

The dimethylamino derivatives, Me_2MNMe_2, (M = Al [32], Ga [33], In [128], Tl [128]) are dimers both in the vapour phase and in benzene. The first three can exist in both crystalline and glassy forms, the latter being believed to consist of cyclic oligomers or polymers.[134] Diphenylamino(dimethyl)aluminium is a crystalline dimer.[130] The diphenylphosphino-, Me_2MPPh_2, (M = Al, Ga[130]), and diphenylarsino-, Me_2MAsPh_2, (M = Al, Ga, In[130]), compounds are all dimers. Trimethylamine is absorbed reversibly by $(Me_2AlPPh_2)_2$ and $(Me_2AlAsPh_2)_2$ but not by the cyclic trimer $(Me_2AlPMe_2)_3$.[32] This is because the donor strength of donor atoms is reduced when they are bound to phenyl groups. The compounds Me_2MPMe_2, (M = Al,[32] Ga, In[94]), Me_2MAsMe_2, (M = Al, Ga, In[94]) and Me_2MPEt_2, (M = Al, Ga, In[94]) are all trimers in benzene solution, and are believed to have cyclic structures, but then form polymeric glasses in the condensed state at room temperature. Amino(dimethyl)indium, $(Me_2InNH_2)_n$, is involatile at room temperature,[128] unlike its gallium analogue.[33]

Phenylphosphine, methylarsine and phenylarsine react to form compounds exemplified by $(MeAlAsMe)_x$ and $(MeGaPPh)_x$, which are non-volatile polymers.[94] The reactions of aniline, m-toluidine and p-toluidine with triphenylaluminium, however, yield crystalline tetramers, e.g., $(PhAlNPh)_4$, the X-ray analysis of which indicates a cubic structure, (32), and dimers, $(Ph_2AlNHAr)_2$, are obtained when ortho-substituents are present on the amine.[123,124]



(32)

The tris(dialkylamino)aluminium derivatives, $(R_2N)_3Al$, have been prepared and found to be dimeric (R = Me) or monomeric (R = Pr^i); bisdimethylaminoalane, $HAl(NMe_2)_2$, has a degree of association of about 2.5, all in benzene, cryoscopically.[117]

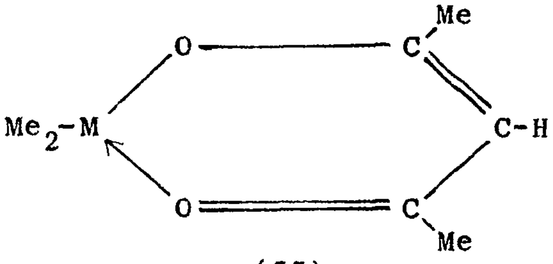
The methoxy- derivatives, Me_2MOMe, (M = Al [32, 118], In[128]), are trimeric, but their gallium [129] and thallium [121] analogues are dimers. Diethylaluminium-methoxide is also trimeric, but diethylaluminium ethoxide and t-butoxide,[8] dimethylaluminium, -gallium and indium t-butoxides,[147] $[Me_2AlOC(Me)Ph_2]_2$[119] and $(Ph_2AlOCPh_3)_2$[120,125] are all dimeric. The aluminium compounds illustrate the fact that there is less steric interaction between bulky groups in dimers than in the corresponding trimers. Dimethylthallium phenoxide has been prepared, but its degree of association was not reported.[116]

The dimeric methylsulphides, $(Me_2MSMe)_2$, (M = Al,[32] Ga [129], In [128], Tl [116,128]), are stable in the vapour phase, although the first two are depolymerised by trimethylamine. Similarly, $(Me_2TlSeMe)_2$[128] is unreactive towards trimethylamine, whereas $(Me_2GaSeMe)_2$[129] is depolymerised. It has been suggested that, in the thallium and indium derivatives, d_π-d_π interaction strengthens the internal coordination.[135] The reason that no higher polymers than dimers have been observed for these thio- and seleno- derivatives, is probably the fact that atoms of higher atomic number undergo valency angle strain more easily than lighter elements.[95] The glassy forms of $Me_2M^{III}NMe_2$, discussed above, can also be explained in terms of gradual relief of valence angle deformation as larger, cyclic, oligomers are formed. The tetrameric dimethylaluminium cyanide and its gallium and thallium analogues [76] also illustrate the influence of angular deformation on the extent of association, and, in fact, higher oligomers of dimethylaluminium cyanide (octamer) and diethylaluminium cyanide (heptamer) are now known.[126] These are believed to be linear polymers, like $(BH_2CN)_x$.[136]

Reactions of trimethylgallium with phenols lead to dimeric products, $(Me_2GaOC_6H_4R)_2$, R = H, CMe_3, similar to the dimeric alkoxides described above. These compounds are split by trimethylamine.[129]

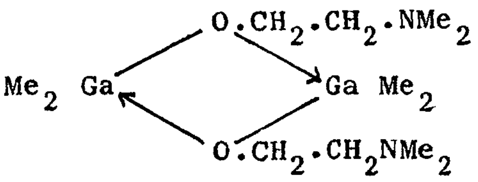
The siloxy-derivatives, $(Me_2MOSiMe_3)_2$, (M = Al [127], Ga [147], In [147], Tl [145]) and $(Me_2MOSiPh_3)_2$, (M = Al, Ga, In [27]), are all dimers in solution.

Several examples of 'internal' coordination complexes formed from molecules which contain a chelating group are known. Trimethylgallium,[129] -indium,[128] -thallium[122] and triethylthallium [122] all react with acetylacetone, forming chelate monomers, (33), and alkane. Trimethyl-, and triethylthallium, with benzoylacetone,[122] and trimethylgallium with salicylaldehyde,[129] also form products analogous to (33).



(33)

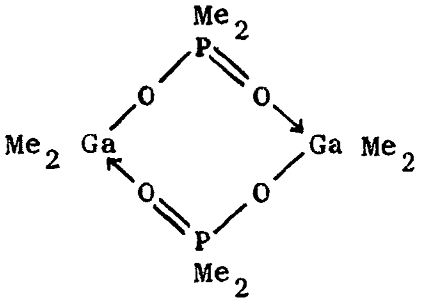
Dimethylethanolamine, on the other hand, yields the dimer (34) in which the amino- nitrogen atoms are not involved in coordination.[129] This is analogous to diethylaluminium 2-ethoxyethoxide, above.



(34)

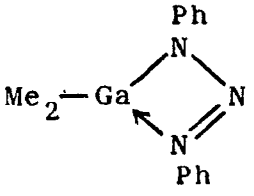
The lowered carbonyl stretching frequency in some acetoxyboranes, $R_2B.OAc$, indicating the presence of a chelating acetate group, has led to the assignment of monomeric structures for these compounds.[131]

By similar methods,[132] the dimeric acetates, dimethylphosphinates, diphenylphosphinates and benzenesulphinates of dimethylgallium and -aluminium have been formulated with cyclic, eight-membered rings, containing, respectively, bridging acetate, phosphinate and sulphinate groups. The cyclic structure of the phosphinate, $Me_2GaO_2PMe_2$, (35), has been confirmed by X-ray analysis.[137]



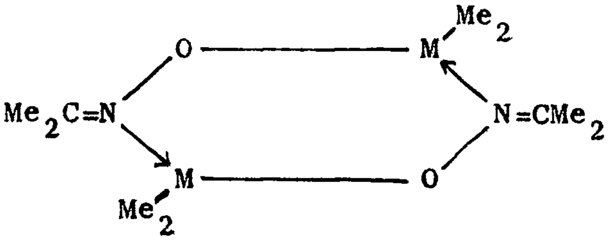
(35)

In contrast to the above, the dimethyldithiophosphinates are chelate monomers. The 1,3-diphenyltriazene derivative, (36), is also nearly monomeric (degree of association in benzene, 1.12).[132]



(36)

The acetoximates, $Me_2C{:}NOM.Me_2$, (M = Al, Ga, In, Tl) have been described.[133] Where M = Al, Ga, In, the compounds are dimeric in benzene solution, and mass spectroscopic studies for M = Al, Ga, Tl indicate a similar degree of association in the vapour phase. The compounds are formulated with six-membered rings (37) as these support the relatively easy loss of methyl groups, as opposed to $Me_2C{=}N$ groups, observed in the course of mass spectroscopy. The boron analogue, $Me_2C{:}NOBMe_2$, is monomeric in the vapour phase, but partially associated in benzene solution. It is probably a dimer in the crystal phase.



(37)

Organoaluminium compounds have been shown to undergo organometallation reactions with ketones,[120,125,138] isocyanates,[139] and cyanides,[140,141] but in the majority of cases, only hydrolysis products, and not intermediates, were isolated. However, benzophenone with triphenylaluminium,[120,125] and trimethylaluminium,[119] yields, respectively, the dimers $(Ph_2AlOCPh_3)_2$ and $[Me_2AlOC(Me)Ph_2]_2$. Adducts, $RCN.AlR'_3$, have now been prepared, and shown to rearrange on heating, with evolution of alkane, and formation of dimeric compounds exemplified by $(Bu^tCMe{:}NAlMe_2)_2$, $(PhMeC{:}NAlMe_2)_2$ and $(PhCH{:}NGaEt_2)_2$.

EXPERIMENTAL.

Apparatus and techniques.

Nitrogen supply.

Most of the compounds studied, as well as many of the starting materials, react rapidly with oxygen and moisture. Much of the work, therefore, was carried out in an inert atmosphere of dry, oxygen-free nitrogen. This was achieved by passing the nitrogen through a column containing 'BTS' catalyst [149] at ca. 120°, to remove oxygen, then through two traps, cooled by liquid nitrogen to -196°, to dry the gas. The 'oxygen-scrubber' was periodically regenerated with hydrogen.

Handling of beryllium compounds.

Beryllium oxide is very toxic, particularly when formed as fumes, on exposure to air, of oxygen-sensitive compounds. Volatile compounds, therefore, were handled in the vacuum system, and only transferred for analyses, molecular-weights etc., in the glove-box. Involatile solids were scraped from the double Schlenk tube [150] into a two-necked flask (fitted to the Schlenk) under an atmosphere of nitrogen, and involatile liquids were transferred from one vessel to another, without exposure to air, by means of a glass teat-pipette. In this way, samples for analysis were sometimes measured out and weighed without use of a glove-box.

Starting materials, such as dimethyl-, diethyl-, di-isopropyl-, and di-t-butyl- beryllium were stored as ether solutions in two-necked flasks fitted with a nitrogen lead and serum cap. These solutions could be transferred using a hypodermic syringe and needle. Taps and ground glass joints were lubricated with Apeizon M grease, as beryllium dialkyls are believed to react with Silicon greases. These greases are slowly dissolved by volatile solvents, so 'Teflon' sleeves, in conjunction with just a small amount of grease, were used at the joints. Solutions of diethylberyllium in hexane were stored in similar fashion.

Glove box.

The glove box was set up in such a way that, after purging the transfer tube with nitrogen and introducing the required materials into the box, the nitrogen could be recycled for up to several days through the nitrogen purification system. This involved the use of a small pump fitted inside the box. The purification system comprised two columns containing copper at 440°, prepared by reducing copper oxide with a stream of hydrogen gas, to remove traces of oxygen, and two traps, cooled to -196°, to freeze out moisture, which might have been desorbed from flasks introduced into the box. To minimise diffusion of oxygen, the box and the purification system were connected by lengths of copper tubing, joined where necessary, by short pieces of rubber pressure tubing, to allow some flexibility. An electrically-operated, single-pan balance was kept in the box, so that accurate weighings could be carried out.

The vacuum line.

A general purpose vacuum line, consisting of three main sections, was built by Mr. W. Tufnell of this department.

Storage section.

Volatile liquids were stored in small tubes, which could also be used for volatile solids, and gaseous reactants were stored in 3l. bulbs, each fitted with a cold-finger to enable condensation of the gases to be effected. Both tubes and bulbs were connected to the main manifold *via* mercury float-valves.

Gas analysis section.

A Töpler pump was used for the measurement of gases evolved from compounds during hydrolysis on the line. Prior to its being incorporated into the line, the pump was calibrated by filling it with mercury and weighing the mercury. The calibration marks corresponded to volumes of 11.52 c.c., and 148.4 c.c., respectively.

Gases which were completely condensable (all except hydrogen and methane) could, alternatively,be measured in calibrated bulbs connected to a manometer. The volume of each bulb was found by condensing known quantities of carbon dioxide into the apparatus.

Vol., small bulb, 489.0 c.c.

Vol., large bulb, 4452 c.c.

Internal radius of manometer tube, 0.45 cm.

Internal radius of mercury reservoir, 2.58 cm.

For a 1 cm., drop in the manometer level, the reservoir level increases by 0.0359 cm.

Fractionation section.

Three small U-traps were interconnected by mercury float-valves, and each trap was separated from the main manifold by another float-valve. By the use of suitable low-temperature baths, volatile gases could be fractionated, at low pressures, in this system.

Infrared spectroscopy.

Infrared (referred to as i.r.) spectra were recorded using Grubb-Parsons GS 2A or Spectromaster prism-grating spectrophotometers, samples having been prepared in the glove box, when the materials were air-sensitive. The range of the two instrumenta was 2-25μ (5000-400 cm.$^{-1}$).

Proton magnetic resonance spectra.

These (referred to as p.m.r. spectra) were recorded on either a Perkin Elmer R10, or an AEI RS2 spectrometer, both operating at 60 Mc./sec.

Samples were prepared in the glove box, and, after the sample tube had been loaded, it was fitted with a Teflon cap, removed from the box, and sealed at a point in the tube which had been constricted prior to taking it into the box.

Ultraviolet and visible spectroscopy.

This was carried out on a Unicam SP 800 visible/ ultraviolet spectrophotometer. Visible absorption spectra of 2,2′-bipyridyl complexes were recorded, over the range 315 to 700 mμ, on saturated solutions, in ether, prepared in the glove box. Ether was used as the reference. The concentration of the bipyridyl solution was then determined by taking a 15 cc., aliquot, evaporating to dryness, dissolving the bipyridyl in 10 cc., of dilute H_2SO_4, and determining the strength of this solution as described below.

Analyses.

Beryllium.

This was determined by titrating, with dilute (N/10) sulphuric acid, the alkaline solution formed on addition of excess potassium fluoride to beryllium hydroxide.

$$Be(OH)_2 + 4F^- \longrightarrow BeF_4^{2-} + 2OH^-$$

The calibration procedure is as follows, and should be strictly adhered to.

Aliquots of a standard beryllium sulphate solution (0.01 M) were taken to cover the range 0 to 6 mg., Be^{2+}, and to each was added 5 cc., of a 0.5 M potassium sodium tartrate solution and three drops of a 0.1% alcoholic

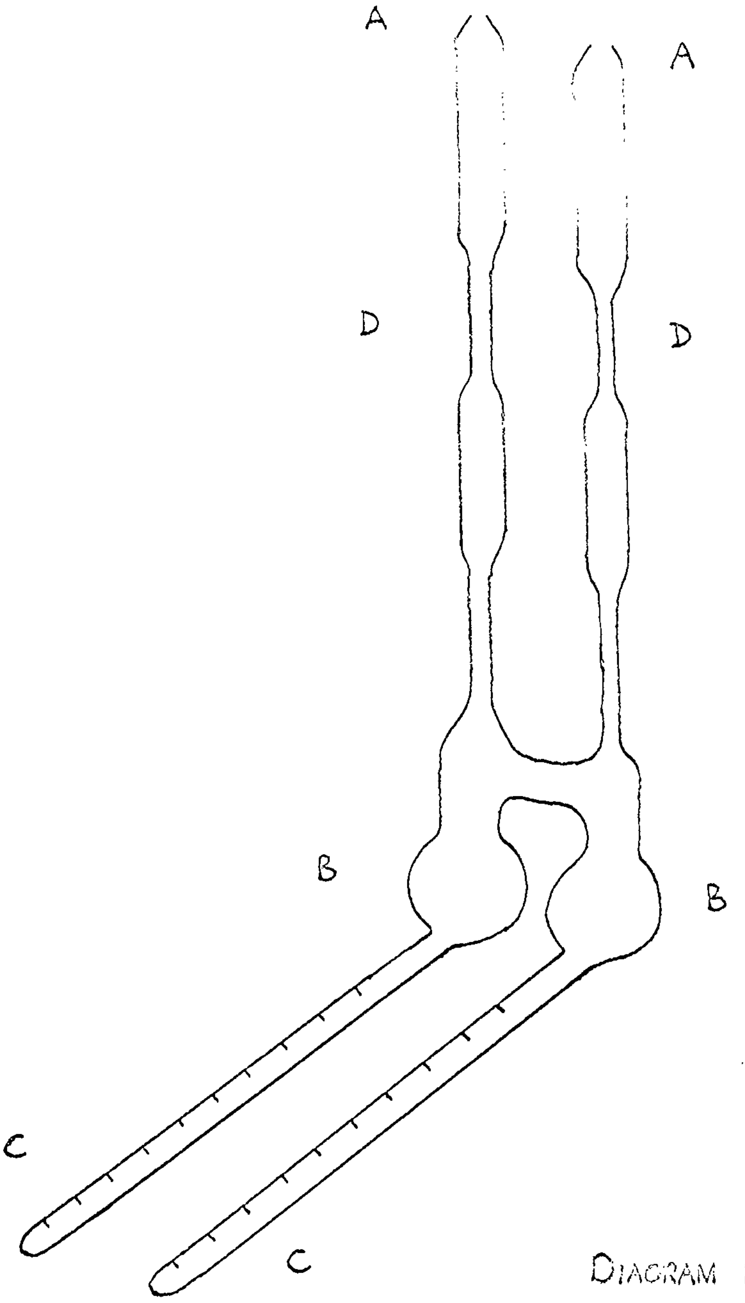


DIAGRAM 1.

solution of bromothymol blue. The solution was titrated, to a green end-point, with dilute sodium hydroxide. Potassium fluoride (5 c.c., of a 1M-solution) was then added, and the resulting blue solution set aside for two minutes, before titrating with 0.1N sulphuric acid to a green end-point. A linear calibration graph, of beryllium concentration against volume of acid, was obtained.

Sodium and lithium.

The strengths of solutions containing these two elements were determined using an 'EEL' flame photometer, calibrated with standard sodium sulphate solutions in the case of sodium, and lithium sulphate in the case of lithium. The unknown solutions were compared with standards of approximately equal strength.

Isothermal molecular-weight measurements.

These were carried out, by the Signer method,[151] in diethyl ether solution, in the apparatus shown in diagram 1. First, the apparatus was placed in a specially-designed oven, evacuated through a tap attached to one of the cones, A, and baked at 380° for twelve hours to remove traces of water. It was then filled with nitrogen via the other cone and allowed to cool to room temperature. A solution of the compound under investigation was syringed, against a counter-current of nitrogen, into one of the bulbs, B, and a solution of the standard, diphenyl, into the other. The apparatus was then inverted, and the volumes of the solutions measured by allowing them to run into the graduated pipettes, C. Thus, a known weight of both standard and unknown was introduced into the apparatus. The solutions were allowed to run back into the bulbs, which were then cooled to -196° to freeze the solutions. The apparatus was evacuated through the cones, sealed at the constrictions D, and allowed to warm to room temperature, after which it was kept in a draught-free cupboard. Solvent distilled from the solution of lower molarity to the more concentrated one, until the two were equimolar. The molecular-weight of the unknown was then calculated from the relationship:

$$M_1 = \frac{G_1MV}{GV_1}$$

where,

M = molecular-weight of standard.
M_1= molecular-weight of unknown.
G = weight of standard.
G_1= weight of unknown.
V = volume of solution of standard.
V_1= volume of solution of unknown.

Cryoscopic molecular-weight measurements.

'Analar' benzene, dried with sodium wire for several days, was used as solvent. Cryoscopic constants for the benzene were determined using biphenyl which had been freshly sublimed on the vacuum line.

Pyridine and 2,2′-bipyridyl.

2,2′-Bipyridyl was determined colorimetrically after addition of ferrous sulphate and ammonium tartrate, the the instrument response being compared to a calibration graph prepared from solutions of known strength.

Samples of compounds to be analysed were hydrolysed and the slightly acid solution made up to 100 c.c. Aliquots of 20 c.c., were then buffered to pH 5 with 20% ammonium tartrate, 1 c.c., of 7% ferrous sulphate added and the solution made up to 100 c.c., with water. The absorption of the red-coloured solution was measured at

522 mμ on an Eel-Spectra spectrophotometer, using a 1 cm. cell. Solutions for the calibration graph were prepared from a standard solution by taking suitable aliquots and treating them in the same fashion.

Where diphenylamine was present, the organic matter was extracted from strong caustic soda solution by diethyl ether, then the bipyridyl re-extracted with dilute H_2SO_4, in which diphenylamine is insoluble.

Pyridine was determined by an adaptation of a spectrophotometric method first employed by Lerosen and Wiley.[152] A standard solution of the base was made up (ca. 0.01M in ca. 0.02N H_2SO_4), suitable aliquots taken, and made up to 100 c.c., with distilled water. The molar absorbances, at 256 mμ, of these solutions were measured, using a Unicam SP800 visible/ultraviolet spectrophotometer and plotted against concentration in $g.l.^{-1}$, to give a straight-line graph. The path length was 1 cm., and the reference distilled water.

Hydrolysis solutions containing pyridine were diluted fifty-fold and their absorbances recorded. From the calibration graph, their concentration, and hence the pyridine content of the compound in question, could be determined.

Interference from other aromatic compounds, which absorb at, or about, the same wavelength (256 mμ) as pyridine, can sometimes be extensive. For example, phenol, unless removed as the tribromo derivative, can reduce the normal accuracy of the method from better than 1% to about 3-4%.

Hydrolysis.

Most of the compounds described are conveniently decomposed by low temperature hydrolysis with

2-methoxyethanol, water, and, finally, dilute sulphuric acid at room temperature, to yield, quantitatively, hydrocarbon gases such as methane, ethane etc.

Gases which are not completely condensable (methane and hydrogen) can be measured, without previous fractionation, by Töplering them from a trap, cooled to -196^{o}, at which temperature all other components are involatile.

Other gases (ethane, propane and butane) were fractionated, then measured in the calibrated bulbs by isolating them and recording the pressure exerted. An alternative procedure, however, was to Töpler them, without fractionation, from a trap cooled by a liquid nitrogen/hydrocarbon slush bath to such a temperature that the gas being measured had an appreciable vapour pressure, but other volatile components a negligible one. For example, ethane can be Töplered from a mixture of pentane and liquid nitrogen, carefully prepared so that the nitrogen is not brought into contact with the pentane until most of the latter is frozen.

Preparation and purification of starting materials and solvents.

Diethyl ether.

'Anhydrous Methylated Ether' was dried over sodium wire for several days, and distilled from lithium aluminium hydride just before use.

Tetrahydrofuran.

This was refluxed with potassium metal, distilled off and transferred, under nitrogen, to a still, where it was distilled from lithium aluminium hydride prior to use.

Benzene, toluene, pentane and hexane.

These solvents were available in a very dry state, and were further dried by standing for several days over sodium wire before use.

Starting materials-amines.

Hexahydro-1,3,5-trimethyl-s-triazine, $(MeNCH_2)_3$.[153]

Equivalent amounts of a 40% aqueous solution of formaldehyde, and a 33% aqueous solution of methylamine, were mixed at 0°. Upon addition of solid potassium hydroxide, the triazine separated from the water as an immiscible liquid. It was dried by standing over potassium hydroxide pellets, then distilled, b.p., 62°/ 17 mm.,Hg pressure. (Yield 95%)

4-Dimethylaminopyridine.

This was purified by vacuum sublimation of the crude material. (80°/10^{-3} mm.,Hg pressure, m.p., 114°).

Dimethylamine.

A solution of dimethylamine hydrochloride was prepared by refluxing N-dimethylnitrosamine, which was available in the laboratory, with 4N hydrochloric acid for 48 hours. By allowing this solution to run onto potassium hydroxide pellets, in a flask attached to the vacuum line, the amine could be freed from its hydrochloride, collected in a trap at -196°, and fractionated from water by trapping the latter out at -78°. The pure, dry amine was then stored in one of the three litre bulbs.

Trimethylamine.

This was available in the laboratory, and was dried by distillation from sodium hydroxide pellets then stored on the vacuum line.

Diethylamine and di-n-propylamine.

These were first fractionated from other volatile components then distilled from potassium hydroxide pellets prior to storage on the vacuum line.

Pyridine.

This was distilled from, and stored over, potassium hydroxide pellets. It was not placed on the line.

2,2'-Bipyridyl

The crude solid was available in the laboratory. Purification was effected by vacuum sublimation at 70-80°/0.001 mm.,Hg pressure, m.p.,72°.

Diphenylamine.

The crude material was purified by vacuum sublimation at 60-70°/0.001mm.,Hg pressure, m.p.,53°.

Alcohols and phenol.

Methanol.

This was dried by reaction with magnesium, then distilled before use, b.p.,65°.

Ethanol, n-propanol, iso-propanol and t-butanol.

All these reagents were dried by refluxing with aluminium turnings, then distilled and stored under nitrogen.

Phenol.

This was sublimed at 45°/0.001mm.,Hg pressure, m.p.,43°.

Diphenylmethanol (benzhydrol).

Crude benzhydrol was sublimed (70°/0.001mm.,Hg pressure, m.p.,69°).

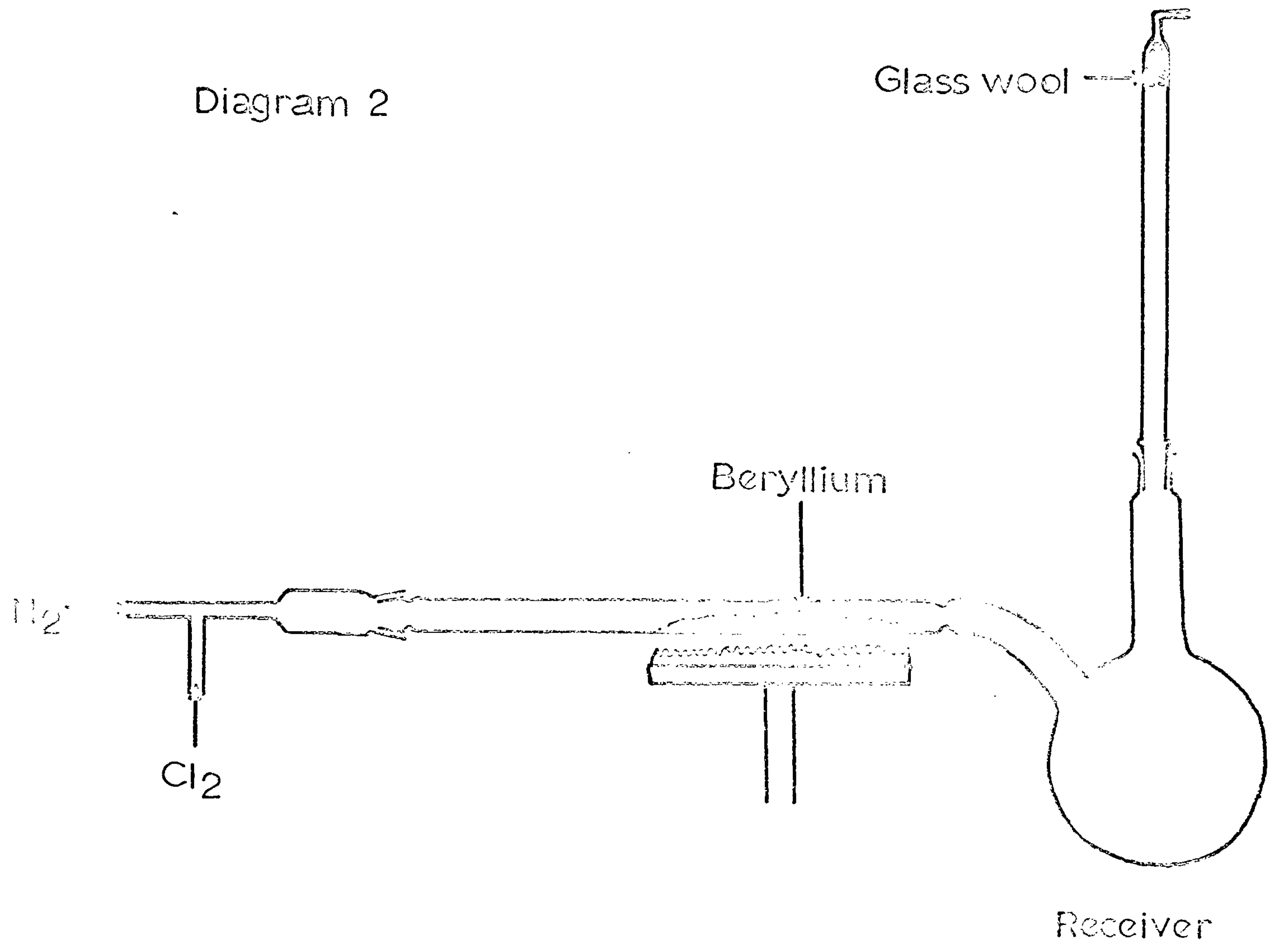
Triphenylmethanol and triethylmethanol.

These were available in a pure state in the laboratory.

2-Dimethylaminoethanol.

This was dried by refluxing with a small amount of magnesium hydride, then fractionally distilled, b.p.,135°.

Diagram 2



2-Methoxyethanol.

This was purified by distillation from magnesium, after first fractionating it, b.p.,125°.

Aldehydes and ketones.

Acetaldehyde and acetone.

These were available in quite a dry state, and were further dried by standing over molecular sieve (Type 5A) for several days.

Diethyl ketone.

This was dried by refluxing with a small amount of lithium aluminium hydride, after which it was distilled and stored under nitrogen, b.p.,103°.

Thiols.

Methanethiol, ethanethiol, iso-propylthiol, t-butylthiol, and thiophenol.

All of these were available in a very dry, pure form.

2-Dimethylaminoethanethiol.

This was bought in the form of the hydrochloride, which was reacted with an equivalent amount of sodium hydroxide solution to liberate the thiol. This was then extracted with ether, and fractionally distilled, b.p., 125°, after removal of ether on a water bath.

Methyl t-butyl ether.

This was prepared by heating methyl iodide and sodium t-butoxide, with sand to keep a clean surface on the butoxide, in a sealed tube, at 60°, for ten days. The ether was fractionated from traces of t-butanol and any methyl iodide was removed by treatment with quinoline. This gave pure methyl t-butyl ether, b.p.,55°.

Beryllium chloride.

This was prepared, in ca. 90% yield, by heating beryllium powder in a stream of chlorine, diluted with nitrogen, in the apparatus shown in diagram 2. The product was sublimed into the receiver and, at the end of the experiment, this was sealed off from thereaction tube. Any chlorine which might have been collected with the product was pumped off before use.

Beryllium bromide.

An ethereal solution of this compound was prepared by the dropwise addition of bromine to a stirred suspension of beryllium in ether. After the solution had become sufficiently concentrated, it was filtered from the excess beryllium, and stored under nitrogen.

Dimethylberyllium.

Ethereal solutions of dimethylberyllium were prepared in 70-80% yield by the addition of two mols., of methylmagnesium bromide to one mol., of beryllium chloride, in diethyl ether. The solution was decanted from precipitated salts, which were washed with diethyl ether, and most of the ether removed by distillation. The product was purified by continuous 'ether distillation' at 200° (24 hours for half a mol., of dimethylberyllium) to separate it from dissolved salts.[13,162] The solution was then analysed by hydrolysis for methane and beryllium.

Diethylberyllium.

This was prepared in 70-80% yield by the addition of two mol., of ethylmagnesium bromide to one of beryllium chloride, in diethyl ether. The solution was decanted from the precipitated salts, which were washed with ether, then distilled down to about 250 c.c., The remaining ether was removed under vacuum, followed by distillation of the diethylberyllium at 60-65°/0.3mm.,Hg. Finally, the strength of the solution was estimated by hydrolysis, for ethane and beryllium.

Di-isopropylberyllium.

This was prepared, in *ca.* 70% yield, from isopropylmagnesium bromide (2 mole) and beryllium chloride (1 mole), in diethyl ether. The solution, after concentration to *ca.* 200 c.c., was distilled at 60°/0.3mm Hg and estimated for propane and beryllium.

Di-t-butylberyllium.

Di-t-butylberyllium (diethyl ether complex), containing approximately one mole of coordinated ether per gram-atom of beryllium, and prepared by the addition of t-butylmagnesium chloride (2 mole) to beryllium chloride (1 mole), in ether, was kindly provided by Mr. P. D. Roberts, of this department.

Ether-free diethylberyllium.

The ether was removed by pumping from a solution of diethylberyllium in diethyl ether. The involatile liquid which remained was exposed to a vacuum at *ca.* 60° for two hours then analysed.

Found: Be, 13.38; hydrolysable ethyl, 84.63%.

$C_4H_{10}Be$ requires Be, 13.45; hydrolysable ethyl, 86.56%

This diethylberyllium was re-dissolved in hexane, and the solution estimated for beryllium and ethane.

Grignard reagents.

These were obtained, in about 90% yield, by the reaction of alkyl bromides with magnesium, in diethyl ether.

n-Butyllithium.

This was purchased as a solution in heptane, analysed for lithium, and found to be 2.45M.

Dimethylaminolithium.

Dimethylamine was passed onto the surface of a well-stirred solution of n-butyllithium in heptane (230 c.c., of a 2.45M-solution, 0.56 mole). Being more dense than nitrogen, it sank into the solution, and a white precipitate of dimethylaminolithium was formed at once. This was filtered and dried *in vacuo*.

Found: Li, 13.65%.

C_2H_6LiN requires Li, 13.72%.

EXPERIMENTAL RESULTS.

Experimental results.

Memmoranda.

1. Where infrared (i.r.) spectra are reported, only absorptions below 2000 cm.$^{-1}$ are noted, except where specified. The absorptions due to Nujol, however, are omitted. The following abbreviations are used: s-strong m-medium, w-weak, br-broad, sh-shoulder.

2. The temperature at which proton magnetic resonance (p.m.r.) spectra were recorded was +33.5°, except where stated. Where shifts are quoted in parts per million (p.p.m.), positive values denote shifts to higher applied field. The concentrations of solutions were of the order 1-2M (see below, 5).

3. All reactions, except where stated, were carried out in a nitrogen-filled double Schlenk tube.[150]

4. Gases were measured as N-c.c.,(1 N-c.c., is one c.c., at s.t.p.) and identified by i.r. spectrum.

5. Where strengths of solutions are quoted in terms of molarity, this is always calculated on the basis of a monomer.

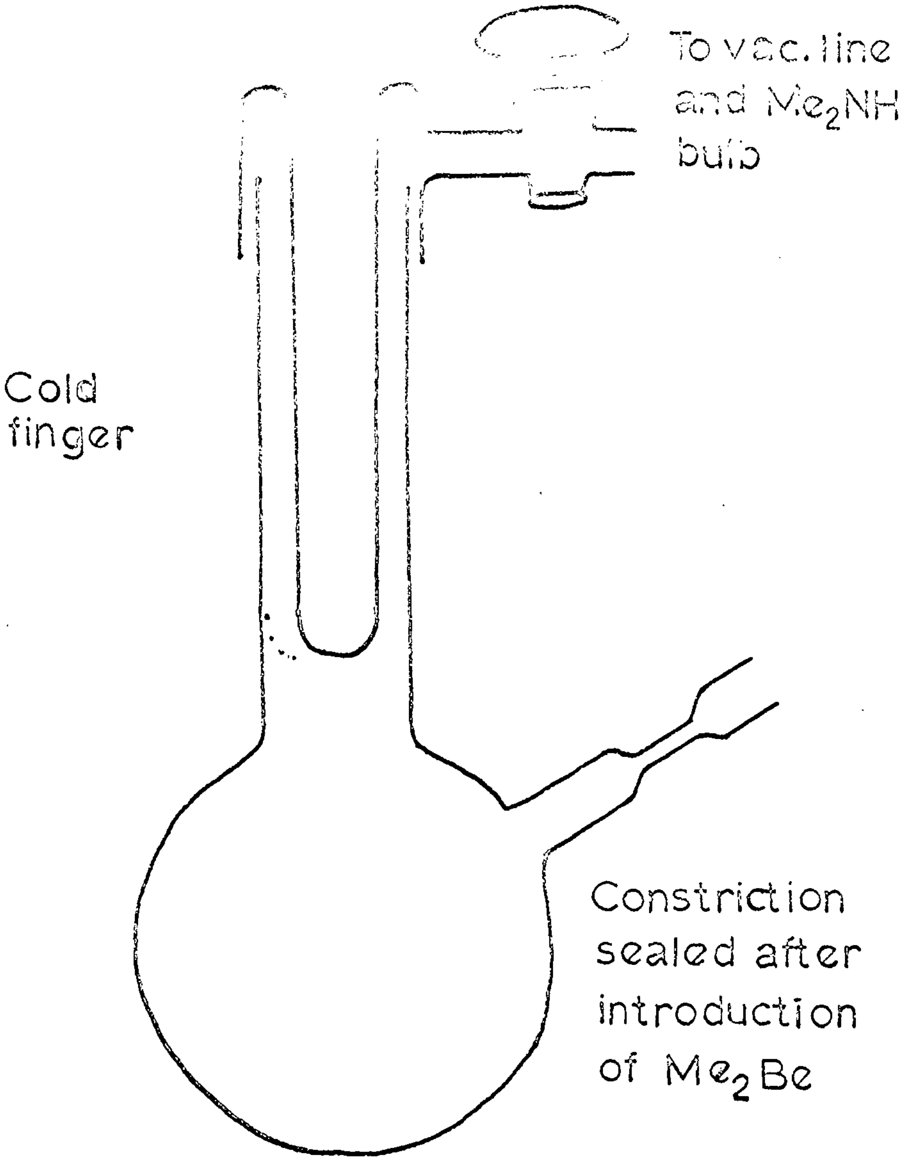

To vac. line and Me_2NH bulb
Cold finger
Constriction sealed after introduction of Me_2Be

Diagram 3

Reactions with amines.

Reaction of dimethylberyllium with dimethylamine - formation of dimethylamino(methyl)beryllium trimer, $(MeBeNMe_2)_3$

The preparation of this compound from ether-free dimethylberyllium is described elsewhere.[63] Here it was made by the reaction of stoichiometric amounts of dimethylberyllium, in diethyl ether, and dimethylamine. In one such experiment, dimethylberyllium (6.61 c.c. of a 1.96M-solution, 0.013 mole), in ether, was cooled to -196^o, and dimethylamine (285 N-c.c., 0.013 mole) condensed on. On warming to room temperature, gas was evolved, and a clear, colourless solution obtained. After removal of ether under reduced pressure, the product was sublimed at $60^o/10^{-3}$mm., m.p., 55^o (lit. value,[63] $55-56^o$). The entire experiment was carried out in the apparatus shown in diagram 3.

Reaction of dimethylberyllium with diethylamine-formation of diethylamino(methyl)beryllium trimer, $(MeBeNEt_2)_3$.

Diethylamine (0.71 g., 0.0097 mole) was added to a slight excess of dimethylberyllium (0.39g., 0.01 mole), in diethyl ether (5c.c.), at -196^o. Gas was evolved vigorously on warming to room temperature. Removal of ether at low pressure left a pale yellow liquid of viscosity about that of conc., H_2SO_4. This was dissolved in hexane, filtered from the excess dimethylberyllium, and dried by exposure to a vacuum.

Found: Be, 9.38; hydrolysable methyl, 15.40%; M, cryoscopically, 0.51, 1.02 wt.-% in benzene, 274, 297. $C_{15}H_{39}Be_3N_3$ requires Be, 9.37; hydrolysable methyl, 15.60%; M, 288.

The i.r. spectrum (contact film) contained absorptions at 525w; 611w,sh; 639m,sh; 676s,br; 797s,br; 896s,br;

1014s,br; 1036s,sh; 1051s,sh; 1077s; 1099s; 1126s; 1142s; 1168s; 1196s; 1252m; 1284w; 1304m; 1337w; 1374s; 1454s; 2809s,sh; 2916s,br cm.$^{-1}$

The p.m.r. spectrum (benzene solvent and reference) consisted of a multiplet (+3.81→4.84 p.p.m.) due to $CH_3\text{-}\underline{CH}_2\text{-}N$, a quintet (+5.88, 5.99, 6.10, 6.19, 6.31) due $\underline{CH}_3\text{-}CH_2\text{-}N$, and a doublet due to $\underline{CH}_3\text{-}Be$ (+7.77, 7.83). In cyclohexane, however, the signal due to the $\underline{CH}_3\text{-}Be$ protons was a singlet (+2.44 p.p.m. with respect to cyclohexane, τ 8.56), and the rest of the spectrum was obscured by the cyclohexane signal. The τ value of benzene is 2.73.

Reaction of dimethylberyllium with di-n-propylamine-formation of di-n-propylamino(methyl)beryllium dimer, $(MeBeNPr^{n}_{2})_{2}$.

Di-n-propylamine (1.01g., 0.01 mole) and dimethylberyllium (0.46g., 0.012 mole), in diethyl ether (6c.c.), gave, after removal of solvent at low pressure, a colourless liquid. This was filtered from the excess dimethylberyllium in hexane (10c.c.) and dried *in vacuo*. Found: Be, 7.39; hydrolysable methyl, 12.05%; M, cryoscopically, 0.97, 1.08 wt.-% in benzene, 258, 251. $C_{14}H_{34}Be_2N_2$ requires Be, 7.26; hydrolysable methyl, 12.09% M, 248.

The i.r. spectrum (contact film) contained absorptions at 680m,br; 726w; 749m; 797s,br; 863m; 881m,sh; 920m; 959m; 1015s; 1082s,br; 1166w; 1202m; 1259s; 1298w; 1324w; 1379m; 1468m; 2874s; 2937s; 2958s cm.$^{-1}$

Proton magnetic resonance spectra were recorded in benzene and cyclohexane. In benzene (benzene reference) there were two multiplets (+4.11→4.80 p.p.m.) and (+5.27 →5.98) due, respectively, to $CH_3\text{-}CH_2\text{-}\underline{CH}_2\text{-}N$ and $CH_3\text{-}\underline{CH}_2\text{-}CH_2\text{-}N$, a triplet (+6.25, 6.40, 6.50) due to

$\underline{CH_3}$-CH_2-CH_2-N, and a singlet due to $\underline{CH_3}$-Be (+7.79). In cyclohexane, there was a multiplet (-1.44→ -0.94 p.p.m.) due to CH_3-$\underline{CH_2}$-CH_2-N, a triplet (+0.50, 0.57, 0.68) due to $\underline{CH_3}$-CH_2-CH_2-N, and a singlet (+2.47) due to $\underline{CH_3}$-Be, all relative to cyclohexane.

This compound becomes glassy at ca. -25°, and, like $(MeBeNEt_2)_3$, fumes in air and is rapidly hydrolysed by water and alcohols.

Reaction of dimethylberyllium with diphenylamine-formation of diphenylamino(methyl)beryllium dimer, $(MeBeNPh_2)_2$.

Dimethylberyllium (6.95c.c. of a 1.96M-solution, 0.014 mole), in diethyl ether, was cooled to -78°, and diphenylamine,(2.31g., 0.014 mole), in diethyl ether (14c.c.), added dropwise. Gas was evolved on warming to room temperature, and when the evolution had ceased, ether was removed at low pressure to leave a white solid which was recrystallized from hexane (5c.c.) as small plates, m.p., 141°, to a yellow liquid, after turning yellow at 115°.

Found: Be, 4.66; hydrolysable methyl, 7.79%; M, cryoscopically, 1.37, 2.06, 4.12 wt.-% in benzene, 372, 374, 370.

$C_{26}H_{26}Be_2N_2$ requires Be, 4.69; hydrolysable methyl, 7.81%; M, 384.

The i.r. spectrum (Nujol mull) contained absorptions at 481m,br; 500m,br; 523m,br; 575m; 599m; 649m,sh; 668s; 686s; 741s; 797s; 867s,br; 922s,br; 952s,sh; 1019s; 1074s; 1096m,sh; 1152s; 1170s; 1195m; 1217m; 1239m,sh; 1258w; 1289s; 1585s cm.$^{-1}$

The p.m.r. spectrum (benzene solvent, TMS reference) contained a singlet (τ 10.43) due to $\underline{CH_3}$-Be, but the $(\underline{C_6H_5})_2N$ sgnal was obscured by that of benzene. This complex turns yellow, and finally green, on exposure to air, and was found to be crystalline by X-ray powder photograph.

Reaction of diethylberyllium with dimethylamine-

a) in equimolar amounts-formation of dimethylamino(ethyl) beryllium trimer, $(EtBeNMe_2)_3$.

Dimethylamine (336 N-c.c., 0.015 mole) was condensed onto diethylberyllium (1.00g., 0.015 mole), in diethyl ether (20c.c.), at -196°. A white solid, presumably $Et_2Be \leftarrow NHMe_2$ adduct, was formed at low temperature, but dissolved on warming. Gas was evolved at room temperature, and removal of solvent, at low pressure, left a colourless oil of viscosity comparable to that of conc., H_2SO_4.

Found: Be, 11.12; hydrolysable ethyl, 35.77%; M, cryoscopically, 0.37, 0.75 wt.-% in benzene, 251, 239. $C_{12}H_{33}Be_3N_3$ requires Be, 10.98; hydrolysable ethyl, 35.37%; M, 246.

The i.r. spectrum (contact film) contained absorptions at 626m,br; 804s,br; 870s,sh; 897s,br; 1038s; 1050s,sh; 1102m,sh; 1116m; 1137m,sh; 1173m; 1205s; 1233m; 1302w; 1367w; 1393m; 1414m; 1466s; 1484s; 2688w; 2762m; 2809s; 2849s; 2878s $cm.^{-1}$

The p.m.r. spectrum in d_{14}-methylcyclohexane (benzene reference) consisted of a singlet (+4.90 p.p.m.) due to $(\underline{CH_3})_2$-N, a triplet (+6.08, 6.21, 6.34) due to $\underline{CH_3}$-CH_2-Be, and a quartet (+7.20, 7.34, 7.47, 7.56) due to CH_3-$\underline{CH_2}$-Be.

This compound becomes glassy on cooling to *ca.* -35°.

b) with an excess-formation of bis(dimethylamino)-beryllium trimer, $[Be(NMe_2)_2]_3$.

A large excess of dimethylamine was condensed onto diethylberyllium (1.00g., 0.015 mole), in diethyl ether

(10c.c.), at -196°. On warming to room temperature, gas was evolved. Removal of volatile material at reduced pressure left a white solid, which was sublimed (60°/10^{-3}mm.), m.p., 88° (lit. value,[52] 88-90°), yield ca. 60%.
Found; Be, 9.19%.
$C_{12}H_{36}Be_3N_6$ requires Be, 9.30%.

The i.r. spectrum (Nujol mull) contained absorptions at 522w,br; 619m,br; 646m; 684m,sh; 715m; 740m; 788s,br; 841w; 921s; 945m,sh; 960m,sh; 991w; 1016m; 1034m,sh; 1063s; 1134s; 1164m; 1236m; 1263w; 1311s; 1406w $cm.^{-1}$

When prepared by this method, bis(dimethylamino)-beryllium was X-ray crystalline (powder pattern).

Reaction of diethylberyllium with diethylamine-formation of diethylamino(ethyl)beryllium dimer, $(EtBeNEt_2)_2$.

Diethylamine (197 N-c.c., 0.0088 mole) was condensed onto a cooled (-196°) solution of diethylberyllium (0.59g. 0.0088 mole), in diethyl ether (8c.c.). On warming, gas was evolved below 0°, and a clear solution was obtained at room temperature. The colourless liquid product remaining after evaporation of ether at low pressure was treated with boiling toluene (30c.c.), then dried by exposure to a vacuum.
Found: Be, 7.96; hydrolysable ethyl, 25.60%; M, cryoscopically, 0.49, 0,94 wt.-% in benzene, 218, 234.
$C_{12}H_{30}Be_2N_2$ requires Be, 8.16; hydrolysable ethyl, 26.40%; M, 220.

The i.r. spectrum (contact film) contained absorptions at 630m; 732m; 798s; 809m,sh; 882s; 911s,sh; 961m; 1013s; 1066m; 1091s,sh; 1105s; 1135m; 1150m; 1185m; 1199m; 1225m; 1262m; 1282w; 1310m; 1337w; 1366m,sh; 2857s; 2958s $cm.^{-1}$

The p.m.r. spectrum in benzene (benzene reference) contained quartets (+4.42, 4.53, 4.65, 4.76 p.p.m.) and (+6.95, 7.09, 7.22, 7.36) due, respectively, to $CH_3-\underline{CH_2}-N$ and $CH_3-\underline{CH_2}-Be$, and unresolved, overlapping signals due to the two methyl groups.

Reaction of diethylberyllium with diphenylamine-formation of diphenylamino(ethyl)beryllium dimer, $(EtBeNPh_2)_2$.

Ethereal diethylberyllium (9.09 c.c. of a 1.1M-solution, 0.01 mole) was cooled to -78°, and diphenylamine (1.69 g., 0.01 mole), in diethyl ether (25c.c.), added dropwise. Considerable heat was generated by the addition. Removal of ether at low pressure left a sticky white solid, which was extracted with boiling hexane(2x20 c.c.) and recrystallized from this solvent as small, glistening plates, m.p., 154° to a clear, viscous liquid.

Found: Be, 4.35; hydrolysable ethyl, 14.14%; M, cryoscopically, 0.76, 1.53 wt.-% in benzene, 423, 434. $C_{28}H_{30}Be_2N_2$ requires Be, 4.38; hydrolysable ethyl,14.08%; M, 412.

The i.r. spectrum (Nujol mull) contained absorptions at 526w,sh; 545w,br; 598w; 621w,br; 659w; 687s; 717m; 742s; 752m,sh; 793m; 859s; 902m; 917m; 961m,sh; 1009s; 1067s; 1151m; 1164m; 1209m; 1251w; 1295w; 1364w; 1572m $cm.^{-1}$

Like its methylberyllium analogue, this compound turns yellow, then green, on exposure to air. It is very soluble in ether, moderately so in benzene, but only dissolves appreciably in hexane on warming.

Reaction of di-isopropylberyllium with dimethylamine-formation of dimethylamino(isopropyl)beryllium trimer, $(Pr^iBeNMe_2)_3$.

This compound has been described before, but no molecular-weight data were reported.[52]

Here it was prepared by condensing dimethylamine (224N-c.c., 0.01 mole) onto a cooled (-196^{o}) solution of di-isopropylberyllium (2.8 c,c. of a 3.50M-solution, 0.01 mole) in diethyl ether. A white solid, probably $Pr^{i}_{2}Be\leftarrow NHMe_{2}$ adduct, was formed at low temperature, but dissolved at about room temperature. Evolution of gas then began and continued slowly for <u>ca.</u> 12 hours. Removal of solvent at low pressure then left a clear, colourless liquid.

Found: Be, 9.19; hydrolysable propyl, 44.40%; M, cryoscopically, 0.76, 1.07 wt.-% in benzene, 293, 300. $C_{15}H_{39}Be_{3}N_{3}$ requires Be, 9.40; hydrolysable propyl, 44.79%; M, 288.

The i.r. spectrum (contact film) contained absorptions at 533m,br; 583m,br; 769s,br; 827s; 893s; 919s,sh; 980m; 1035s; 1053w,sh; 1116m; 1136w; 1153w; 1172w; 1222m; 1264w; 1377w; 1439m,sh; 1462s; 1484m,sh; 2833s; 2907s cm.$^{-1}$

The p.m.r. spectrum (benzene solvent and reference) consisted of a singlet (+5.09 p.p.m.) due to $(\underline{CH}_{3})_{2}$-N, a doublet (+5.89, 6.01) due to $(\underline{CH}_{3})_{2}$-CH-Be, and a quintet due to -C-$\underline{H}$ (+6.51, 6.63, 6.75, 6.88, 7.00)

Like all the other liquids described, this compound was violently hydrolysed by hydroxylic solvents.

<u>Reaction of di-isopropylberyllium with pyridine-formation of di-isopropyl(dipyridine)beryllium, $Pr^{i}_{2}Be.py_{2}$.</u>

Addition of pyridine (3c.c., an excess) to di-isopropylberyllium (1.5c.c. of a 3.5M-solution, 0.0053 mole), in diethyl ether, at room temperature, resulted in a golden-yellow solution. Removal of solvent by pumping left a yellow solid, which was recrystallized from benzene-hexane (1:1) mixture (10c.c.) as golden needles, m.p.,111-112°, to a red liquid.

Found: Be, 3.54; hydrolysable propyl, 34.01; pyridine, 61.49%; M, cryoscopically, 0.66, 1.32 wt.-% in benzene, 250, 256.

$C_{16}H_{24}BeN_2$ requires Be, 3.57; hydrolysable propyl, 33.99; pyridine, 62.46%; M,253.

The i.r. spectrum (Nujol mull) contained absorptions at 579m; 627w; 652w; 667m; 703s; 746m; 759w; 774w,sh; 800m,br; 873m; 881w,sh; 901w; 927m; 1016m; 1050s; 1067m; 1092m,br,sh; 1138w; 1155w; 1178m; 1215m; 1266m; 1381s; 1582w; 1613m cm.$^{-1}$

The p.m.r. spectrum (in benzene with this as reference) contained a doublet (+5.67, 5.79 p.p.m.) due to $(\underline{\mathrm{CH}}_3)_2$-C groups.

Reaction of di-t-butylberyllium with dimethylamine-formation of di-t-butylberyllium-dimethylamine adduct, $Bu^t_2Be.NHMe_2$.

Di-t-butylberyllium diethyl ether complex (1.569g., 0.009 mole) was dissolved in diethyl ether (20c.c.) and dimethylamine (192N-c.c., 0.009 mole) condensed onto it at -196°. On warming to room temperature, a pale yellow solution was obtained. Ether was removed at low pressure and hexane (12c.c.) added. The solution was boiled, hexane was removed by pumping, and the liquid *product* dried *in vacuo*. No evolution of gas was observed.

Found: Be, 5.41; hydrolysable butyl, 67.27%.

$C_{10}H_{25}BeN$ requires Be, 5.36; hydrolysable butyl, 67.86%.

The i.r. spectrum (contact film) contained absorptions at 544s; 671m,sh; 695s; 752m; 763w,sh; 807m,sh; 813s; 862s; 892s; 917m; 929m,sh; 1000m; 1019s; 1034s; 1115m; 1132w; 1197m; 1219m; 1259m; 1355w; 1381m; 1410w; 1466s; 2684w; 2717w; 2747m; 2801s; 2907s; 3289m (N-H stretch) cm.$^{-1}$

The p.m.r. spectrum (benzene solvent; TMS reference) consisted of two signals, one rather broad, due to $(\underline{CH_3})_2$-N, centred on τ 8.25, the other, sharp, due to $(\underline{t-C_4H_9})_2$-Be, at τ 8.94. They were in the ratio, on integration, $t-C_4H_9:CH_3$ = 3.10:1.00 (calculated for the adduct 3:1). The signal expected for N-$\underline{H}$ was probably weak and broad, and was not observed.

Attempted preparations of dimethylamino(t-butyl)beryllium Bu^tBeNMe_2.

a) by pyrolysis of $Bu^t_2Be.NHMe_2$ adduct.

The adduct (0.294g.,0.0018mole) was pyrolysed in a flask, attached to the vacuum line, at a nitrogen pressure of 3.603 cm.Hg. At about 50°, distillation of the adduct was observed, so the nitrogen pressure was increased to 4.603 cm.,Hg. At 70-80°, isobutane (12.60 N-c.c.,identified by i.r. spectrum) was evolved, but raising of the temperature caused rapid decomposition to a brown oil. The evolved gases did not contain either isobutene or dimethylamine, but the volume of isobutane calculated for complete rearrangement to Bu^tBeNMe_2 was 39.17N-c.c. The oily residual liquid had an i.r. spectrum (contact film) which contained an N-H stretch (3289 cm^{-1}) weaker than that in the spectrum of the adduct. It was not investigated further.

b) by reaction of di-t-butylberyllium with dimethylamine and trimethylamine in equimolar amounts.

Di-t-butylberyllium diethyl ether complex (2.135g., 0.012 mole), in pentane (20c.c.), was cooled to -196°, and dimethylamine and trimethylamine (269N-c.c.,0.012 mole of each) condensed on. On warming to room temperature a clear, colourless solution was obtained. No gas had been evolved, so the solution was stirred overnight, then the solvent removed at low pressure to leave a colourless

liquid, which was dried in vacuo.
Found: Be, 7.30; hydrolysable butyl, 44.86%; Be:butyl molar ratio, 1.00:0.97.
$C_6H_{15}BeN$ requires Be, 8.18; hydrolysable butyl, 51.82%; Be:butyl molar ratio, 1:1.

The i.r. spectrum (contact film) contained a weak N-H stretch (3289 cm.$^{-1}$).

The p.m.r. spectrum (in d_6-benzene, with TMS reference) consisted of singlets, τ 7.78 and 8.25, due to CH_3-N groups, and τ 8.86 and 8.94, due to t-C_4H_9-Be groups. Their ratios, on integration, were 4:1:6:3.

Distillation of the liquid product in an all glass apparatus attached to the vacuum line (60°/0.1mm.) yielded a colourless, liquid distillate.
Found: Be, 7.10; hydrolysable butyl, 52.59; hydrolysable hydride, 0%; Be:butyl molar ratio, 1:1.17.

The i.r. spectrum (contact film) contained an N-H stretch (3289 cm.$^{-1}$), and the p.m.r. spectrum (in d_6-benzene with TMS reference) contained the same resonances as that of the undistilled liquid, but the ratios were changed, viz., 2.66:5:4:15. (cf. 4:1:6:3, above).

The white residue left behind after distillationhad a Be:butyl ratio of 14.66:1, and its i.r. spectrum was very similar to that of bis(dimethylamino)beryllium.

c) by reaction of the $Bu^t_2Be.NHMe_2$ adduct with excess trimethylamine.

Trimethylamine (1593N-c.c.,0.0711 mole) was condensed onto the adduct (1g., 0.006 mole) at -196°, in a tube fitted with a capilliary side-arm. The tube was sealed under vacuum and left at room temperature for three days. The capilliary was then sealed into the vacuum line, broken, and the volatile material (trimethylamine and isobutane by i.r. spectrum) condensed onto the line, leaving a glassy solid in the tube. This was dissolved in hexane (10c.c.) and transferred to a double Schlenk tube, but it could not be recrystallized, even at -78°. Hexane was removed at low pressure, and the glass dried in vacuo.

Found: Be, 3.70; hydrolysable butyl, 21.52%; Be:butyl molar ratio, 1:1.08.

$C_6H_{15}BeN$ requires Be, 8.18; hydrolysable butyl 51.82%; Be:butyl molar ratio, 1:1.

The i.r. spectrum of the glass did not contain an N-H stretch, nor did its p.m.r. spectrum contain the broad signal associated with $(CH_3)_2$-N in the adduct. It was, however, complex, and indicated that the glass contained a large proportion of other types of CH_3-N groups.

Reaction of di-t-butylberyllium with t-butylamine.

Di-t-butylberyllium diethyl ether complex (1.136g., 0.007 mole) was syringed into a nitrogen-filled tube fitted with a capilliary side-arm. The liquid complex was then cooled to -196° and t-butylamine (0.73c.c., 0.007 mole) added. With the contents frozen, the tube was evacuated and sealed. On warming to room temperature, evolution of gas was observed. After two days, the tube was sealed into the vacuum line, opened, and the volatile contents condensed onto the line. A very viscous liquid was left behind in the tube. After fractionation, it was found that the volatile contents contained 202N-c.c. of isobutane (identified by i.r. spectrum), and no isobutene. The viscous liquid was dissolved in hexane (10c.c.),and transferred to a nitrogen-filled double

Schlenk tube. It could not, however, be recrystallized even on cooling to -78^o, and was, therefore, dried *in vacuo.*

Found: Be, 7.91; hydrolysable butyl, 32.37%.

$C_8H_{19}BeN$ (Bu^{t}BeNHBu^t) requires Be, 6.54; hydrolysable butyl, 41.30%.

C_4H_9BeN (BeNBu^t) requires Be, 11.26; hydrolysable butyl, 0%.

The i.r. spectrum (contact film) contained a weak N-H stretch absorption at 3289 cm.$^{-1}$

The p.m.r. spectrum (benzene standard and solvent) consisted of overlapping signals from +5.81-6.10, but singlets due, respectively, to t-C_4H_9 protons bound to nitrogen (+5.94) and beryllium (+6.10) could be resolved.

Reaction of di-t-butylberyllium with pyridine-formation of di-t-butyl(dipyridine)beryllium, Bu$^t_2$Be.py$_2$.

Pyridine (*ca.* 3c.c., an excess) was added to di-t-butylberyllium diethyl ether complex (*ca.* 1g.,), in ether (10c.c.), at room temperature. An orange-yellow solution was obtained. On pumping off about half of the ether, yellow crystals were deposited. Addition of hexane (30c.c.) caused further crystallization. The bright yellow crystals were filtered, washed with ether (2x25c.c.), and pumped dry, m.p., 112-114^o to an orange liquid.

Found: Be, 3.15; hydrolysable butyl, 41.10; pyridine, 55.56%; M, cryoscopically, 0.76, 1.09 wt.-% in benzene, 201, 213.

$C_{18}H_{28}BeN_2$ requires Be, 3.20; hydrolysable butyl, 40.57; pyridine, 56.23%; M, 281.

The i.r. spectrum (Nujol mull) contained absorptions at 573m; 613m; 658s; 662s,sh; 700s,sh; 706s; 715s; 759m;

804m,sh; 813s; 871w; 933w; 1000w; 1014m; 1048s; 1066s; 1157w; 1214m; 1239w; 1261w; 1572w; 1610m cm.$^{-1}$

The p.m.r. spectrum (benzene solvent and reference) contained a singlet (+6.02 p.p.m.), due to $(C_4H_9)_2$-Be; the signals due to the pyridine molecules were obscured by the benzene peak.

Reaction of dimethylaminolithium with beryllium bromide-attempted preparation of bis(dimethylamino)beryllium.

Dimethylaminolithium (1.24g.,0.024 mole) was covered with diethyl ether (30c.c.) in a three-necked flask fitted with a stirrer and a reflux condenser. Beryllium bromide, (2.06g.,0.012 mole), in ether (181c.c.), was added by syringe at room temperature. Some heat was generated. After stirring for twelve hours, ether was removed at low pressure to leave a yellow solid, from which nothing could be sublimed on heating to 110-120°/10^{-3}mm. It was not investigated further.

Reaction of dimethylaminolithium with beryllium chloride-formation of bis(dimethylamino)beryllium.

Dimethylamine,(847N-c.c.,0.038 mole), was condensed onto diethyl ether (24c.c.) cooled to -196°. After the solution had been allowed to warm to room temperature, and mixed thoroughly, it was cooled to *ca.* 10° and n-butyllithium (2.42g.,0.038 mole), in ether (15c.c.), added. A white, flocculent precipitate was formed at once but, on addition of beryllium chloride (1.51g.,0.019 mole), in ether (30c.c.), heat was generated, and the precipitate coagulated and sank to the bottom of the solution. The colourless solution was filtered from the solid matter, and evaporated to dryness, at low pressure, to leave a white solid. This was transferred to a sublimation apparatus and sublimed as white crystals,

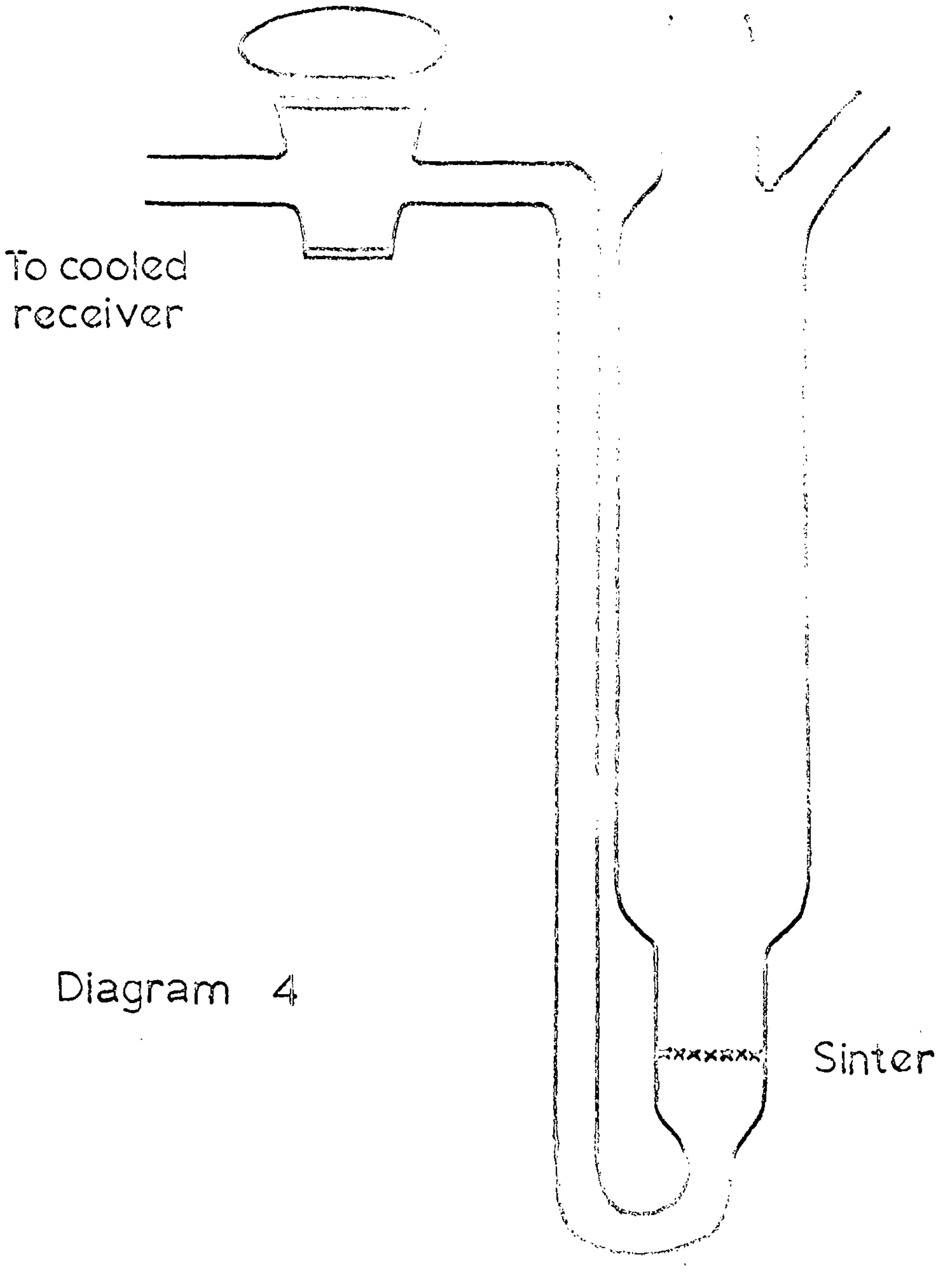


Diagram 4

$95^{o}/10^{-3}$mm. The crystals were identified as bis(dimethylamino)beryllium by m.p.,90^{o}. (Lit, value,[52] 88-90^{o}). Yield, 5.85%.

Reactions of aminoberyllium alkyls with bases.

Reaction of dimethylamino(methyl)beryllium with 2,2'-bipyridyl-attempted formation of dimethylamino(methyl)-bipyridylberyllium, Me(bipy)BeNMe$_2$,

a) at room temperature.

Addition of bipyridyl (1.72g.,0.011 mole), in diethyl ether (12c.c.), to dimethylamino(methyl)beryllium (0.63g.,0.009 mole), in ether (12c.c.), resulted in a red solution, which quickly turned browny-green. Evaporation of ether at low pressure left an olive-green solid from which an orange solution could be obtained by extraction with hot benzene (10x40c.c.). Addition of pentane (30 c.c.) resulted in the crystallization of yellow needles. Found: Be, 4.59; bipyridyl, 78.89%.

$C_{12}H_{14}BeN_2$ (Me_2Be.bipy) requires Be, 4.61; bipyridyl, 79.98%.

b) at -78^{o}.

Dimethylamino(methyl)beryllium (0.47g.,0.007 mole), and bipyridyl (1.08g.,0.007 mole), were found to be soluble in diethyl ether (15c.c. and 25c.c. respectively) at -78^{o}.

The solution of MeBeNMe$_2$ was syringed into the apparatus shown in diagram 4, where it was kept on the sinter by means of a slight pressure of nitrogen. Addition of the bipyridyl (at -78^{o}) resulted in a red solution, which was stable at this temperature. Very little solid could be crystallized, however, so the solution was filtered into a receiver, cooled to -78^{o}, where it was evaporated to dryness, at low pressure, to leave a brick-red solid. On warming to room temperature, this solid turned brown after 30 mins., and, after 12 hrs., it was olive-green in colour. It was not investigated, except to record its i.r. spectrum (Nujol mull), which contained absorptions at 619m; 653w; 667w; 727m,sh; 741s,sh; 753s; 796m; 892w; 992m; 1022m,sh; 1039s; 1063m; 1087s; 1138m; 1208w; 1253m; 1299w; 1416s; 1553m; 1580s,cm.$^{-1}$

Reaction of dimethylamino(methyl)beryllium with pyridine- a) in equimolar quantities-formation of dimethylamino-(methyl)monopyridineberyllium dimer, $(MepyBeNMe_2)_2$.

Pyridine (0.66g.,0.008 mole) was added to a stirred solution of dimethylamino(methyl)beryllium (0.57g., 0.008 mole), in diethyl ether (18c.c.), at room temperature. On concentration of the clear, colourless solution to about 5 c.c., the complex crystallized as small, white needles, and was recrystallized from ether, m.p., 225-238^{0} (decomposition, i.e. loss of pyridine).

Fpund: Be, 6.09; hydrolysable methyl, 10.08%; M, cryoscopically, 0.30, 0.61 wt.-% in benzene, 290, 289. $C_{16}H_{28}Be_2N_4$ requires Be, 6.13; hydrolysable methyl, 10.20%; M, 294.

The i.r. spectrum (Nujol mull) contained absorptions at 646w; 662m; 692s; 749s; 784s,br; 833m,sh; 858m; 909m; 936s; 1006m; 1035s; 1057s; 1101s; 1129s; 1157m; 1193w; 1225m; 1245w; 1387w; 1550w; 1586m cm.$^{-1}$

b) with an excess-formation of dimethylamino(methyl)-dipyridineberyllium monomer, $Mepy_2BeNMe_2$.

To a solution of dimethylamino(methyl)beryllium (0.68g.,0.01 mole), in diethyl ether (20c.c.), an excess (2c.c.) of pyridine was added. The solution became fawn-coloured, and evaporation of ether at low pressure left a cream solid. This was dissolved in boiling pentane (15c.c.) and recrystallized at ca. -50^{0} as small plates, m.p., 175-180^{0} (decomposition, i.e. loss of pyridine).

Found: Be, 3.91; hydrolysable methyl, 6.57%; M, cryoscopically, 0.71, 0.76 wt.-% in benzene, 223, 220. $C_{13}H_{19}BeN_3$ requires Be, 3.98; hydrolysable methyl, 6.61%; M, 226.

The i.r. spectrum (Nujol mull) contained absorptions at 666m; 697s; 743s; 796s,br; 813m,sh; 840m; 894m; 933m; 1012s; 1046s; 1090s; 1158m,sh; 1183w,sh; 1237w; 1253w; 1564w; 1602w cm.$^{-1}$

Reaction of dimethylamino(methyl)beryllium with hexahydro-1,3,5,-trimethyl-s-triazine, $(MeNCH_2)_3$.

The triazine (0.285g.,0.0067 mole) was added to dimethylamino(methyl)beryllium (0.42g.,0.0062 mole), in diethyl ether (20c.c.), at room temperature. Heat was evolved, but no product could be crystallized from ether or pentane, even at -78°. Evaporation of solvent at low pressure left a yellow, viscous liquid, involatile at room temperature. This smelled of the triazine, and discoloured in air, but was not investigated further, except to record its i.r. spectrum (contact film) which contained absorptions at 491w,br; 621w; 679w; 797m,br; 857m; 913s; 979w; 1002s; 1022m; 1048m; 1116s; 1156m; 1235s; 1263s; 1370m; 1385m; 1422m; 1441m; 1466m; 2591w; 2625w; 2725w; 2849s; 2882m; 2924s cm.$^{-1}$

Reaction of diphenylamino(methyl)beryllium with 2,2'-bipyridyl-formation of diphenylamino(methyl)-bipyridylberyllium monomer, $Me(bipy)BeNPh_2$.

Diphenylamino(methyl)beryllium (*ca.* 1g.,) was dissolved in benzene (15c.c.). Bipyridyl (1.10g., an excess), in benzene (20c.c.), was added, with stirring, at room temperature. The solution became wine-red in colour immediately, and did not undergo any colour change. The solution was evaporated to *ca.* 10c.c. at low pressure and hexane (20c.c.) added. The *complex* then crystallized

as a red powder, which was filtered, washed with benzene (5x10c.c.) and dried *in vacuo*, m.p., 110-170° (decomp.)
Found: Be, 2.61; hydrolysable methyl, 4.33; bipyridyl, 44.70%.
$C_{23}H_{21}BeN_3$ requires Be, 2.59; hydrolysable methyl, 4.31; bipyridyl, 44.82%.

The i.r. spectrum (Nujol mull) contained absorptions at 523w; 540w; 646w; 693m; 709s; 744s; 756s; 770s; 802m; 819w,sh; 862w; 876m; 894m; 945m; 986m; 1019m; 1031m; 1044m; 1054m; 1068m; 1082m; 1152w; 1167w; 1186w; 1215w; 1263w; 1297s; 1333w; 1377m; 1582s; 1607m $cm.^{-1}$

The *complex* is not soluble enough for cryoscopic molecular-weight determinations in benzene. It is hydrolysed slowly by water and alcohols, and turns white on exposure to air.

The visible absorption spectrum consisted of two absorptions at 552 (ϵ = 4010) and 375(ϵ= 3923), mμ. The path length was 3 cm., and the concentration of the solution of the complex 6.034×10^{-5} $mole.l^{-1}$.

Reaction of diphenylamino(methyl)beryllium with pyridine, a) in equimolar quantities-formation of diphenylamino-(methyl)monopyridineberyllium, $MepyBeNPh_2$.

Pyridine (0.52g.,0.0066 mole) was added, with stirring, to a hot (*ca.* 70°) solution of diphenylamino-(methyl)beryllium (1.27g.,0.0066 mole), in benzene (20c.c.). The solution became bright yellow and, on cooling, deposited a lemon-coloured powder which was recrystallized from boiling benzene. On heating, it decomposed (loss of pyridine) from 100°, and melted to a golden wax at 209°.
Found: Be, 3.33; hydrolysable methyl, 5.47%.
$C_{18}H_{18}BeN_2$ requires Be, 3.32; hydrolysable methyl, 5.51%.

The i.r. spectrum (Nujol mull) contained absorptions at 526w; 572w; 596m; 642m; 651w,sh; 674m,sh; 687s,sh; 699s; 746s; 763m,sh; 774m; 791m; 875m; 886m; 929s; 986w; 1016w; 1027w; 1049m; 1065s; 1079m; 1148w; 1165w; 1176w; 1207w; 1216w; 1282s; 1302s; 1329m; 1477s; 1577s; 1589s $cm.^{-1}$

This compound was not soluble enough to permit cryoscopic molecular-weight determinations in benzene. It was not hydrolysed by water at all, and only slowly by dilute H_2SO_4.

b) with an excess-formation of diphenylamino(methyl)-dipyridineberyllium monomer, $Mepy_2BeNPh_2$.

Pyridine (1.18g.,0.015 mole, an excess) was added to diphenylamino(methyl)beryllium (0.6g.,0.0031 mole), in benzene (20c.c.), at room temperature, giving a bright yellow solution. Addition of hexane (30c.c.) caused the complex to precipitate, and it was recrystallized from boiling benzene/hexane (1:2) mixture (30c.c.) as needles, m.p., 83-85^{o} (decomposition).

Found: Be, 2.56; hydrolysable methyl, 4.26%; M, cryoscopically, 0.58 wt.-% in benzene, 342.

$C_{23}H_{23}BeN_3$ requires Be, 2.57; hydrolysable methyl, 4.28%; M, 350.

The i.r. spectrum (Nujol mull) contained absorptions at 504m; 524w; 528w; 567w; 601w; 616w; 645m,sh; 667m; 672m; 687s; 700s; 745s; 797s,br; 874m; 934m,sh; 991s,sh; 1020s; 1050s; 1066s; 1080s; 1147m; 1172m; 1218w; 1241w; 1258w; 1289m; 1592s $cm.^{-1}$

The complex turns white immediately when placed in the open air.

Reaction of diphenylamino(ethyl)beryllium with 2,2'-bipyridyl -formation of diphenylamino(ethyl)bipyridylberyllium monomer, $Et(bipy)BeNPh_2$.

Addition of a slight excess (*ca.* 1.0g.) of bipyridyl in benzene (15c.c.), to diphenylamino(ethyl)beryllium

(0.808g., 0.0039 mole), in benzene (30c.c.), resulted in the formation of a dark red solution. Concentration, at low pressure, to *ca.* 10c.c., and addition of hexane (40c.c.), caused the *complex* to separate as a brick-red powder, which was washed with a little benzene and dried *in vacuo,* m.p., 139° (decomposition to a purple mass). Found: Be, 2.46; hydrolysable ethyl, 7.95; bipyridyl, 43.12%; M, cryoscopically, 0.35, 0.69 wt.-% in benzene, 352, 345.

$C_{24}H_{23}BeN_3$ requires Be, 2.49; hydrolysable ethyl, 8.01; bipyridyl, 43.09%; M, 362.

The i.r. spectrum (Nujol mull) contained absorptions at 572w; 605m; 616w; 652w,sh; 676m; 691m; 706m; 719m; 743s; 752s; 770s; 790w; 858w; 877w; 888m; 934m; 946m; 988m; 1022m,sh; 1031m; 1039w; 1052w; 1082w,sh; 1154m; 1167m; 1185w; 1218m; 1307s; 1333w; 1575s; 1607s cm.$^{-1}$

This compound dissolved in benzene at 50° to give a brown solution which did not redeposit any solid on cooling back to room temperature. Molecular-weight determinations were carried out on such a solution. It is relatively air stable (goes white in air after *ca.* 20 mins.), and is only slowly hydrolysed by water and dilute H_2SO_4.

The visible absorption spectrum contained absorption maxima at 554 (ϵ = 4100) and 378 (ϵ = 2109) mμ. (Path length = 3 cm., concentration = 7.204x10^{-5} mole.l^{-1}).

Reaction of diphenylamino(ethyl)beryllium with pyridine, a) in equimolar quantities-attempted formation of diphenylamino(ethyl)monopyridineberyllium, EtpyBeNPh$_2$.

Pyridine (0.79g.,0.01 mole) was added, with stirring, to diphenylamino(ethyl)beryllium (2.05g.,0.0099 mole), in benzene (20c.c.), at room temperature. A golden yellow solution was obtained. Removal of solvent at low pressure left a sticky yellow solid which was recrystallized from hexane (40c.c.) at -78°. On filtering, however, it was seen that the precipitate was still semi-solid. It was, therefore, redissolved in benzene (10c.c.) and transferred to a nitrogen-filled two-necked flask, where it was pumped as dry as possible.

Found: Be, 2.83; hydrolysable ethyl, 5.74%; Be:ethyl molar ratio, 1.59:1.

$C_{19}H_{20}BeN_2$ requires Be, 3.19; hydrolysable ethyl, 10.17%; Be:ethyl molar ratio, 1:1.

The i.r. spectrum (Nujol mull) contained absorptions at 483m; 501w; 525s; 557m,br; 576m; 592m; 606m; 618m; 642m; 649m; 690s,br; 746s,br; 790m; 807m; 872m; 890m; 941m; 988s; 1018s; 1050s; 1068s; 1152m; 1176m; 1215s; 1297s; 1333s; 1484s; 1587s cm.$^{-1}$

b) with an excess-formation of diphenylamino(ethyl)-dipyridineberyllium monomer, $EtPy_2BeNPh_2$.

An excess of pyridine (1.23g.,0.0155 mole) was added with stirring, to diphenylamino(ethyl)beryllium (1.506g., 0.0073 mole), in benzene (45c.c.), at room temperature. A golden-yellow solution was obtained. On removal of *ca.* two-thirds of the solvent at low pressure, the complex crystallized as fine yellow particles, m.p., 194° to a yellow wax after decomposition (loss of pyridine) from *ca.* 85°.

Found: Be, 2.44; hydrolysable ethyl, 7.90%; M, cryoscopically, 0.52, 1.04 wt.-% in benzene, 345, 346.

$C_{24}H_{25}BeN_3$ requires Be, 2.47; hydrolysable ethyl, 7.97%; M, 364.

The i.r. spectrum (Nujol mull) contained absorptions at 504m; 527m; 554w; 567m; 578m; 590w; 602w; 612w; 628w;

637m; 645w; 662m; 670s; 678s; 694s; 726w; 741s; 784m; 854m; 861m; 877m; 940w; 978m; 1006m; 1019m; 1035m; 1059m; 1073w; 1137m; 1164m; 1202s; 1228w; 1285s; 1300m; 1557s; 1572s; 1587s cm.$^{-1}$

Reaction of di-n-propylamino(methyl)beryllium with pyridine in eqimolar quantities-formation of dipyridine-(dimethyl)beryllium, $Me_2Be.py_2$.

The reaction of pyridine (0.8g.,0.01 mole) and di-n-propylamino(methyl)beryllium (1.24g.,0.01 mole), in hexane (10c.c.), resulted in the formation of a pale yellow solution which, on standing at -78° for 30 mins., deposited white needles.

Found: Be, 4.53; hydrolysable methyl, 15.13%.

$C_{12}H_{16}BeN_2$ ($Me_2Be.py_2$) requires Be, 4.57; hydrolysable methyl 15.23%.

Reaction of bis(dimethylamino)beryllium with 2,2'-bipyridyl -formation of bis(dimethylamino)bipyridylberyllium, $(Me_2N)_2Be.bipy$.

Bis(dimethylamino)beryllium (0.1074g., 0.0011 mole) was dissolved, with warming, in a mixture of ether (25c.c.) and benzene (10c.c.). Bipyridyl (0.1909g., 0.0012 mole), in ether (12c.c.), was added, at room temperature, giving a bright yellow solution which turned into a pale yellow suspension when stirred overnight. Filtration yielded a pale cream solid, which did not dissolve when stirred with benzene, and could not be purified. On heating, it softened slightly at 320-325°, but did not melt below 360°.

Found: Be, 3.47; Me_2N (by measurement of evolved Me_2NH on the vacuum line), 33.29; bipyridyl, 61.35%.

$C_{12}H_{14}BeN_4$ requires Be, 3.56; Me_2N, 33.50; bipyridyl, 61.66%.

The complex was insoluble in both benzene and nitrobenzene.

Reaction of bis(dimethylamino)beryllium with pyridine.

When pyridine (0.275g., 0.0035 mole) was mixed with bis(dimethylamino)beryllium (0.509g., 0.0053 mole), in benzene (10c.c.), at room temperature, a pale yellow solution was obtained. The yellow solid left after evaporation of solvent by pumping was dissolved in hexane (5c.c.) but could not be recrystallized, even at -78°. On prolonged exposure to a vacuum, it slowly turned white and was then identified, by i.r. spectrum, as bis(dimethylamino)beryllium.

Reaction of bis(dimethylamino)beryllium with 4-dimethylaminopyridine.

Bis(dimethylamino)beryllium (0.32g.,0.0033 mole), in benzene (15c.c.), was stirred at room temperature whilst 4-dimethylaminopyridine (0.27g.,0.0022 mole), in benzene (15c.c.), was added. A very pale yellow solution was obtained. On concentration to *ca.* 5c.c., addition of hexane (20c.c.), and cooling to *ca.* -50°, a small quantity of white solid was crystallized.

Found: Be, 2.88%.

This figure does not correspond to any of the possible products (see discussion, below) in a pure state so the solid was not investigated further, except to record its i.r. spectrum (Nujol mull), which contained absorptions at 530w; 541w; 752m; 806s; 862w,br; 945w; 990s; 1020m; 1071m; 1105m; 1229s; 1263m; 1346w; 1520m; 1538m; 1608s cm.$^{-1}$

Reactions with alcohols and phenol.

Reaction of dimethylberyllium with methanol-formation of methylberyllium methoxide tetramer, $(MeBeOMe)_4$.

Dimethylberyllium, in diethyl ether, (17.2c.c., of a 1.16M-solution, 0.02 mole) was cooled to -196^{0}, and methanol (0.64g.,0.02 mole) added slowly. On warming, gas was evolved rapidly from ca. -100^{0}. Solvent was removed at low pressure, and the product sublimed at $70^{0}/10^{-3}$mm., m.p., $23-25^{0}$.

Found: Be, 16.22; hydrolysable methyl, 27.09%; M, cryoscopically, 0.49, 0.99 wt.-% in benzene, 218, 224. $C_8H_{24}Be_4O_4$ requires Be, 16.36; hydrolysable methyl, 27.27%. M, 220.

The i.r. spectrum (contact film) contained absorptions at 667m; 752s,br; 759s,br; 910w; 958m; 1039s; 1104s; 1208m; 1262w; 1408w,sh; 1464w; 1538w,sh; 2849s; 2941s cm^{-1}.

Proton magnetic resonance spectra were recorded in benzene and d_8-toluene. In benzene (benzene reference), there was a doublet (+3.77, 4.04 p.p.m.), due to $\underline{CH_3}$-O, and a singlet (+7.88) due to $\underline{CH_3}$-Be. On integration, these signals were in the ratio CH_3-O (total):CH_3-Be = 1.00:1.05. [$(MeBeOMe)_4$ requires 1:1]. On heating up to 100^{0}, both these signals remained unchanged. In d_8-toluene, (TMS as reference), the $\underline{CH_3}$-O doublet was at τ 6.81, 6.91 and the $\underline{CH_3}$-Be singlet at τ 10.76. Cooling of this sample to -90^{0} produced no change in the spectrum. In all these spectra, the $\underline{CH_3}$-O signal was split into two equal components.

The preparation of this compound from ether-free dimethylberyllium has been described elsewhere.[53]

Reaction of dimethylberyllium with ethanol-formation of methylberylliumethoxide tetramer, $(MeBeOEt)_4$.

Ethanol (0.92g.,0.02 mole), in diethyl ether (15c.c.), was added, with stirring, to a slight excess of dimethylberyllium (0.819g.,0.021 mole), in ether (11c.c.), at ca. -50°. On warming to room temperature, a clear, colourless solution was obtained. Evaporation of all the solvent at low pressure left a sticky, white solid, which was extracted with hot hexane, and dried *in vacuo*, m.p.,28-30°.

Found: Be, 13.19; hydrolysable methyl, 21.34%; M, cryoscopically, 0.31, 0.47, 0.94 wt.-% in benzene, 293, 287, 301.

$C_{12}H_{32}Be_4O_4$ requires Be, 13.07; hydrolysable methyl, 21.74%; M, 276.

The i.r. spectrum (contact film) contained absorptions at 769s,br; 901m,sh; 917m; 1026m,sh; 1050s; 1075s; 1122s; 1170m; 1221m; 1300w; 1366w,sh; 1389m; 1445w; 1462w,sh; 2825m; 2890s; 2915s; 2963s $cm.^{-1}$

The p.m.r. spectrum (benzene solvent; TMS reference) consisted of a quartet (τ 5.92, 6.03, 6.15, 6.27), due to CH_3-$\underline{CH_2}$-O, a triplet (τ 8.81, 8.93, 9.04), due to $\underline{CH_3}$-CH_2-O and a singlet (τ 10.71), due to $\underline{CH_3}$-Be.

Reaction of dimethylberyllium with n-propanol-formation of methylberyllium n-propoxide tetramer, $(MeBeOPr^n)_4$.

Dimethylberyllium (0.49g.,0.0125 mole), in diethyl ether, (10c.c.), reacted with n-propanol (0.75g., 0.0125 mole), in ether (20c.c.), at ca. -50°, with evolution of gas, to give a clear solution. The white solid left after pumping off the ether was extracted with hexane (15c.c.) and crystallized, on concentration to ca. 5c.c., as plates, m.p.,38-40°.

Found: Be, 10.64; hydrolysable methyl, 18.19%; M, cryoscopically, 0.64, 1.28 wt.-% in benzene, 325, 345. $C_{16}H_{40}Be_4O_4$ requires Be, 10.84; hydrolysable methyl, 18.07%; M, 332.

The i.r. spectrum (Nujol mull) contained absorptions at 667m; 676m; 754m,br; 798s; 880m; 890m; 922m; 964s; 1015s; 1044s; 1098m; 1117m,sh; 1174w; 1211m; 1266m; 1290w; 1312w cm.$^{-1}$

The p.m.r. spectrum (benzene solvent and reference) contained a triplet (+3.18, 3.29, 3.41 p.p.m.), due to $-\underline{CH_2}-CH_2-CH_3$, a multiplet (+5.51→5.98), due to $-CH_2-\underline{CH_2}-CH_3$, a triplet (+6.39, 6.51, 6.63), due to $-CH_2-CH_2-\underline{CH_3}$, and a singlet (+8.04), due to $\underline{CH_3}$-Be. On integration, these four signals were in the ratio 1:1:1.47:1.47. [$(MeBeOPr^n)_4$ requires 1:1:1.5:1.5].

The above three alkoxides all decomposed rapidly, with charring, on exposure to air.

Reaction of dimethylberyllium with isopropanol-formation of methylberyllium isopropoxide tetramer, $(MeBeOPr^i)_4$.

isoPropanol (0.90g.,0.015 mole) was added to a cooled (-196°) solution of dimethylberyllium (0.58g.,0.015 mole) in diethyl ether (13c.c.). Gas was evolved rapidly at *ca.* -80°, and, at room temperature, a clear solution was obtained. Removal of ether at low pressure left a white solid, which was recrystallized from hexane. The product could also be sublimed (100°/10^{-3}mm.), m.p.,134-136°. Found: Be, 10.48; hydrolysable methyl, 18.21%; M, cryoscopically, 0.30, 0.60 wt.-% in benzene, 336, 340. C16H40Be4O4 requires Be, 10.84; hydrolysable methyl, 18.07%; M, 332.

The i.r. spectrum (Nujol mull) contained absorptions at 538m,br; 576m,br; 722m,sh; 790s,br; 936s; 1015s; 1117s; 1140m; 1173m; 1210m; 1258m; 1287w; 1335w cm.$^{-1}$

The p.m.r. spectrum in benzene (benzene reference) consisted of a septet (+2.86, 2.96, 3.06, 3.17, 3.28,3.39 3.49 p.p.m.), due to O-C$\underline{H}$Me$_2$, a doublet (+5.92, 6.03), due to O-CH$\underline{Me}_2$, and a singlet (+8.04) due to $\underline{CH}_3$-Be. In d$_8$-toluene (TMS as standard) the isopropoxy resonances (τ 8.70, 8.80) were unaffected by reducing the temperature, but the $\underline{CH}_3$-Be resonance (τ 10.75) developed a shoulder on the high-field side at -5°, and was split into an unequal doublet (high-field component less intense) at -45°. Recording of the spectrum at lower temperature was not feasible on account of reduced solubility.

Reaction of dimethylberyllium with t-butanol,
a) in equimolar quantities-formation of methylberyllium t-butoxide tetramer, $(MeBeOBu^t)_4$.

Addition of t-butanol (0.86g., 0.012 mole), in diethyl ether (10c.c.), to dimethylberyllium (10c.c. of a 1.16M-solution, 0.012 mole), at -80°, resulted in a clear solution which evolved gas on warming to *ca.* -20°. On concentration, the product crystallized, m.p.,93° (sharp).

Found: Be, 9.20; hydrolysable methyl, 15.47%; M, cryoscopically, 0.43, 0.86 wt.-% in benzene, 388, 399. M, isothermally, in ether (0.088M-solution), 369.
$C_{20}H_{48}Be_4O_4$ requires Be, 9.27; hydrolysable methyl, 15.46%; M, 388.

The i.r. spectrum (Nujol mull) contained absorptions at 494w; 532w; 598w; 676m; 671m,sh; 806s; 819s; 847s; 971s,sh; 990s; 1012s; 1027s; 1055m; 1080m,sh; 1200s; 1236m; 1256s; 1366s cm.$^{-1}$

The p.m.r. spectrum (benzene solvent and standard) consisted of a singlet (+5.80p.p.m.), due to O-$\underline{Bu}^t$, and one due to $\underline{CH}_3$-Be (+7.73). This spectrum was unaffected by heating up to65^{o}. In d_{14}-methylcyclohexane, however, the signals were split into doublets (τ 8.52, 8.64), due to Bu^{t}-O, and (τ 10.70, 10.94), due to CH_3-Be. The reference was TMS, and, on integration, the ratios were Bu^{t}(total):Me(total) = 3.24:1. [(MeBeOBu^{t})$_4$ requires 3:1]. Heating of this sample up to 100^{o} caused no significant change in the shifts or relative intensities of the signals, which were still split into doublets. Variation of concentration also had no effect on the spectrum.

b) with an excess-formation of beryllium t-butoxide trimer, [Be(OBu^{t})$_2$]$_3$.

t-Butanol, an excess, in diethyl ether (40c.c.), was added, with stirring, to dimethylberyllium (5c.c. of a 1.16M-solution, 0.0058 mole), in ether, at room temperature. Gas was evolved and heat generated. Ether was removed at low pressure to ca. 10c.c., and benzene (20c.c.) added. The solution was boiled to ensure complete elimination of methane then the white product pumped dry and exposed to a vacuum to remove volatile impurities, m.p.,106-107^{o}. Found: Be, 5.85%; M, cryoscopically, 0.53, 1.06 wt.-% in benzene, 454, 458.

$C_{24}H_{54}Be_3O_6$ requires Be, 5.81%; M, 465.

The i.r. spectrum (Nujol mull) contained absorptions at 676w,sh; 725m,sh; 806s; 819s,sh; 971s; 1021s; 1089m; 1209m; 1262m cm.$^{-1}$

The p.m.r. spectrum in benzene (TMS reference) consisted of a singlet (τ 8.56), due to Bu^{t}-O, but in d_{14}-methylcyclohexane, this resonance was split into an unequal doublet (τ 8.60, 8.75, ratio on integration 2.01:1.00), which was unaffected on heating up to 100^{o}. Similar splitting was observed in carbon tetrachloride (τ 8.62, 8.78, in ratio 2:1).

When beryllium t-butoxide (0.225g.,0.0015 mole), in toluene (4c.c.), was added to ether-free dimethylberyllium (0.070g.,0.0018 mole), an equimolar amount of the latter dissolved to give, on filtration from the excess, a colourless solution. On concentration of the solution to ca. 1c.c., the product crystallized and was identified as $(MeBeOBu^t)_4$ by m.p. (94-95°) and i.r. spectrum. This sample gave p.m.r. spectra (in benzene and d_{14}-methylcyclohexane) identical with those of the product of the reaction of dimethylberyllium and t-butanol.

All the above alkoxides dissolve readily in diethyl ether and aliphatic or aromatic hydrocarbons.

Reaction of dimethylberyllium with diphenylmethanol-formation of methylberyllium diphenylmethoxide dimer, $(MeBeOCHPh_2)_2$.

The reaction of these two compounds, in ethereal solution, to give $MeBeOCHPh_2.OEt_2$, has been described elsewhere.[70]

A solution of dimethylberyllium (0.29g.,0.0075 mole) in diethyl ether (3.8c.c.), was concentrated under reduced pressure until no liquid remained. The residue was heated at 50° for 15 min., with continuous pumping, after which all the Me_2Be had sublimed onto the upper part of the Schlenk limb. The sublimate was then stirred with benzene (15c.c.), and a solution of diphenylmethanol (1.38g., 0.0075 mole), in benzene (50c.c.), was added over two hr. Evaporation of solvent left a sticky white residue, which was boiled three times with hexane, the latter being removed each time under reduced pressure. The product was finally recrystallized from hexane as star-like clusters, melting range 97-108° to a viscous liquid. Found: Be, 4.41; hydrolysable methyl, 7.31%; M, cryoscopically, 0.87, 1.73 wt-% in benzene, 401, 419. $C_{28}H_{28}Be_2O_2$ requires Be, 4.35; hydrolysable methyl, 7.25%; M, 414.

The i.r. spectrum (Nujol mull) contained absorptions at 507w,br; 609w; 633w; 697s; 741m; 792m; 844w; 871m; 887m; 914m; 923w; 1027s; 1060s; 1088s; 1198m; 1245w; 1264m; 1517m $cm.^{-1}$

The p.m.r. spectrum (d_6-benzene; TMS reference) consisted of a multiplet (τ 2.60→3.04), due to $(\underline{C}_6\underline{H}_5)_2$-C, and singlets ($\tau$ 4.18 and 11.06) due, respectively, to -C-$\underline{H}$ and $\underline{CH}_3$-Be. The ratio of these signals was 11:1:3. $[(MeBeOCHPh_2)_2$ requires 10:1:3].

Reaction of dimethylberyllium with triphenylmethanol, a) in ether-formation of methylberyllium triphenylmethoxide diethyl ether complex, $MeBeOCPh_3.OEt_2$.

Triphenylmethanol (0.87g.,0.0033 mole), in diethyl ether (20c.c.), was added, with stirring, to dimethylberyllium in ether (1.7c.c. of a 1.96M-solution, 0.0033 mole) at *ca.* -50°. A clear solution was obtained but, on warming to room temperature, gas was evolved, and a white precipitate formed. This was recrystallized from benzene (20c.c.) as a white powder, which softens at 82-84° then melts at 182-183° (the melting point of the ether-free triphenylmethoxide, below).

Found: Be, 2.55%; hydrolysable methyl, 4.25; M, cryoscopically, 1.15, 1.50 wt.-% in benzene, 360, 351. $C_{24}H_{28}BeO_2$ requires Be, 2.53; hydrolysable methyl, 4.20%; M, 357.

The i.r. spectrum (Nujol mull) contained absorptions at 638w; 666w; 699m; 758m; 800s; 816m,sh; 869w,br; 1018s; 1029s,sh; 1093s; 1152w,sh; 1201w,sh; 1264s; 1475m $cm.^{-1}$

The p.m.r. spectrum, in d_6-benzene with TMS as reference consisted of a multiplet (τ 2.54→3.16), due to $(C_6\underline{H}_5)_3$-C-, a quartet (τ 6.52, 6.64, 6.75, 6.87), due to CH_3-$\underline{CH}_2$-, a triplet (τ 8.79, 8.92, 9.04), due to $\underline{CH}_3CH_2$, and a singlet (τ 11.53) due to $\underline{CH}_3$-Be, in the ratio 5.21:1.34:1.95:1.00. ($MeBeOCPh_3.OEt_2$ requires 5.00:1.33: 2.00:1.00).

b) in the absence of ether-formation of methylberyllium triphenylmethoxide dimer, $(MeBeOCPh_3)_2$.

Ether-free dimethylberyllium (0.29g.,0.0075 mole) was prepared as described above, covered with benzene (20c.c.), and stirred with occasional cooling while triphenylmethanol (1.95g.,0.0075 mole), in benzene (50c.c.), was added slowly. Gas was evolved and, after addition was complete, a clear solution was left. Evaporation to dryness at low pressure left a white solid which was boiled with hexane twice, the latter being removed each time by pumping, then recrystallized from hexane, m.p., 183-184°.

Found: Be, 3.23; hydrolysable methyl, 5.22%; M, cryoscopically, 0.54, 1.08 wt.-% in benzene, 592, 582. $C_{40}H_{36}Be_2O_2$ requires Be, 3.18; hydrolysable methyl, 5.30%; M, 566.

The i.r. spectrum (Nujol mull) contained absorptions at 500w; 519w; 532w; 633m; 650w; 684m; 697s; 707m; 752m; 759m; 800m,br; 890m; 905m; 921m; 934m; 995s; 1012s; 1037m; 1083m; 1158w; 1205m; 1216m; 1261m; 1600w $cm.^{-1}$

The p.m.r. spectrum was recorded in d_6-benzene with TMS as reference, and consisted of a multiplet (τ 2.62→3.14), due to $(C_6\underline{H}_5)_3$-C-, and a singlet (τ 11.43) due to $\underline{CH}_3$-Be, in the ratio 5.35:1.00 [$(MeBeOCPh_3)_2$ requires 5:1].

Reaction of dimethylberyllium with 2-dimethylaminoethanol -formation of methylberyllium 2-dimethylaminoethoxide oligomer, $(MeBeOC_2H_4NMe_2)_{6.7\rightarrow 7.1}$

Dimethylberyllium (5.1 c.c. of a 1.96M-solution, 0.01 mole) was cooled to ca. -40°, and 2-dimethylaminoethanol (0.89g.,0.01 mole), in ether (10c.c.), added dropwise, with stirring. As the addition proceeded, gas was evolved, and white crystals deposited. These were washed with ether (2x10c.c.), in which they were only sparingly soluble, m.p., $208-212^{\circ}$.

Found: Be, 7.97; hydrolysable methyl, 13.40%; M, cryoscopically, 1.33, 1.57, 2.00 wt.-% in benzene, 749, 761, 792.

$C_5H_{13}BeNO$ requires Be, 8.04; hydrolysable methyl, 13.40%; M, 112.

The i.r. spectrum (Nujol mull) contained absorptions at 465m,br; 568w; 640m; 689m,br; 776s; 809s; 837m; 864s; 906s; 965s; 1032s; 1071s; 1085s; 1101m,sh; 1175m; 1183m,sh; 1266m; 1284m cm^{-1}.

The p.m.r. spectrum (benzene solvent and reference) contained a singlet (+5.17p.p.m.), due to $(\underline{CH_3})_2$-N, and one due to $\underline{CH_3}$-Be (+8.10). The resonances due to C_2H_4 protons were not observed. This compound is very soluble in benzene but does not dissolve in hexane. Water and 2-methoxyethanol do not hydrolyse it at all, but dil. H_2SO_4 does so at once.

Reaction of dimethylberyllium with phenol, a) in ether-formation of methylberyllium phenoxide diethyl ether complex, $MeBeOPh.OEt_2$.

Phenol (1.88g.,0.02 mole), in ether (20c.c.), was added slowly, with stirring, to dimethylberyllium in ether (10c.c. of a 1.96M-solution, 0.02 mole), at -96°. Gas was evolved and a white precipitate formed. This was only sparingly soluble in ether, but was recrystallized from a small amount of benzene as needles, which softened at 114° then decomposed into a colourless sublimate and an involatile residue at *ca.* 160°.

Found: Be, 4.62; hydrolysable methyl, 7.91%; M, cryoscopically, 0.59, 1.19 wt.-% in benzene, 231, 269.
$C_{11}H_{18}BeO_2$ requires Be, 4.71; hydrolysable methyl, 7.85%; M, 191.

The i.r. spectrum (Nujol mull) contained absorptions at 467w,br; 509m,br; 597w; 694s; 765s; 800s; 826m; 867s,br; 908m; 1002m; 1023s; 1038s; 1075m; 1094m; 1153m; 1193m; 1263s; 1597m $cm.^{-1}$

The p.m.r. spectrum in d_6-benzene (TMS reference) consisted of the following: $\underline{C_6H_5}$-O triplet (τ 2.70, 2.76, 2.82), CH_3-$\underline{CH_2}$- quartet (τ 6.32, 6.42, 6.54, 6.64), $\underline{CH_3}$-CH_2- triplet (τ 9.04, 9.16, 9.28) and $\underline{CH_3}$-Be singlet (τ 10.48), in ratio, 1.67:1.50:2.00:1.00. ($MeBeOPh.OEt_2$ requires 1.67:1.33:2.00:1.00).

The volatile material removed, on pumping, from a benzene (10c.c.) solution of this complex (0.0012 mole) was shown to contain 33.44 per cent. by weight of the coordinated ether, by comparison of its integrated p.m.r. spectrum with those of standard solutions of ether in benzene.

b) in benzene-attempted formation of methylberyllium phenoxide, MeBeOPh.

Dimethylberyllium (0.01 mole) was stirred with benzene (20c.c.) whilst phenol (0.95g.,0.01 mole), in benzene (40c.c.), was added dropwise, at room temperature. Gas was evolved and a white, insoluble solid formed. On filtering and pumping dry, the filtrate was seen to contain very little soluble material. The insoluble solid therefore, was washed with ether to remove dimethylberyllium and dried *in vacuo*, m.p., not below 360°.

The solid did not evolve methane on treatment with water, but was not investigated further, except to record its i.r. spectrum. (see discussion).

Reaction of diethylberyllium with triethylmethanol,

a) in equimolar quantities-formation of ethylberyllium triethylmethoxide trimer, $(EtBeOCEt_3)_3$.

Diethylberyllium (9.1c.c. of a 1.1M-solution, 0.01 mole), in diethyl ether, was cooled to *ca.* -60°, and triethylmethanol (1.16g.,0.01 mole), in ether (10c.c.), added, with stirring. Gas was evolved slowly as the reaction proceeded, leaving a colourless solution, removal of solvent from which gave a colourless liquid. Found: Be, 5.84; hydrolysable ethyl, 18.94%; M, cryoscopically, 0.45, 0.90 wt.-% in benzene, 470, 450. $C_{27}H_{60}Be_3O_3$ requires Be, 5.90; hydrolysable ethyl, 18.95%; M, 459.

The i.r. spectrum (contact film) contained bands at 565w,br; 667w; 689m,sh; 760s,br; 793s; 818m,sh; 859m; 918m; 963m; 1020s; 1049m; 1078s; 1121m; 1152m; 1209w; 1233w; 1264m; 1311w; 1385w; 1418w; 1458m; 2874m,sh; 2924s,sh; 2959s cm.$^{-1}$

b) in the molar ratio 1:2-formation of beryllium triethylmethoxide dimer, $[Be(OCEt_3)_2]_2$.

Triethylmethanol (0.58g.,0.005 mole) was added to a cooled (-196°) solution of diethylberyllium (2.25c.c. of a 1.1M-solution, 0.0025 mole), in diethyl ether, in a two-necked flask attached to the vacuum line. The flask was evacuated, then allowed to warm to room temperature. At *ca.* -30°, ethane (110.6 N-c.c., 0.0049 mole), identified by i.r. spectrum, was evolved. Removal of solvent at low pressure left a white paste, which was sublimed (50-60°/10^{-3}mm.) as a white solid, m.p., 36-37°.

Found: Be, 3.74%; M, cryoscopically, 0.36, 0.72 wt.-% in benzene, 474, 486.

$C_{28}H_{60}Be_2O_4$ requires Be, 3.77%; M, 478.

The i.r. spectrum (Nujol mull) contained absorptions at 483m; 564w; 606w,br; 667m; 714w; 754m; 797s; 856s; 914s; 988s,br; 1018s; 1044s; 1078s; 1205m; 1245s,sh; 1261s; 1350m cm.$^{-1}$

This compound gave an X-ray diffraction pattern. Its p.m.r. spectra in benzene and d_{14}-methylcyclohexane were recorded. In benzene, a quartet, centred at τ 8.30 (relative to benzene, 2.73), and a triplet, centred at τ 8.91, were observed, and in C_7D_{14}, these were at τ 8.47 and 9.18 respectively, relative to TMS.

Reaction of diethylberyllium with 2-methoxyethanol-formation of ethylberyllium 2-methoxyethoxide tetramer, $(EtBeOC_2H_4OMe)_4$.

To a cooled (*ca.* -50°) solution of diethylberyllium (0.01 mole), in diethyl ether (20c.c.), was added 2-methoxyethanol (0.76g.,0.01 mole), in ether (10c.c.). Gas was evolved at *ca.* 0°, and a colourless solution obtained. The white solid obtained on pumping dry was recrystallized from hot hexane (20c.c.) as needles, m.p., 79-80° to a colourless liquid.

Found: Be, 7.91; hydrolysable ethyl, 25.46%; M, cryoscopically, 1.25, 1.66 wt.-% in benzene, 457, 448.

$C_{20}H_{48}Be_4O_8$ requires Be, 7.98; hydrolysable ethyl, 25.66%; M, 452.

The i.r. spectrum (Nujol mull) contained absorptions at 532w; 574w,sh; 588m,br; 659s; 674s; 794s,br; 863s; 926s; 950m,sh; 988s; 1012s; 1087s,br; 1181m; 1198m,sh; 1236m; 1263s; 1416w cm.$^{-1}$

The p.m.r. spectrum in benzene, using this as reference consisted of a triplet (+3.53, 3.62, 3.70 p.p.m.), due to $-\underline{CH}_2-\underline{CH}_2-$, a singlet (+4.11), due to $\underline{CH}_3-O$, a triplet (+5.65, 5.79, 5.92), due to $\underline{CH}_3-CH_2-Be$ and a quartet (+7.24 7.37, 7.51, 7.65), due to $CH_3-\underline{CH}_2-Be$.

Reaction of diethylberyllium with phenol, a) in benzene-attempted formation of ethylberyllium phenoxide, EtBeOPh.

Ether-free diethylberyllium (0.01 mole) was dissolved in benzene (20c.c.) and phenol (0.95g.,0.01 mole), in benzene (40c.c.), added dropwise, with evolution of gas, to give a faintly turbid solution. The addition was carried out at room temperature. Filtration from the small amount of insoluble matter, and removal of solvent at low pressure, left a sticky white solid which, on further pumping, yielded a white solid, insoluble in hexane and benzene, and an involatile liquid, presumably diethylberyllium. The solid did not melt below 360°.

Found: Be, 4.68; hydrolysable ethyl, 2.20%.

$C_{12}H_{10}BeO_2$ $[(C_6H_5O)_2Be]$ requires Be, 4.62; hydrolysable ethyl, 0%.

The i.r. spectrum (Nujol mull) contained bands at 507m; 547w; 686s; 726s; 752s; 784s; 867s,br; 884s,sh; 995w; 1016m; 1062m; 1144w; 1159m; 1232s; 1468s; 1572s $cm.^{-1}$

b) in toluene.

When the reaction was repeated using toluene, instead of benzene, as solvent, the same result was obtained. The white solid isolated did not melt below 360°.

Found: Be, 4.81; hydrolysable ethyl, 5.24%.

$C_{12}H_{10}BeO_2$ requires Be, 4.62; hydrolysable ethyl, 0%.

The i.r. spectrum (Nujol mull) was identical to that of the product from a), above.

Reaction of di-isopropylberyllium with methanol,

a) in equimolar quantities-formation of isopropylberyllium methoxide tetramer, $(Pr^iBeOMe)_4$.

Methanol (0.6c.c.,0.015 mole), in diethyl ether (10c.c.), was added, with stirring, to di-isopropylberyllium (4.2c.c. of a 3.50M-solution, 0.015 mole), in diethyl ether, at *ca.* -80°. Vigorous evolution of gas occurred at *ca.* -50° and, on warming to room temperature, and filtration from the small amount of insoluble material a clear solution was obtained. Ether was removed at low pressure, to leave a white solid which was recrystallized from hexane as plates, m.p.,133-5°.

Found: Be, 10.73; hydrolysable propyl, 51.85%; M, 324, 326 (cryoscopically, 0.49, 0.97 wt.-% in benzene).

$C_{16}H_{40}Be_4O_4$ requires Be, 10.84; hydrolysable propyl, 51.81%; M, 332.

The i.r. spectrum (Nujol mull) contained absorptions at 513w,br; 727m,sh; 781s,sh,br; 795s,br; 846s; 863m,sh; 936m; 1042s; 1109m; 1152w,sh; 1199w; 1222w; 1263w $cm.^{-1}$

The p.m.r. spectrum (benzene solvent and standard) consisted of a broad singlet (+3.83p.p.m.), due to $\underline{CH}_3$-O, and a doublet (+5.74, 5.80) due to $(\underline{CH}_3)_2$-C-. The signal expected for C-$\underline{H}$ was not observed.

b) in excess-formation of beryllium methoxide polymer, $[Be(OMe)_2]_x$.

Methanol (1.4c.c.,an excess) was added, with stirring to di-isopropylberyllium (1.4c.c., of a 3.5M-solution, 0.005 mole) at *ca.* -80°.Evolution of gas and precipitation of a white, insoluble, involatile solid, m.p., not below 360°, occurred at *ca.* -50°. This solid was washed with ether.

Found: Be, 12.63%.

$C_2H_6BeO_2$ requires Be, 12.68%.

The i.r. spectrum (Nujol mull) contained bands at 756s,br; 799s,br; 818m,sh; 1026m,sh; 1045s; 1114s; 1202w; 1263m cm.$^{-1}$

Beryllium methoxide was insoluble in boling ether, benzene and toluene to which pyridine had been added. It was similarly insoluble in boiling ether or hexane solutions of $(MeBeOMe)_4$. It did, however, dissolve in dimethylberyllium in refluxing ether to give a clear solution, after filtration from the excess beryllium methoxide. The white solid obtained by pumping this solution dry was identified as $(MeBeOMe)_4$ by its i.r. spectrum. Its p.m.r. spectrum in benzene (benzene standard) consisted of a doublet (+3.87, 4.13 p.p.m.), due to $\underline{CH_3}$-O and a singlet (+7.88) due to $\underline{CH_3}$-Be, in the ratio CH_3-O(total):$\underline{CH_3}$-Be = 1:1. [$(MeBeOMe)_4$ requires 1:1].

Reaction of di-t-butylberyllium with methanol-formation of t-butylberyllium methoxide tetramer, $(Bu^tBeOMe)_4$.

Di-t-butylberyllium diethyl ether complex (1.34g., 0.009 mole), in hexane (20c.c.), was cooled to ca. -60° and methanol (0.28g.,0.009 mole), in hexane (20c.c.), added. The yellow solution, formed initially, became colourless at room temperature. The solution was boiled for ten minutes and, on cooling, small plates slowly crystallized, m.p.,199°, after softening at 155°. Found: Be, 9.12; hydrolysable butyl, 59.25%; M, cryoscopically, 0.35, 0.70 wt.-% in benzene, 408, 412. $C_{20}H_{48}Be_4O_4$ requires Be, 9.27; hydrolysable butyl, 58.76%; M,388.

The i.r. spectrum (Nujol mull) contained absorptions at 505w; 690s,sh; 719s; 800s; 893s; 934w; 1004s,sh; 1033s; 1099s; 1182w; 1210m; 1266m cm.

This compound was only moderately soluble in benzene, but p.m.r. spectra could be recorded in this solvent. The spectrum of the recrystallized material consisted of singlets (τ 6.59, 8.97) due, respectively, to $\underline{CH}_3$-O and t-$\underline{C}_4\underline{H}_9$-Be protons, ratio on integration 1.0:3.2, but that of a sample which had not been recrystallized, but was pure by analysis, showed splitting of both signals into doublets. The $\underline{CH}_3$-O doublet was at τ 6.47, 6.69 and the t-$\underline{C}_4\underline{H}_9$-Be one at τ 8.63, 9.03, ratio 1.00:2.82. [$(Bu^tBeOMe)_4$ requires 1:3]. In both cases, TMS was the internal standard.

Reaction of di-t-butylberyllium with t-butanol-formation of t-butylberyllium t-butoxide dimer, $(Bu^tBeOBu^t)_2$.

t-Butanol (0.68g.,0.009 mole), in hexane (15c.c.), was added, with stirring, to di-t-butylberyllium diethyl ether complex (1.57g.,0.009 mole), in hexane (15c.c.), at room temperature, and caused the solution to be warmed to *ca.* 50°. The hexane was boiled then removed at low pressure to leave a white solid whichwas sublimed (40-50°/10^{-3}mm.), melting range 177-189° after previous softening at 53° and apparent decomposition at 108°. Found: Be, 6.44; hydrolysable butyl, 41.25%; M, cryoscopically, 0.49, 0.98, 1.36 wt.-% in benzene, 289, 294, 291.

$C_{16}H_{36}Be_2O_2$ requires Be, 6.48; hydrolysable butyl, 41.01%; M, 278.

The i.r. spectrum (Nujol mull) contained bands at 540w,sh; 547m; 617w; 667w; 694w; 800m,sh; 813s; 843s; 917m; 930m,sh; 958s; 1008m; 1033m; 1193m; 1252m; 1366m cm^{-1}.

The p.m.r. spectrum consisted of two singlets, τ 8.58 and 8.71 due, respectively, to t-$\underline{C}_4\underline{H}_9$-O and t-$\underline{C}_4\underline{H}_9$-Be, in the ratio 1.20:1.00. [$(Bu^tBeOBu^t)_2$ requires

1:1]. Benzene was used as solvent and TMS as reference.

Reaction of dimethylberyllium with ethylene oxide, a) in equimolar quantities-formation of methylberyllium n-propoxide tetramer, $(MeBeOPr^n)_4$.

Ethylene oxide (285N-c.c.,0.0127 mole) was condensed onto a cooled (-196°) solution of dimethylberyllium (0.0132 mole, a slight excess), in diethyl ether (7.5 c.c.). On warming to *ca.* 0°, a clear, colourless solution was obtained, and at room temperature, an exothermic reaction took place. Removal of solvent at low pressure left a white solid. The product was extracted with hot hexane (10c.c.) and crystallized by concentration of the solution to *ca.* 3c.c. Its i.r. and p.m.r. spectra were identical to those of $(MeBeOPr^n)_4$. It melted at 37-39°. (cf. 38-40° for a sample prepared from Me_2Be and Pr^nOH.)

b) in the molar ratio 1:2-formation of $(MeBeOPr^n)_4$.

The n-propoxide, in diethyl ether (5c.c.), was prepared as above and a further, equimolar, quantity of ethylene oxide condensed on. On warming to room temperature a clear solution was obtained, but no further evolution of heat was observed. Hexane (15c.c.) was added, the solution boiled, then the solvent removed, at low pressure, to leave a white solid. This was recrystallized after filtration from the very slight excess of dimethylberyllium, from hexane, m.p., 38-40°. Examination of its i.r. and p.m.r. spectra enabled it to be identified as $(MeBeOPr^n)_4$.

Reaction of dimethylberyllium with di-t-butyl peroxide-formation of methylberyllium t-butoxide tetramer.

Ether-free dimethylberyllium (0.005 mole) was covered with toluene (5c.c.), cooled to -196°, and di-t-butyl peroxide (0.4g., 0.0027 mole) added. On warming to room temperature, and filtering from the excess dialkyl, a colourless solution was obtained. On concentration of this solution, colourless crystals, identified by i.r. and p.m.r. (in benzene) spectra as $(MeBeOBu^t)_4$, were obtained. The volatile material from the reaction was shown, after fractionation, to contain methyl t-butyl ether by comparison of its i.r. spectrum (gas phase) with that of an authentic sample.

Reactions with aldehydes and ketones.

Reaction of dimethylberyllium with acetaldehyde-formation of methylberyllium isopropoxide tetramer, $(MeBeOPr^i)_4$.

Acetaldehyde (45.41 N-c.c., 0.002 mole) was condensed onto dimethylberyllium in diethyl ether (1.04 c.c. of a 1.96M-solution, 0.002 mole), at -196°, in a two-necked flask attached to the vacuum line. On warming to room temperature, a colourless solution was obtained, and no evolution of methane had taken place. Removal of solvent at low pressure left a white solid, identified as $(MeBeOPr^i)_4$ by i.r. and p.m.r. spectra.

Reaction of dimethylberyllium with acetone,

a) in equimolar quantities-formation of methylberyllium t-butoxide tetramer, $(MeBeOBu^t)_4$.

Acetone (36.35 N-c.c., 0.0016 mole) and dimethylberyllium (0.0016 mole), in diethyl ether (0.83c.c.), reacted together as above. No methane was evolved. Concentration of the solution caused $(MeBeOBu^t)_4$, identified by p.m.r. and i.r. spectra, to crystallize.

b) with an excess-formation of beryllium t-butoxide trimer $[Be(OBu^t)_2]_3$.

Methylberyllium t-butoxide (0.067g., 0.00068 mole), prepared as in a) reacted with acetone (15.23 N-c.c., 0.00068 mole) to yield $[Be(OBu^t)_2]_3$, identified by i.r. spectrum and analysis, but no methane.

Found: Be, 5.84; hydrolysable methyl, 0%.

$C_{24}H_{54}Be_3O_6$ requires Be, 5.81; hydrolysable methyl, 0%.

Reaction of diethylberyllium with diethylketone,

a) in equimolar amounts-formation of ethylberyllium triethylmethoxide trimer, $(EtBeOCEt_3)_3$.

The reaction of diethyl ketone (0.86g., 0.01 mole) and diethylberyllium (8.85c.c. of a 1.13M-solution, 0.01 mole), in diethyl ether (20c.c.), resulted in the formation of a yellow-coloured solution. At *ca.* -30°, the yellow colour disappeared with evolution of heat and formation of a colourless solution, from which, by pumping off the solvent, a colourless liquid was obtained.
Found: Be, 5.77; hydrolysable ethyl, 18.90%;
$C_9H_{20}BeO$ requires Be, 5.90; hydrolysable ethyl, 18.95%.

b) with an excess,-attempted formation of beryllium triethylmethoxide.

An excess (1.86g., 0.022 mole) of diethyl ketone, in diethyl ether (10c.c.), was added to diethylberyllium (9.1c.c. of a 1.1M-solution, 0.01 mole), in ether, at room temperature. Evaporation of solvent from the yellow solution so obtained gave a very viscous semi-solid, which could not be recrystallized from hexane at -70°, and was not investigated further.

Reactions of alkylberyllium alkoxides with bases.

Reaction of methylberyllium methoxide with 2,2'-bipyridyl-attempted formation of methyl(bipyridyl)beryllium methoxide, Me(bipy)BeOMe.

A slight molar excess of bipyridyl, in benzene (30c.c.), was added to methylberyllium methoxide (*ca.* 0.3 g.,), in benzene (10c.c.), to give an orange-yellow solution. Yellow crystals were slowly deposited and, on addition of hexane (10c.c.), there was further crystallization. These crystals were filtered, washed free from adherent bipyridyl with ether, and dried *in vacuo*.

Found: Be, 7.67; hydrolysable methyl, 7.10; bipyridyl, 38.64%.

$C_{12}H_{14}BeN_2O$ requires Be, 4.28; hydrolysable methyl, 7.11; bipyridyl, 73.92%.

Reaction of methylberyllium methoxide with pyridine, a) in equimolar quantities-attempted formation of methyl(monopyridine)beryllium methoxide, Me(py)BeOMe.

The reaction of methylberyllium methoxide (0.55g., 0.01 mole) and pyridine (0.79g., 0.01 mole), in diethyl ether (30c.c.), at room temperature, gave a pale yellow solution. Removal of ether, addition of hexane (10c.c.), and standing at -78° for two hours, caused a pale yellow substance to be deposited from solution.

Found: Be, 6.50; hydrolysable methyl, 13.05; pyridine, 68.96%.

$C_7H_{11}BeNO$ requires Be, 6.71; hydrolysable methyl, 11.19; pyridine, 58.95%.

The product did not completely redissolve in ether, but crystallization from the filtrate yielded the complex $Me_2Be.py_2$, m.p.,90-92° (Lit.[36] 91-92°), also identified by i.r. spectrum.

b) with an excess-formation of methyl(dipyridine)beryllium methoxide monomer, $Me(py_2)BeOMe$.

Pyridine (an excess) was added to methylberyllium methoxide (0.30g., 0.0055 mole), in hexane (10c.c.), at room temperature, to give a colourless solution. On standing, this solution deposited small, white crystals, which were recrystallized from benzene-hexane (2:1) mixture as plates, m.p.,112-114°.

Found: Be, 4.24; hydrolysable methyl, 7.07%; M, cryoscopically, 0.61, 1.21 wt.-% in benzene, 218, 229.

$C_{12}H_{16}BeN_2O$ requires Be, 4.23; hydrolysable methyl, 7.04%; M, 213.

The i.r. spectrum (Nujol mull) contained absorptions at 582w; 631w,sh; 650m,sh; 687s,sh; 700s; 754s; 794s,br; 876m,sh; 1014s,sh; 1040s; 1069s; 1095s; 1151m; 1179m; 1212m; 1259m; 1572w; 1608m cm.$^{-1}$

Reaction of methylberyllium t-butoxide with pyridine, a) in equimolar quantities-formation of methyl(monopyridine)beryllium t-butoxide, Me(py)BeOBu^t.

To a solution of methylberyllium t-butoxide (0.3g., 0.003 mole), in diethyl ether (15c.c.), was added pyridine (0.24g., 0.003 mole), in ether (10c.c.). A clear colourless solution was obtained, but, on concentration to *ca.* 10c.c., the complex crystallized, and was recrystallized from hot ether by the dropwise addition of hexane, as small plates, m.p., 134-136^o.

Found: Be, 5.04; hydrolysable methyl, 8.60; pyridine, 45.01%; M, cryoscopically, 0.35, 0.70 wt.-% in benzene, 217, 248.

$C_{10}H_{17}BeNO$ requires Be, 5.13; hydrolysable methyl, 8.52; pyridine, 44.89%; M, 176.

The i.r. spectrum (Nujol mull) contained bands at 634w; 649w; 699m; 732m; 760m; 798s; 838m; 977m; 1013s; 1042s; 1070s; 1088s; 1176m; 1208m; 1259s; 1605w cm.$^{-1}$

The p.m.r. spectrum in benzene, with TMS as internal standard, consisted of a multiplet (τ 3.17-3.25), due to $\underline{C_5H_5}N$, and two singlets (τ 8.82 and 10.26), due, respectively, to t-$\underline{C_4H_9}$-O and $\underline{CH_3}$-Be, in the ratio 1.73:3.10:1.00. [Me(py)BeOBu^t requires 1.67:3.00:1.00].

The volatile material pumped from a benzene (5c.c.) solution of this complex (0.00055 mole) was shown, by u.v. spectrophotometry, to contain 37.20% by weight of the pyridine originally contained in the complex.

b) with an excess-formation of methyl(monopyridine) beryllium t-butoxide.

Pyridine (2c.c., an excess) was added, with stirring, to methylberyllium t-butoxide (0.94g., 0.0097 mole), in diethyl ether (10c.c.). On concentration to ca. 5c.c., and addition of hexane (10c.c.), white crystals separated, m.p., 135-136°.

Found: Be, 5.07; hydrolysable methyl, 8.56%.

$C_{10}H_{17}BeNO$ requires Be, 5.10; hydrolysable methyl, 8.52%.

Reaction of methylberyllium phenoxide diethyl ether complex with pyridine-attempted formation of methyl-(monopyridine)beryllium phenoxide, Me(py)BeOPh.

Pyridine (0.31g., 0.0039 mole), in benzene (15c.c.), was added to the ether complex (0.74g., 0.0039 mole), in benzene (15c.c.). As the addition proceeded, white crystals were formed, and were recrystallized, after filtration from some insoluble matter, from boiling benzene, as colourless needles.

Found: Be, 4.70; hydrolysable methyl, 6.18; pyridine, 37.26%.

$C_{12}H_{13}BeNO$ requires Be, 4.59; hydrolysable methyl, 7.65; pyridine, 40.28%.

Reaction of t-butylberyllium t-butoxide with pyridine-attempted formation of t-butyl(monopyridine)beryllium t-butoxide, $Bu^t(py)BeOBu^t$.

Addition of pyridine (0.87g., 0.0011 mole), in diethyl ether (20c.c.), to t-butylberyllium t-butoxide (1.53g., 0.0011 mole), in ether (20c.c.), resulted in the formation of a pale yellow solution. Removal of most of the ether at low pressure, and addition of hexane (30c.c.), caused the separation of pale yellow crystals, which decomposed at 105° then melted over the range 180-186°.

Found: Be, 3.75; hydrolysable butyl, 33.82; pyridine, 47.92%.

$C_{13}H_{23}BeNO$ requires Be, 4.14; hydrolysable butyl, 26.15; pyridine, 36.23%.

The p.m.r. spectrum (benzene solvent and reference) contained singlets at +5.71 and +5.99 p.p.m., identifiable as due to t-$\underline{C_4H_9}$-O and t-$\underline{C_4H_9}$-Be protons respectively, and in the ratio 1:4.

Reaction of t-butylberyllium t-butoxide with 4-dimethylaminopyridine-attempted formation of t-butyl(mono-4-dimethylaminopyridine)beryllium t-butoxide, $Bu^t(Me_2N.C_5H_4N)BeOBu^t$.

Addition of the amine (1.43g., 0.012 mole), in benzene (20c.c.), to a stirred solution of the butoxide (1.62g., 0.012 mole), in ether (40c.c.), resulted in the formation of a yellow solution. Removal of solvent, at low pressure, down to ca. 20c.c., caused the separation of yellow crystals, which could be recrystallized from hot benzene by addition of hexane.

Found: Be, 2.19; hydrolysable butyl, 27.53%.

$C_{15}H_{28}BeN_2O$ requires Be, 3.46; hydrolysable butyl, 21.84%.

Reaction of beryllium t-butoxide with 2,2'-bipyridyl-attempted formation of bipyridylberyllium t-butoxide.

Bipyridyl (ca. 0.6g., a slight excess) in ether (10c,c.), was added to the butoxide (ca. 0.5g.,), in ether (10c.c.), to give a faintly yellow solution. Removal of solvent, at low pressure, left a cream solid, which was redissolved in hexane (10c.c.). Cooling of this solution to ca. -30° caused a white solid to crystallize, leaving the filtrate colourless. This solid was identified, by its i.r. spectrum and melting point, as 2,2'-bipyridyl. It did not contain any Bu^t-O groups (p.m.r. spectrum in benzene). The filtrate, on pumping dry, was seen to contain a white solid, identifiable as $[(Bu^tO)_2Be]_3$, contaminated with a small amount of 2,2'-bipyridyl, by i.r. and p.m.r. spectra.

Reactions with thiols and thiophenol.

Reaction of dimethylberyllium with isopropylthiol-attempted preparation of methylberyllium isopropylsulphide, $MeBeSPr^i$, a) in ether.

The thiol (0.76g., 0.01 mole), in hexane (10c.c.), was added, with stirring, to dimethylberyllium in ether (5.7c.c. of a 1.96M-solution, 0.012 mole), at -50°. Gas was evolved at *ca.* 0°. Removal of solvent at low pressure left a sticky white solid, which was treated with boiling hexane in an attempt to remove coordinated ether, but this yielded a very viscous glue. Its p.m.r. spectrum, in benzene with TMS as reference, consisting of an unresolved multiplet (τ 6.07→6.84), a doublet due to $(\underline{CH}_3)_2$-C (τ 8.52, 8.63), a triplet, due to coordinated ether (τ 8.90, 9.02, 9.13) and a singlet, due to $\underline{CH}_3$-Be (τ 10.49), was recorded, but it was not investigated further.

b) in benzene.

Ether-free dimethylberyllium (0.011 mole) was covered with benzene (20c.c.) and stirred whilst the thiol (0.76g., 0.01 mole), in benzene (10c.c.), was added dropwise, at room temperature, over thirty minutes. The addition was accompanied by steady evolution of gas, and, after filtration from the excess dimethylberyllium, a clear solution was obtained. Removal of solvent at low pressure left a sticky, white solid, which, after several minutes' exposure to a good vacuum, would not completely redissolve in benzene and appeared, even after treatment with boiling hexane (10c.c.), to be inhomogeneous. The p.m.r. spectrum of the benzene-soluble material was recorded (benzene solvent and standard) and consisted of a doublet, due to $(\underline{CH}_3)_2$-C (+5.78, 5.90 p.p.m.) and a singlet, due to $\underline{\text{CH}}_3$-Be (+7.59), in the ratio 3:1. After it had been left for sixteen hours, the same sample contained much solid matter, insoluble in benzene, and the ratio of the above signals was then 4.4:1. (MeBeSPr^i requires 2:1). The solid material was filtered off and shown to consist partly of dimethylberyllium by isolation of the pyridine complex, $\text{Me}_2\text{Be.py}_2$, m.p., 91° (lit.[36], 91-92°), from the ether extract.

<u>Reaction of dimethylberyllium with t-butylthiol-formation of methylberyllium t-butylsulphide tetramer, (MeBeSBu^t)$_4$.</u>

t-Butylthiol (0.81g., 0.009 mole), in ether (20c.c.), was added to a cooled (*ca.* -50°) solution of dimethylberyllium (0.009 mole), in ether (4.6c.c.). Gas was evolved on warming to room temperature, and removal of solvent at low pressure left a sticky, white solid, which was exposed to a vacuum for twelve hours, then recrystallized from hot benzene as a fine powder, decomposing at 142° with formation of a white sublimate. Found: Be, 7.86; hydrolysable methyl, 13.05%; M, cryoscopically, 0.37, 0.74 wt.-% in benzene, 460, 444. $\text{C}_{20}\text{H}_{48}\text{Be}_4\text{S}_4$ requires Be, 7.98; hydrolysable methyl, 13.27%; M, 452.

The i.r. spectrum (Nujol mull) contained bands at 510m,br; 543w,br,sh; 581m,br; 799s; 814m,sh; 859m,sh; 1018s; 1089s; 1159m; 1172m,sh; 1219w; 1263s; 1366m cm.$^{-1}$

The p.m.r. spectrum (benzene solvent; TMS reference) consisted of a singlet (τ8.46), due to $(\underline{\text{CH}}_3)_3$-C, and a singlet ($\tau$10.23), due to $\underline{\text{CH}}_3$-Be, in the ratio 3.11:1.00. [(MeBeSBu^t)$_4$ requires 3:1]. Benzene solutions (*ca.* 0.1M) of this compound slowly deposited a white solid (containing dimethylberyllium, identified as above) on standing.

Reaction of dimethylberyllium with thiophenol-formation of methylberyllium phenylsulphide diethyl ether complex dimer, $(MeBeSPh.OEt_2)_2$.

Thiophenol (1.02c.c., 0.009 mole), in ether (10c.c.), was added to a stirred solution of dimethylberyllium (0.01 mole), in ether (5c.c.), at ca. -80°. Gas was evolved on warming to ca. 0°, and subsequent removal of ether at reduced pressure left a viscous oil, treatment of which with boiling hexane (10c.c.) gave a white solid. This was recrystallized from toluene/hexane (1:2) mixture (10c.c.) as a microcrystalline powder, decomposing over the range 66-96°.

Found: Be, 4.31; hydrolysable methyl, 7.26%; M, cryoscopically, 0.43, 0.86 wt.-% in benzene, 414, 428. $C_{22}H_{36}Be_2O_2S_2$ requires Be, 4.35; hydrolysable methyl, 7.25%; M, 414.

The i.r. spectrum (Nujol mull) contained absorptions at 571w,br; 691s; 741s; 776m,sh; 800s,br; 836w,sh; 886w; 904w,sh; 1026s; 1071m,sh; 1087s; 1149w,sh; 1179w,sh; 1263m; 1563w,sh; 1580m cm^{-1}.

The p.m.r. spectrum (in d_6-benzene with TMS as reference) was made up of a triplet, due to phenyl groups (τ 2.86, 2.97, 3.05), a quartet, due to $CH_3-\underline{CH_2}-O$ (τ 6.29 6.40, 6.51, 6.61), a broad triplet, $\underline{CH_3}-CH_2-O$ (centred on τ 8.93) and a singlet, due to $\underline{CH_3}-Be$ (τ 10.38).

Reaction of dimethylberyllium with 2-dimethylaminoethanethiol-formation of methylberyllium 2-dimethylaminoethylsulphide trimer, $(MeBeSC_2H_4NMe_2)_3$.

Dimethylberyllium (0.39g., 0.01 mole), in ether (10c.c.), was cooled to ca. -50° and the thiol (1.05g., 0.01 mole), in ether (20c.c.), added slowly. Gas was evolved, and white crystals deposited. These were filtered and washed with ether (3x10c.c.). On heating,

they decomposed from 194°.
Found: Be, 7.12; hydrolysable methyl, 11.81%; M, cryoscopically, 1.31, 1.36 wt.-% in benzene, 398, 399. $C_{15}H_{39}Be_3N_3S_3$ requires Be, 7.05; hydrolysable methyl, 11.71%; M, 384.

The i.r. spectrum (Nujol mull) contained absorptions at 523w,br; 552w,br; 682m,sh; 707s,br; 776m; 802s; 816s,ssh; 894m; 950m; 1005s; 1025s; 1033s; 1098m; 1121m; 1170w; 1189m; 1220w; 1247w; 1263m; 1304m cm.$^{-1}$

This compound, though only very sparingly soluble in ether at room temperature, nevertheless dissolved quite readily in benzene. Its p.m.r. spectrum in this solvent (benzene reference also) consisted of a broad signal centred at +4.75 p.p.m., due to $-\underline{CH_2}-\underline{CH_2}-$, an unequal doublet (+5.25, 5.32, in ratio 1:2), due to $(\underline{CH_3})_2-N$, and a singlet (+7.89), due to $\underline{CH_3}-Be$.

Reaction of diethylberyllium with methanethiol-attempted preparation of ethylberyllium methylsulphide, EtBeSMe.

Methanethiol (306N-c.c., 0.014 mole) was condensed onto diethylberyllium in hexane (7.2c.c. of a 1.90M-solution, 0.014 mole), at -196°. Gas was evolved vigorously on warming to ca. -70°, and a white, insoluble precipitate formed. This was filtered, and pumped dry. The filtrate was observed to contain a colourless liquid, involatile at room temperature, which gave the characteristic orange $Et_2Be.py_2$ (turning brown at ca. 90-95°), on addition of pyridine.
Analysis of the precipitate was as follows:
Found: Be, 10.06; hydrolysable ethyl, 31.42%.
C_3H_8BeS requires Be, 10.61; hydrolysable ethyl, 34.12%.

The i.r. spectrum (Nujol mull) contained absorptions at 549m,br,sh; 628s,br,sh; 649s,br; 704m; 717w; 767m,sh;

790m; 884w; 908w; 959w,br,sh; 1013s; 1082m; 1135w,sh; 1171w,sh; 1253m cm.$^{-1}$

Reaction of diethylberyllium with ethanethiol, a) in equimolar quantities, formation of ethylberyllium-ethylsulphide tetramer, $(EtBeSEt)_4$.

Ethanethiol (240N-c.c., 0.0107 mole) was condensed onto diethylberyllium (0.0107 mole), in hexane (5.6c.c.), at -196^{o}. Gas was evolved at *ca.* -30^{o}, and subsequent removal of solvent, at low pressure, from the colourless solution, left a white solid which was purified by exposure to a vacuum for one hour followed by washing with pentane (5c.c.), m.p.,$75-77^{o}$.

Found: Be, 9.03; hydrolysable ethyl, 29.52%; M, cryoscopically, 0.94, 1.42 wt.-% in benzene, 405, 413. $C_{16}H_{40}Be_4S_4$ requires Be, 9.11; hydrolysable ethyl, 29.29%; M, 396.

The i.r. spectrum (Nujol mull) contained bands at 512m,br,sh; 530m,br; 646m; 664s; 670m,sh; 759w,sh; 764w; 798s; 856m; 915w; 954w; 978m,sh; 990m; 1017s; 1055m; 1091m; 1193w; 1264s; 1412w cm^{-1}.

The p.m.r. spectrum (in benzene, with this as reference) consisted of quartets (+4.35, 4.48, 4.59, 4.72 p.p.m.) and (+6.81, 6.92, 7.05, 7.18) due, respectively, to $CH_3-\underline{CH_2}-S$ and $CH_3-\underline{CH_2}-Be$, and unresolved, overlapping signals (+5.55→6.23), due to the two methyl groups.

b) with an excess-formation of beryllium ethylsulphide polymer, $[(EtS)_2Be]_x$.

Ethanethiol (448N-c.c., 0.02 mole) reacted with diethylberyllium (0.01 mole), in ether (9c,c.), at *ca.* -30^{o}, to give a white, insoluble precipitate. This was filtered, washed with ether (2x10c.c.) and dried *in vacuo.* It did not melt below 360^{o}.

Found: Be, 6.84%.

$C_4H_{10}BeS_2$ requires Be, 6.89%.

The i.r. spectrum (Nujol mull) contained absorptions at 537s,br; 591s; 664m; 724w; 735w,br; 763w; 800m,br; 971m; 1020m; 1057m; 1075m; 1096m,br; 1149w,sh; 1266s; 1359m cm^{-1}.

This compound was insoluble in boiling ether and in hydrocarbons, but when a sample (0.207g., 0.0016 mole) was covered with diethyl ether (10c.c.) and mixed with a slight deficiency of diethylberyllium, in ether (1.45c.c.) most of it dissolved immediately at room temperature. After filtration from the excess, the solution was evaporated to dryness and the residue identified as $(EtBeSEt)_4$ by i.r. and p.m.r. spectra.

Reaction of diethylberyllium with isopropylthiol-formation of ethylberyllium isopropylsulphide tetramer, $(EtBeSPr^i)_4$.

Reaction of diethylberyllium (0.011 mole), in hexane (5.6c.c.), and isopropylthiol (1.00c.c., 0.011 mole), in hexane (10c.c.), at ca. -20°, gave a colourless solution which yielded a white solid on pumping dry. This was washed with pentane (3c.c.), m.p.,58-60°.

Found: Be, 8.04; hydrolysable ethyl, 25.79%; M, cryoscopically, 0.86, 1.30 wt.-% in benzene, 448, 434.

$C_{20}H_{48}Be_4S_4$ requires Be, 7.98; hydrolysable ethyl, 25.66%; M, 452.

The i.r. spectrum (Nujol mull) contained absorptions at 477s,br, 502m,br,sh; 619m,sh; 642s,br; 652s,sh; 667m,sh; 718s,br; 795s; 818m,sh; 879m; 910m; 921m; 948m; 982s; 1046s; 1082w; 1094w,sh; 1144s; 1179w; 1241s; 1295w; 1404m cm^{-1}.

The p.m.r. spectrum (benzene solvent and standard) consisted of a quintet (+3.51, 3.62, 3.73, 3.84, 3.94 p.p.m.), due to C-H, a doublet (+5.73, 5.84), due to $(\underline{CH_3})_2$-C and a quartet (+6.62, 6.76, 6.90, 7.03), due to CH_3-$\underline{CH_2}$-Be. The signal expected for $\underline{CH_3}$-CH_2-Be was obscured by that of the $(\underline{CH_3})_2$-C group.

Reaction of diethylberyllium with t-butylthiol-formation of ethylberyllium t-butylsulphide tetramer, $(EtBeSBu^t)_4$.

Diethylberyllium (0.011 mole), in hexane (5.6c.c.), was cooled to -40°, and t-butylthiol (1.20c.c.,0.011 mole), in hexane (10c.c.), added. Evolution of gas occurred at ca. 0°, and evaporation to dryness (at low pressure) of the colourless solution left a viscous, white solid. Prolonged (ca. two hours) pumping of this solid, followed by washing with pentane (3c.c.), yielded a white solid, which softened and became wet (decomp.) on heating to 65°.

Found: Be, 7.19; hydrolysable ethyl, 22.62%; M, cryoscopically, 0.43, 0.86 wt.-% in benzene, 522, 512. $C_{24}H_{56}Be_4S_4$ requires Be, 7.10; hydrolysable ethyl, 22.83%; M, 508.

The i.r. spectrum (Nujol mull) contained absorptions at 510m,br; 587s,br; 722w; 730w,sh; 798m; 818m,sh; 862w; 909w,br; 1019s; 1075m,br,sh; 1158s; 1169m,sh; 1224w; 1262m; 1369s cm^{-1}.

The p.m.r. spectrum in benzene, with this as reference, consisted of a singlet (+5.71p.p.m.), due to $(\underline{CH_3})_3$-C, and a quartet (+6.78, 6.91, 7.00, 7.12), due to CH_3-$\underline{CH_2}$-Be. The triplet expected for the $\underline{CH_3}$-CH_2-Be group was not distinguishable, owing to its proximity to that of the $(\underline{CH_3})_3$-C group.

A solution of this compound, in hexane, was warmed to ca. 50°. At this temperature, a white solid was precipitated immediately. It was identified, by i.r. spectrum, as beryllium t-butylsulphide, $[Be(Bu^tS)_2]_x$.

Reaction of di-isopropylberyllium with ethanethiol-formation of isopropylberyllium ethylsulphide diethyl ether complex dimer, $(Pr^iBeSEt.OEt_2)_2$.

Di-isopropylberyllium (2.85c.c. of a 3.5M-solution, 0.01 mole) was cooled to -196° while ethanethiol (224N-c.c., 0.01 mole) was condensed on. On warming to ca. 0°, gas was evolved and a clear solution obtained. Removal of solvent at low pressure left a white solid, which was recrystallized from hexane (10c.c.). On heating, it decomposed, with loss of ether, from ca. 160°.
Found: Be, 4.82; hydrolysable propyl, 23.10%; M, cryoscopically, 0.88, 1.76 wt.-% in benzene, 370, 385. $C_{18}H_{44}Be_2O_2S_2$ requires Be, 4.82; hydrolysable propyl, 23.00%; M, 374.

The i.r. spectrum (Nujol mull) contained absorptions at 545m,br,sh; 580s,br; 652s; 660s,sh; 672m,sh; 736w; 760m; 802m; 833w,sh; 886m; 946m; 972m; 1021m; 1036m,sh; 1092m; 1131w,sh; 1208w; 1266s cm^{-1}.

The p.m.r. spectrum contained unresolved, overlapping signals, centred at +4.42 and +5.91 p.p.m., relative to benzene as standard.

Reaction of di-isopropylberyllium with isopropylthiol-attempted preparation of isopropylberyllium isopropylsulphide, Pr^iBeSPr^i.

isoPropylthiol (0.94c.c., 0.01 mole), in diethyl ether (10c.c.), was added to di-isopropylberyllium (0.01 mole), in ether (2.8c.c.), at ca. -50°. Gas was evolved at ca. 0° to give a colourless solution which, on removal of solvent at low pressure, left a viscous glue. This dissolved in hexane (10c.c.), but could not be recrystallized, even at -60°. It was not investigated further.

Reaction of di-isopropylberyllium with t-butylthiol-formation of beryllium t-butylsulphide polymer, $[(Bu^tS)_2Be]_x$.

Di-isopropylberyllium (0.01 mole), in diethyl ether (2.8c.c.), was cooled to ca. -100° whilst t-butylthiol (1.12c.c., 0.01 mole), in ether (10c.c.), was added slowly. Evolution of gas occurred on warming to ca. 0°, and a colourless solution was obtained. On standing, this solution slowly deposited a white precipitate, and further precipitation occurred on addition of hexane (10c.c.). This precipitate would not redissolve in ether, so it was filtered and washed with this solvent (10c.c.). Subsequent removal of solvent, by pumping, from the filtrate left a colourless liquid, identified as di-isopropylberyllium by isolation of the dipyridine complex, $Pr^i_2Be.py_2$, m.p.,110° (cf. 111-112°, above). The solid decomposed (turned grey) at 336°, but did not melt below 360°.

Found: Be, 4.84; hydrolysable propyl, 0%.

$C_8H_{18}BeS_2$ requires Be, 4.82; hydrolysable propyl, 0%.

The i.r. spectrum (Nujol mull) contained absorptions at 506m,br; 585s; 605s,sh; 722w; 735w,sh; 799m; 819m,sh; 862m; 1018m; 1092m; 1155s; 1220w; 1261m cm^{-1}.

Reaction of diethylberyllium with diethyl disulphide-formation of ethylberyllium ethylsulphide tetramer.

Diethylberyllium (1.45c.c. of a 1.09M-solution, 0.0016 mole), in diethyl ether, was cooled to -196° and diethyl disulphide (0.192c.c., 0.0016 mole) added. On warming to room temperature, a clear solution was obtained. This was evaporated to dryness to leave a white residue, which was washed with pentane (0.5c.c.) and identified as $(EtBeSEt)_4$ by i.r. and p.m.r. spectra.

The volatile condensate from the reaction contained diethyl sulphide, which could be separated from ether by fractionation under vacuum and identified by i.r. spectrum.

Reactions of alkylberyllium alkylsulphides with bases.

Reaction of impure ethylberyllium methylsulphide with excess diethyl ether-attempted preparation of ethylberyllium methylsulphide diethyl ether complex.

The sulphide (mainly EtBeSMe) was washed with ether (10c.c.), which caused it to diminish in volume. On evaporation of ether from the filtrate, at low pressure, diethylberyllium, identified by isolation of its dipyridine complex, was left. The solid left behind was analysed. It could not be completely dissolved in ether.

Found: Be, 9.26; hydrolysable ethyl, 14.46%. These figures do not correspond to any simple compound.

Reaction of impure ethylberyllium methylsulphide with excess pyridine-attempted preparation of ethylberyllium methylsulphide pyridine complex.

Pyridine (3c.c., an excess) was added to the impure sulphide (*ca.* 0.5g.,), covered with toluene (20c.c.). On stirring, the solid dissolved to give a yellow solution from which, by addition of hexane (20c.c.), pale cream crystals could be separated.

Found: Be, 5.66; hydrolysable ethyl, 4.25%. These figures do not correspond to any simple compound.

Reaction of ethylberyllium ethylsulphide with excess pyridine-attempted preparation of ethylberyllium ethylsulphide pyridine complex.

The sulphide (*ca.* 0.5g.), in diethyl ether (10c.c.), was mixed with pyridine (4c.c., an excess), to give a solution which was faintly yellow in colour. The yellow syrup obtained by removal, at low pressure, of all the ether, could not be recrystallized, even from hexane at -50°, and, on exposure to a vacuum, it slowly lost its colour, becoming, finally, a white solid, identified, by i.r. spectrum, as $(EtBeSEt)_4$.

Reaction of ethylberyllium isopropylsulphide with excess pyridine-attempted preparation of ethylberyllium isopropylsulphide pyridine complex.

Yellow solutions of the sulphide and pyridine (in excess), in hexane, deposited no solid material at *ca.* -60°, and, on pumping dry followed by exposure to a vacuum, gave pure $(EtBeSPr^i)_4$, identifiable by i.r. spectrum.

Reaction of ethylberyllium t-butylsulphide with excess tetrahydrofuran-formation of ethylberyllium t-butylsulphide tetrahydrofuran complex, monomer, $EtBeSBu^t.THF$.

t-Butylthiol (0.9c.c.,0.008 mole), in hexane (10 c.c.), was added to diethylberyllium in hexane (4.2c.c. of a 1.90M-solution, 0.008 mole), as described above. After reaction was complete, tetrahydrofuran (5c.c., an excess) was added and the solution concentrated at low pressure to *ca.* 3c.c., by which time the adduct had crystallized. Pentane (5c.c.) was added, and the *product* recrystallized from the pentane/hexane mixture, m.p.,88°. Found: Be, 4.57; hydrolysable ethyl, 14.41%; M, cryoscopically, 0.67, 1.00 wt.-% in benzene, 210, 206. $C_{10}H_{22}BeOS$ requires Be, 4.53; hydrolysable ethyl, 14.57%; M, 199.

The i.r. spectrum (Nujol mull) contained absorptions at 491m,br; 546m,br; 590m; 630m; 654m; 665w,sh; 690w,br; 720w; 776m,sh; 790s,br; 814m,sh; 869s; 912w; 937w; 951w; 977m; 1020s; 1062m; 1147m; 1164m,sh; 1200w; 1247m; 1324w,sh; 1342m cm^{-1}.

The p.m.r. spectrum (benzene solvent and standard) was complex, but a multiplet (+3.25→3.48 p.p.m.), due to THF protons, a singlet (+5.59), due to $(\underline{CH_3})_3$-C, and a quartet (+6.70, 6.84, 6.97, 7.09), due to CH_3-<u>CH_2</u>-Be, could be distinguished.

<u>Reaction of ethylberyllium t-butylsulphide with pyridine-</u>
<u>a) in equimolar amounts-formation of ethyl(monopyridine)-beryllium t-butylsulphide dimer, $(EtpyBeSBu^t)_2$.</u>

Diethylberyllium (0.005 mole) and t-butylthiol (0.005 mole) reacted together in ether (10c.c.), then pyridine (0.005 mole), in hexane (5c.c.), was added. A colourless solution was obtained. The solvent was removed by pumping to leave a white solid, which was recrystallized from toluene/hexane (1:2) mixture (15c.c.) at <u>ca.</u> -30°, m.p., 99-107° with decomposition.

Found: Be, 4.34; hydrolysable ethyl, 14.18; pyridine, 37.98%; M, cryoscopically, 0.65, 1.30 wt.-% in benzene, 357, 372.

$C_{22}H_{38}Be_2N_2S_2$ requires Be, 4.38; hydrolysable ethyl, 14.08; pyridine, 38.34%; M, 412.

The i.r. spectrum (Nujol mull) contained bands at 547m; 591w; 662w; 667w; 685w; 703m; 721w; 757m; 800s,br; 865w; 986m,sh; 1018s; 1050s; 1073s; 1094s,sh; 1160m; 1217m; 1266m; 1575w; 1613m cm^{-1}.

<u>b) with an excess-formation of ethyl(dipyridine)beryllium t-butylsulphide monomer, $Etpy_2.BeSBu^t$.</u>

Pyridine (4c.c., an excess) was added to a hexane solution of ethylberyllium t-butylsulphide (0.008 mole), to give a yellow solution. After five minutes, a yellow compound had been precipitated from the solution. It was recrystallized from boiling toluene/hexane (2:1) mixture (15c.c.) as lemon-coloured needles, m.p., 129-130° to a yellow liquid.

Found: Be, 3.17; hydrolysable ethyl, 10.17; pyridine, 56.44%; M, cryoscopically, 0.64, 1.28 wt.-% in benzene, 300, 292.

$C_{16}H_{24}BeN_2S$ requires Be, 3.17; hydrolysable ethyl, 10.17; pyridine, 55.46%; M, 285.

The i.r. spectrum (Nujol mull) contained absorptions at 484m,br; 544s,br; 593w,br; 633m,sh; 647s; 655s; 664s,sh; 686s,br; 703s,br; 764s; 794s; 826w; 912m; 943m; 955m,sh; 982s; 1014m; 1048s; 1069s; 1098w,sh; 1159s; 1180m,sh; 1215m; 1244w; 1264w; 1355s; 1572w; 1610m cm^{-1}.

The complex rapidly turned white on exposure to air.

Reaction of ethylberyllium t-butylsulphide tetrahydrofuran complex with 2,2'-bipyridyl-formation of ethyl(bipyridyl)-beryllium t-butylsulphide monomer, Et(bipy)BeSBu^t.

Addition of 2,2'-bipyridyl (0.25g., 0.0016 mole) to the tetrahydrofuran complex (0.32g., 0.0016 mole), in diethyl ether (15c.c.), resulted in a blood-red solution, which slowly deposited orange plates, m.p., 133-5° with decomposition.

Found: Be, 3.22; hydrolysable ethyl, 10.16; bipyridyl, 54.79%.

$C_{16}H_{22}BeN_2S$ requires Be, 3.19; hydrolysable ethyl, 10.24; bipyridyl, 55.12%.

This complex was insoluble in hexane and benzene, and was only presumed monomeric.

The i.r. spectrum (Nujol mull) contained absorptions at 616m; 679s; 736m; 754m; 767s; 776s; 797m; 812m,sh; 822w,sh; 943w; 976m; 1020m; 1033m; 1056m; 1099m; 1120w,sh; 1156m; 1263m; 1316m; 1355m; 1562w; 1610m; cm^{-1}.

Reaction of isopropylberyllium ethylsulphide diethyl ether complex with an equimolar amount of pyridine-formation of isopropyl(monopyridine)beryllium ethylsulphide dimer, $(Pr^i py.BeSEt)_2$.

The diethyl ether complex (1.87g., 0.01 mole) was dissolved in diethyl ether (10c.c.) and pyridine (0.79g., 0.01 mole), in ether (10c.c.), added slowly. A yellow-coloured solution was obtained. The yellow product

obtained when solvent was removed at low pressure, was recrystallized from toluene/hexane (1:3) mixture (12c.c.) as plates, m.p., 96-8°, with decomposition.
Found: Be, 4.68; hydrolysable propyl, 22.43; pyridine, 41.31%; M, cryoscopically, 0.86, 1.72 wt.-% in benzene, 373, 376.
$C_{20}H_{34}Be_2N_2S_2$ requires Be, 4.70; hydrolysable propyl, 22.40; pyridine, 41.14%; M, 384.

The i.r. spectrum (Nujol mull) contained bands at 544s; 568s; 656m; 667m; 670m,sh; 690s; 704s,sh; 722w; 746m; 752m,sh; 765m; 773w,sh; 796w; 876m; 940m; 975w; 1018m; 1053s; 1072s; 1092w,sh; 1155w; 1193w; 1220m; 1263m; 1570w; 1613m cm^{-1}.

The p.m.r. spectrum (benzene solvent and reference) was complex, due to overlapping signals, but the triplet due to $\underline{CH}_3$-CH_2-S (+5.41, 5.53, 5.66 p.p.m.) and the doublet due to $(\underline{CH}_3)_2$-C-Be (+5.71, 5.82) could be resolved on an expanded scale factor.

Reaction of impure isopropylberyllium isopropylsulphide with excess pyridine-formation of isopropyl(dipyridine)-beryllium isopropylsulphide monomer, $Pr^i py_2.BeSPr^i$.

The glue obtained from the reaction of di-isopropylberyllium with isopropylthiol (above) was redissolved in hexane (10c.c.) and pyridine (5c.c., an excess) added. A yellow solution resulted, and, on stirring of this solution for five minutes, a bright yellow solid separated and was recrystallized from the hexane as needles, melting range 75-81° (decomposition).
Found: Be, 3.15; hydrolysable propyl, 14.99; pyridine, 54.81%; M, cryoscopically, 0.97, 1.93 wt.-% in benzene, 287, 292.
$C_{16}H_{24}BeN_2S$ requires Be, 3.17; hydrolysable propyl, 15.09;

pyridine, 55.46%; M, 285.

The i.r. spectrum (Nujol mull) contained absorptions at 551m,br; 590m,br; 643m; 666m; 671m; 703s; 739s; 759m; 772m,sh; 799m; 870m; 886w,sh; 939m; 1014s; 1046s; 1065s; 1093m,sh; 1148m; 1208m; 1242m; 1263m; 1309w; 1570m; 1610s cm^{-1}

Reaction of beryllium t-butylsulphide with 2,2'-bipyridyl -formation of (bipyridyl)beryllium t-butylsulphide monomer, $(Bu^tS)_2Be.bipy$.

The sulphide (0.76g., 0.0041 mole) was covered with toluene (15c.c.). The toluene was boiled and kept at *ca.* 100° whilst bipyridyl (0.66g., 0.0042 mole), in toluene (15c.c.), was added. An orange solution was formed, but not all the solid would dissolve, even in boiling toluene. The suspension was stirred overnight, after which, filtration yielded the ochre-coloured *complex*, decomposing to a black tar at 290-295°.

Found: Be, 2.61; bipyridyl, 45.87%.

$C_{18}H_{26}BeN_2S_2$ requires Be, 2.63; bipyridyl, 45.47%.

The complex was relatively air-stable, only turning white in air after about two hours' exposure. It did not dissolve to any appreciable extent in benzene, hence it is only presumed to be monomeric.

The i.r. spectrum (Nujol mull) contained absorptions at 513w; 594w; 615m; 646m,sh; 654m; 667w; 671w,sh; 721s; 742s; 756w; 771m; 782s; 800s; 817m,sh; 865w; 1022s; 1039s,sh; 1049s,sh; 1060s; 1093s; 1163s; 1264s; 1316m; 1359m; 1577w; 1613m cm^{-1}.

Reaction of beryllium t-butylsulphide with pyridine- formation of dipyridineberyllium t-butylsulphide monomer $(Bu^tS)_2Be.py_2$.

Pyridine (4c.c., an excess) was added to a suspension of beryllium t-butylsulphide in boiling toluene (20c.c.).

The sulphide dissolved to give a very pale yellow solution. Solvent was removed, at reduced pressure, to leave the pale cream adduct, which was recrystallized from toluene/hexane (1:4) mixture (5c.c.) at -60°. On heating, it decomposed, with formation of a brown residue, at 140°. Found: Be, 2.63; pyridine, 45.39%; M, cryoscopically, 0.24, 0.42 wt.-% in benzene, 204, 221.
$C_{18}H_{28}BeN_2S_2$ requires Be, 2.61; pyridine, 45.81%; M, 345.

The i.r. spectrum (Nujol mull) contained bands at 528w; 550m; 600w,br; 643m; 661m; 680m; 687m,sh; 698m,sh; 705s; 777m; 798s,br; 861m,br; 1018s; 1050s; 1073s; 1092s,sh; 1163m; 1220m; 1264m; 1577w; 1613m cm^{-1}.

Reactions with selenophenol.

Reaction of diethylberyllium with selenophenol, a) in equimolar quantities-formation of ethylberyllium phenylselenide diethyl ether complex dimer, $(EtBeSePh.OEt_2)_2$.

Selenophenol (1.05c.c., 0.01 mole), in diethyl ether (10c.c.), was added to a cooled (-40°) solution of diethylberyllium (0.01 mole), in diethyl ether (7c.c.). Evolution of gas occurred at ca. 0° to give a colourless solution. Removal of solvent from this solution left a white foam which, on treatment with boiling hexane (2x10c.c.), became a white solid. This was washed with hexane (10c.c.). It melted with decomposition at $150-152^{\circ}$. Found: Be, 3.34; hydrolysable ethyl, 10.64; diethyl ether, 27.44%; M, cryoscopically, 0.64, 1.28 wt.-% in benzene, 524, 529.

$C_{24}H_{40}Be_2O_2Se_2$ requires Be, 3.37; hydrolysable ethyl, 10.82; diethyl ether, 27.62%; M, 536.

The i.r. spectrum (Nujol mull) contained bands at 464m,br; 488m,sh; 498m,br; 543m,br,sh; 561m,br; 616m,sh; 631s; 665w; 691s; 732s; 741s; 770s; 793m,sh; 836m; 885m; 910w; 946w; 992m; 1001m,sh; 1022s; 1071m; 1090m; 1151w; 1185w; 1266w; 1548w,sh; 1577m $cm.^{-1}$

This complex turned yellow after about one minute's exposure to the air.

b) in molar ratio 1:2-attempted preparation of beryllium phenylselenide, $Be(SePh)_2$.

Diethylberyllium (0.005 mole), in ether (5c.c.), and selenophenol (0.01 mole), in ether (10c.c.), reacted together at ca. 0° to give a clear solution. Removal of ether at low pressure left a white foam, which yielded a white solid on treatment with boiling hexane (2x10c.c.), in which it was insoluble. This solid decomposed, with loss of a volatile liquid, from ca. 100°, to leave a white residue which did not melt below 360°.

Found: Be, 2.44; diethyl ether, 12.97%.

These figures do not correspond to any simple compound.

Reaction of the above product with 2,2'-bipyridyl- formation of (bipyridyl)beryllium phenylselenide monomer, $(PhSe)_2Be.bipy$.

The above diethyl ether complex (0.295g., 0.0008 mole) was dissolved in benzene (10c.c.) and bipyridyl (0.125g., 0.0008 mole), in benzene (8c.c.), added. An ochre-coloured solid was deposited at once. This solid was extracted with hot benzene (3x10c.c.) and crystallized on cooling back to room temperature. On heating, it decomposes to a brown mass over the range 125-135°.

Found: Be, 1.92; bipyridyl, 32.48%.

$C_{22}H_{18}BeN_2Se_2$ requires Be, 1.89; bipyridyl, 32.70%.

This bipyridyl complex is not sufficiently soluble for cryoscopic molecular-weight determinations in benzene to be carried out, so it is only presumed to be monomeric.

The i.r. spectrum (Nujol mull) contained bands at 596w; 610m; 667w; 685w; 696m; 722m; 736s; 740s,sh; 770m,sh; 777s; 800s; 865w; 976w,sh; 1024s; 1052s; 1059s; 1075s; 1093s; 1155m; 1169w,sh; 1266s; 1312m; 1577w; 1615m cm.$^{-1}$

DISCUSSION.

DISCUSSION.

Reactions with amines.

Dimethylamino(methyl)beryllium, prepared by the elimination of methane from dimethylberyllium and dimethylamine, was described several years ago.[63] Several other aminoberyllium alkyls, $RBeNR'_2$, have now been prepared, and these are listed in Table IV. Except where acknowledged by reference, they were prepared for the first time in the course of this investigation.

Table IV.

Trimers[a]	$(MeBeNMe_2)_3$[63]	$(MeBeNEt_2)_3$	$(PhBeNMe_2)_3$[62]
	$(EtBeNMe_2)_3$	$(Pr^iBeNMe_2)_3$[52]	
Dimers[a]	$(MeBeNPr^n_2)_2$	$(MeBeNPh_2)_2$	$(EtBeNEt_2)_2$
	$(PhBeNPh_2)_2$[62]	$(EtBeNPh_2)_2$	$[MeBeN(CH_2Ph)Ph]_2$[70]

a-in benzene solution, cryoscopically.

As can be seen, all these compounds are either trimeric or dimeric in solution, and it is concluded that a balance between the entropy, angular valence strain, and steric, effects, discussed above, determines their degree of association.

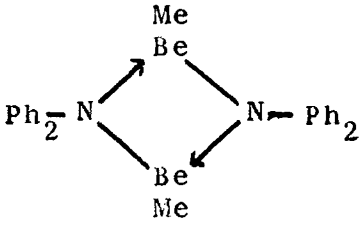
The formation of monomers is excluded because a two-coordinate, strongly acceptor, beryllium atom could not co-exist with a strongly donor, three-coordinate nitrogen atom, unless there is very severe steric hindrance to association, as in $[(Me_3Si)_2N]_2Be$. The formation of dimers rather than more associated species would be favoured by the entropy effect, but the average internal ring angle in a dimer must be 90°, and this would result in quite appreciable angular valence strain. Though nothing is known about the energy required to deform three-coordinate beryllium from an angle of 120^{o} to 90^{o}, by analogy with the strain energy in cyclobutane, (about 6-7 kcal. per g.atom of carbon [154]), one may guess that the strain energy at the nitrogen atoms would be something like 10-15 kcal. per mole of dimer $(RBeNR'_2)_2$. The difference in translational entropy between one mole of trimer and 1.5 moles of dimer is unlikely to contribute, at room temperature, more than about 1-3 kcal. per mole to the free energy change in favour of dimers, so trimers (in which little angular strain is to be expected) are likely to be favoured relative to dimers.

Reference to Table IV will show that all of the dimethylamino derivatives are the expected trimers, also that, with the exception of $(MeBeNEt_2)_3$, the complexes in which two groups larger than methyl are bound to nitrogen are all dimers. Experiments with molecular models show that steric interference between the groups bound to nitrogen, and that bound to beryllium, is less in the planar dimer than in the corresponding trimer. Thus it would appear that trimers are preferred for small substituents, and, on account of steric interference, dimers for large substituents.

All of the above compounds were prepared from the organoberyllium compound, R_2Be, and the appropriate amine, R'_2NH, with the exception of $[MeBeN(CH_2Ph)Ph]_2$, which was obtained from methylberyllium hydride and benzalanil.[70] Dimethylamino(isopropyl)beryllium was prepared some time ago,[52] but its molecular-weight was not measured.

Dimethylamino(methyl)beryllium, although trimeric in solution, is now known to be a glass in the condensed state at room temperature. It is isotropic in polarised light, and affords no X-ray diffraction pattern.[53] In contrast to this, $(MeBeNEt_2)_3$, $(EtBeNMe_2)_3$, $(Pr^iBeNMe_2)_3$, $(MeBeNPr^n_2)_2$ and $(EtBeNEt_2)_2$ are all mobile liquids at room temperature, although $(EtBeNMe_2)_3$ and $(MeBeNPr^n_2)_2$ become glassy on cooling to ca. -35° and -25° respectively. It is possible that these complexes resemble the derivatives $(R_2M\text{-}DR'_2)_n$, (M = Group III element, D = Group V donor)[94,134] in so far as they are glasses in the condensed state, but dissolve in hydrocarbons as dimers or trimers.

Diphenylamino(methyl)beryllium is X-ray crystalline, and it, as well as its ethylberyllium analogue, probably has a structure involving a four-membered, very nearly planar, beryllium-nitrogen ring (38), similar to that found by X-ray diffraction analysis of $(MeZnNPh_2)_2$.[75]



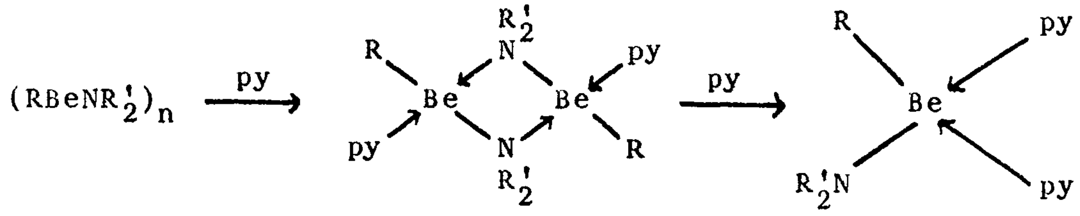
(38)

Such a ring would be expected to be subject to considerable valence angle strain, particularly as it contains a small metal atom. There is, however, considerable, and growing, evidence that even the lighter elements can tolerate the strain required for the formation of four-membered rings. The ethylideneaminoboranes, $(MeCH{:}N.BR_2)_2$,[160] some diphenylketimino derivatives, $(R_2M.N{:}CPh_2)_2$, where M is a Group III element, B, Al or Ga,[161] and $(Pr^iMgNPr^i_2)_2$[11] most probably all contain metal atoms in four-membered metal (or boron)-

nitrogen rings.

The trimers can reasonably be assumed to consist of six-membered puckered rings containing three-coordinate beryllium and four-coordinate nitrogen in a chair-like configuration.

Since, in hypothetical monomers, $RBeNR'_2$, the beryllium atom has two vacant orbitals while the nitrogen has only one lone pair, the beryllium will be coordinatively unsaturated whatever the degree of association, n, in $(RBeNR'_2)_n$. Therefore, these compounds should react with bases, though the dimethylamino complex, $MeBeNMe_2$, has been found not to react with trimethylamine.[63] Since then, it has been established that the three-coordinate beryllium compounds, $Et_2Be.NMe_3$ and $Me_2Be.NMe_3$ form unstable bistrimethylamine adducts having dissociation pressures of 11 mm. at -16° $(Et_2Be.2NMe_3)$[44] and 23 mm. at 0° $(Me_2Be.2NMe_3)$.[35] In contrast, dimethyl- and diethyl- beryllium form stable bispyridine and 2,2'-bipyridyl complexes,[36] and the adduct, $Mepy_2ZnNPh_2$, can be isolated from the reaction of excess pyridine with $MeZnNPh_2$ which, like its beryllium analogue, must contain three-coordinate metal.[83] It is now found that $RBeNR'_2$ readily adds pyridine or 2,2'-bipyridyl, though the reactions are, in some cases, complicated by disproportionation processes, or by thermal decomposition of the products.



(I) (II)

The addition of pyridine to $(MeBeNMe_2)_3$ takes place without complication; addition of only one molecule of pyridine for each beryllium atom gives colourless (I, R = R' = Me) whereas pyridine in excess gives pale cream coloured (II, R = R' = Me). In this instance, the first reaction involves a change in ring size, from trimer to dimer, due, in all probability, to increased steric congestion about the metal atom. Similarly, the dimer, $(MeBeNPh_2)_2$, gives pale yellow (I, R = Me, R' = Ph) and (II, R = Me, R' = Ph), according to the reactant ratios. However, (I, R = Me, R' = Ph) was too insoluble in benzene for its molecular-weight to be measured cryoscopically, so it is only presumed dimeric. It had the unique property, amongst methylberyllium compounds, of not being decomposed by cold water, although there is now one further instance of such a compound (see below). It is likely that steric hindrance, by the pyridine molecule and the diphenylamino group, hinders coordination of water molecules, making the hydrolysis of the Be-C bond a slow process. The monomeric bispyridine complex (II, R = Me, R' = Ph) has a bright yellow colour similar to that of $Me(Ph_2N)py_2Zn$.[83]

Whereas the addition of pyridine in excess to the dimer $(EtBeNPh_2)_2$, gives (II, R = Et, R' = Ph), no complex of the type (I, R = Et, R' = Ph) could be isolated from its reaction with two moles of pyridine. A yellow solid could be crystallized from hexane at <u>ca.</u> -70°, but, on warming to room temperature, this became slightly viscous, and analysis figures indicated that slow disproportionation into diethylberyllium and a complex containing no ethyl groups bound to beryllium, was taking place, so that a mixture of the two pyridine complexes was isolated.

$$[\mathrm{Et(Ph_2N)Be.py}]_2 \rightleftharpoons \mathrm{Et_2Be} + \mathrm{py_2Be(NPh_2)_2}$$

The reaction of $(\mathrm{MeZnNPh_2})_2$ with two moles of pyridine gives $\mathrm{py_2Zn(NPh_2)_2}$, which can be crystallized, and dimethylzinc, by a similar process,[83] which, in this case, goes to completion.

When pyridine (one mole per g. atom of beryllium) was added to $(\mathrm{MeBeNPr^n})_2$, the product of crystallization at -78° was $\mathrm{Me_2Be.py_2}$, again formed, presumably, by a disproportionation process, in which it is likely to be the least soluble component.

$$\begin{array}{c} (\mathrm{MeBeNPr^n})_2 + 2\mathrm{py} \rightarrow (\mathrm{I},\ \mathrm{R} = \mathrm{Me},\ \mathrm{R'} = \mathrm{Pr^n}) \\ \downarrow\uparrow \\ \mathrm{Me_2Be.py_2} + (\mathrm{Pr^n_2N})_2\mathrm{Be}. \end{array}$$

In all these reactions, as in those with 2,2'-bipyridyl below, it may well be that solubility decides which product, or products, are isolated.

The observation that $\mathrm{Me(Me_2N).py_2Be}$ has a slight, and $\mathrm{Me(Ph_2N).py_2Be}$ a strong, yellow colour, prompted an attempt to form 2,2'-bipyridyl complexes.

Addition of the base to $(\mathrm{MeBeNMe_2})_3$, in ether solution, resulted in an immediate red precipitate, which quickly decomposed, becoming olive-green. Even when the reaction was carried out at -78°, and the red precipitate isolated, it decomposed before it could be analysed. Benzene extraction of the precipitate yielded the previously described [36] $\mathrm{Me_2bipyBe}$. The initially formed red precipitate was probably $\mathrm{Me(Me_2N)bipyBe}$, which decomposes, though not quantitatively, by disproportionation.

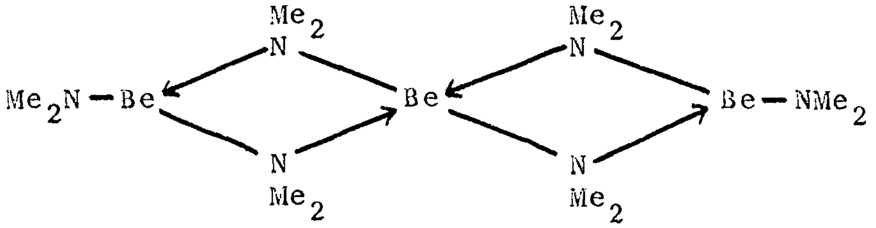
$$2\ \mathrm{Me(Me_2N)bipy.Be} \rightleftharpoons \mathrm{Me_2bipy.Be} + \mathrm{(Me_2N)_2bipy.Be}$$

Bis(dimethylamino)bipyridylberyllium was prepared from $(Me_2N)_2Be$ and bipyridyl and found to be insoluble in benzene, which explains why it did not extract from the above equilibrium.

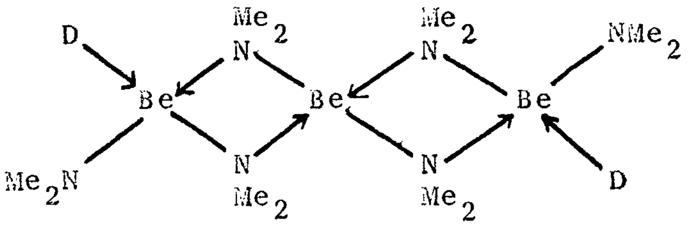
In contrast, both $(MeBeNPh_2)_2$ and $(EtBeNPh_2)_2$ yielded brick-red 2,2'-bipyridyl adducts which did not disproportionate. The ethyl compound, $Et(Ph_2N)bipyBe$, was monomeric in benzene, but the methyl analogue was not sufficiently soluble to permit cryoscopic molecular-weight determinations in benzene.

The colours of bipyridyl complexes of beryllium alkyls have earlier been discussed in terms of electron-transfer from beryllium-carbon bonds to the heterocyclic π-electron system.[36] In these amino-compounds, thereis the additional possibility of the nitrogen lone-pair acting as an electron source for the transition, and the strong absorption of visible light by aluminium complexes (e.g. with phenanthridine), in which alkyl groups and amino-nitrogen are bound to the same metal atom, has been discussed in similar terms.[155] The beryllium complexes provide further examples of these effects.

The reactions of bis(dimethylamino)beryllium with pyridine and 4-dimethylaminopyridine were carried out, not only in the hope of isolating complexes, but also in an attempt to add some evidence to the linear structure proposed for this compound by Fetter and Peters.[64] [(14), above, but shown again below].



In such a molecule, there would be one four-, and two three-, coordinate beryllium atoms. Thus, it was hoped that complexes of type (III, D = pyridine or 4-dimethylaminopyridine) might be obtained, and the reactant quantities were chosen with this possibility in mind.



(III)

Unfortunately, however, though coloured solutions, giving an indication of some degree of coordination, were obtained in both cases, no pure complexes could be crystallized. Pyridine could be removed (by pumping) from its reaction with $[(Me_2N)_2Be]_3$, and, in the case of 4-dimethylaminopyridine, only a white substance, probably a mixture, could be crystallized, even at low temperature. Its beryllium content did not correspond to that required by (III, D = 4-dimethylaminopyridine) nor to any other possible product, e.g., $(Me_2N)_2Be.D_2$.

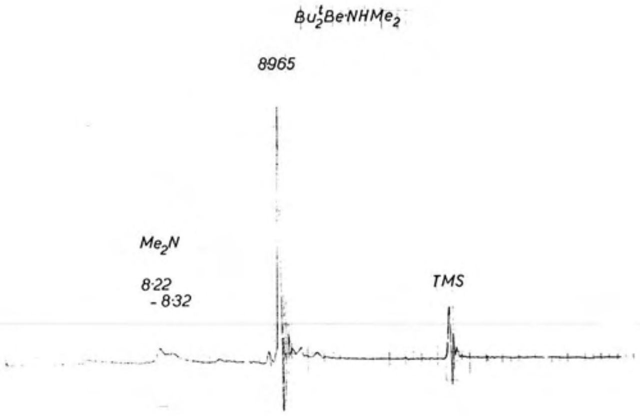
The reaction of diethylberyllium with two moles of dimethylamine,[64] gives bis(dimethylamino)beryllium which, on purification by sublimation, yields ca. 50 mole per cent of the calculated yield of trimer (65°/0.01 mm.) and 30 mole per cent of a product which appears to contain the trimer and at least one other form of $[Be(NMe_2)_2]_n$, n being unknown (100°/0.01 mm.). The rest of the product is insoluble in benzene, and may be a polymeric form of the amino compound. An investigation into the possibility of improving this yield was carried out. Reaction of beryllium bromide with dimethylaminolithium gave a yellow solid, which was completely involatile at 110-120°/10^{-3}mm. and only a very small amount of the trimer could be sublimed from the white solid obtained from the reaction of dimethylamine with n-butyllithium, followed by addition of beryllium chloride. In each case, heat was generated on addition of the halide, so it is possible that polymeric forms are being prepared, or that coating of the reactants with alkali halides is impairing the reaction.

Proton magnetic resonance spectra.

The p.m.r. spectra of some of the compounds $RBeNR'_2$ are given in the experimental section. Those of $(MeBeNMe_2)_3$[53] and $[(Me_2N)_2Be]_3$[64] have been discussed elsewhere, and the only notable feature of the spectra reported above is the splitting of the methylberyllium resonance of $(MeBeNEt_2)_3$ into a doublet at τ 10.50, 10.56 when the complex is examined in benzene solution. It is unlikely that this is due to slow interchange between the two conformations similar to the chair form of cyclohexane, as no such splitting is observed in the spectrum of $(MeBeNMe_2)_3$, even at -90°. As the splitting was absent when cyclohexane was used as solvent, it is more likely to be a solvent effect.

Di-t-butylberyllium-dimethylamine adduct.

Reactions between organoberyllium compounds, R_2Be, and secondary amines readily proceed to completion, and in some instances, both alkyl groups can be replaced by secondary amino groups.[64,65] In contrast, di-t-butylberyllium formed a 1:1 complex with dimethylamine, from which complete elimination of isobutane could not be obtained. Inspection of a model of the complex, $Bu^t_2Be.NHMe_2$, shows that the amino-hydrogen is so shielded



(38a)

Photograph 1. $Pr^i_2Be.py_2$

by methyl and t-butyl groups that it could not come within reaction distance of carbon bound to beryllium either in the same, or in a neighbouring, molecule. Though for steric reasons, the eqilibrium

$$Bu^t_2Be.NHMe_2 + Me_3N \rightleftharpoons Bu^t_2Be.NMe_3 + Me_2NH$$

would be expected to lie to the left, nevertheless, addition of trimethylamine may liberate enough dimethylamine to allow faster isobutane elimination. Though a product in which the Bu^t:Be ratio was 0.97:1 was obtained from Bu^t_2Be, Me_2NH and Me_3N in equimolar proportions, its analysis and p.m.r. spectrum were consistent with a mixture of Bu^tBeNMe_2 and $Bu^t_2Be.NHMe_2$. Attempted purification by distillation resulted in disproportionation,

$$2\ Bu^tBeNMe_2 \longrightarrow Bu^t_2Be + Be(NMe_2)_2$$

as the distillate was enriched in butyl groups bound to beryllium (ratio Bu^t:Be = 1.17:1) and the residue contained very little butyl bound to beryllium and could be identified as being largely composed of $(Me_2N)_2Be$ by its i.r. spectrum.

Reaction of the adduct with a large excess of trimethylamine gave a product with Bu^t:Be ratio 1.08:1, whose i.r. spectrum did not contain an N-H stretch. However, analysis figures, and its p.m.r. spectrum, indicated that it was mixed with a large amount of inseparable trimethylamine.

The broad, poorly resolved, doublet, centred on τ 8.25, due to Me_2N groups in the p.m.r. spectrum of the adduct is likely to be due to coupling between $N-\underline{CH}_3$ and $N-\underline{H}$, poorly resolved on account of the nitrogen quadrupole in an unsymmetrical environment. [(38a), above]

Reaction of di-t-butylberyllium with t-butylamine.

The reaction of di-t-butylberyllium (diethyl ether complex) and t-butylamine, in equimolar amounts, liberated about two-thirds of the available isobutane at or below room temperature, forming a product of composition intermediate between that required for $Bu^tBeNHBu^t$ and $Be{\cdot}NBu^t$. Similar results were obtained, several years ago, for the reaction of dimethylberyllium with methylamine.[63] These observations support the conclusion that the second alkylberyllium group is much less reactive than the first, but, in the case of t-butylamine, shielding of the protons attached to nitrogen, by t-butyl groups, as in the adduct, $Bu^t_2Be.NHMe_2$, may preclude elimination of alkane. In the same way, triphenylaluminium reacts with, for example, aniline at ca. 80°, to form $(PhAl.NPh)_4$, but the adduct $Ph_3Al.NH_2Bu^t$ is stable even in boiling toluene.[124]

Reactions of di-isopropyl-, and di-t-butyl- beryllium with pyridine.

Some years ago,[36] the complexes $Me_2Be.py_2$ (colourless) and $Et_2Be.py_2$ (orange-yellow) were reported. Their colours were ascribed to electronic transitions, similar to those obtaining in the 2,2'-bipyridyl complexes, from the Be-C bond into the pyridine molecules. The two complexes described in this thesis, $Pr^i_2Be.py_2$ (golden-yellow) and $Bu^t_2Be.py_2$ (bright yellow) constitute further examples of the same effect. The isopropyl- derivative is monomeric in benzene solution, but the t-butyl analogue dissociates (n = 0.72, 0.76 in 0.76, 1.09 wt.-% solution) due, presumably, to increased steric congestion around the beryllium atom. [n.b. Photograph 1, above, $Pr^i_2Be.py_2$.]

Reactions with alcohols and phenol.

A series of alkylberyllium alkoxides has been prepared by alcoholysis of beryllium dialkyls, and is summarised in Table V.

Table V.

Alkylberyllium Alkoxides.

Tetramers[a]	$(MeBeOMe)_4$	$(MeBeOEt)_4$	$(MeBeOPr^n)_4$
	$(MeBeOPr^i)_4$	$(MeBeOBu^t)_4$	$(MeBeOCH_2Ph)_4$[70]
	$(Pr^iBeOMe)_4$[52]	$(Bu^tBeOMe)_4$	$(PhBeOMe)_4$[62]
Trimer[a]	$(EtBeOCEt_3)_3$		
Dimers[a]	$(MeBeOCHPh_2)_2$	$(MeBeOCPh_3)_2$	$(Bu^tBeOBu^t)_2$

a - in benzene solution, cryoscopically.

Alkylmetal alkoxides, RMOR', in which M is a Group II metal, are of interest because the presence of two lone pairs (on the oxygen) and at least two acceptor sites (at the metal atom) in each monomer unit could result in a wide range of associated species, containing metal and oxygen in three-, or four-, coordinate states. Cyclic dimers and trimers, formation of the former being favoured on account of greater translational entropy per unit mass, can be formulated with not more than three-coordinate metal, examples being $(PhZnOCPh_3)_2$, $(EtZnOCHPh_2)_3$,[82] $(PhHgOMe)_3$[68], $(MeCdOBu^t)_2$[96], and $(Bu^nMgOPr^i)_3$[19].

In contrast, tetramers can be formulated with both metal and oxygen in four-coordinate states, as a near-cubic [83] structure, which would be favoured over a polymer by entropy, and disfavoured by valence angle, considerations. Tetramers, exemplified by $(MeCdOEt)_4$[96]

$(EtMgOBu^t)_4$[17], $(MeZnOMe)_4$[83], and many others, all referred to above, are seen to be a relatively common state of aggregation of Group II alkylmetal alkoxides in benzene solution.

In like fashion, most of the alkylberyllium alkoxides studied were found to be tetrameric (cryoscopically in benzene). Methylberyllium t-butoxide was also a tetramer in ether (by isothermal measurement at room temperature). The degree of association of methylberyllium n-propoxide in ether (by the same method) was found to 4.8. This is mentioned, not as an indication that the compound is more associated in ether, as the result is probably erroneous, but merely to further illustrate the observation that an alkoxy-bridge does not appear to be broken by ether, at least at room temperature. Coates and Ridley concluded [83] that even pyridine coordinates only weakly, if at all, to tetrameric alkylzinc alkoxides.

Ethylberyllium triethylmethoxide, $(EtBeOCEt_3)_3$, formed by elimination of ethane from 3-ethylpentan-3-ol and diethylberyllium, is unique among the alkylberyllium alkoxides so far known in being trimeric in benzene solution, and may have a cyclic Be_3O_3 skeleton. This and the dimers $(Bu^tBeOBu^t)_2$, $(MeBeOCHPh_2)_2$ and $(MeBeOCPh_3)_2$ illustrate the reduction in degree of association brought about by steric interference between large organic groups. These must all be formulated with three-coordinate metal. In this connection, it should be remembered that $(PhZnOCPh_3)_2$[82], and $(Bu^tZnOBu^t)_2$[56], are dimers in benzene, and that the degree of association, <u>n</u>, of methylzinc t-butoxide falls significantly below four as the concentration is reduced.[86]

The relative melting points of the methylberyllium alkoxides, MeBeOR, deserve comment; they are, R = Me, 23-25^{o}, Et, 28-30^{o}, Pr^{n}, 38-40^{o}, Pr^{i}, 134-136^{o}, and Bu^{t}, 93^{o}. Methyl compounds commonly have higher melting points than higher homologues, and t-butyl compounds, usually, are higher melting than isopropyl. Here the reverse is observed. That MeBeOPr^{i} and Pr^{i}BeOMe have nearly identical m.p.'s (134-136^{o} and 133-135^{o} respectively) may be a coincidence, but if the crystals of each have cubane-type structures similar to that of methylzinc methoxide, then both molecules would have a very similar size and shape.

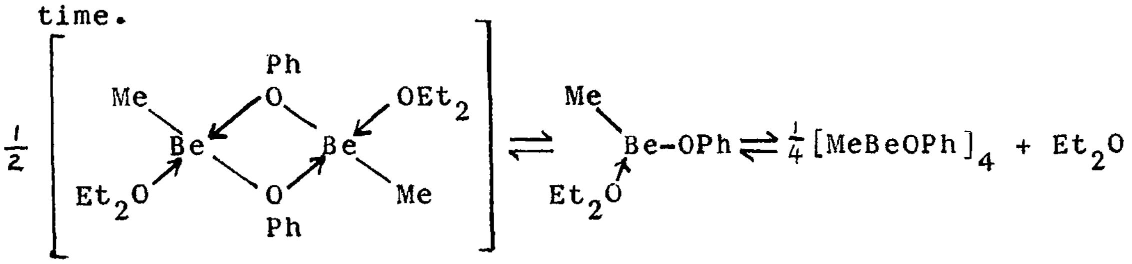
In three instances, reactions of dialkylberyllium compounds with two mol. alcohol per beryllium, to give beryllium alkoxides, were carried out. Beryllium methoxide, $Be(OMe)_2$, from di-isopropylberyllium and methanol, is involatile, insoluble even in a mixture of boiling toluene and pyridine, and, therefore, presumed to be polymeric. On the other hand, beryllium t-butoxide, $[Be(OBu^{t})_2]_3$, is trimeric, and beryllium triethylmethoxide, $[Be(OCEt_3)_2]_2$, dimeric, both in benzene, cryoscopically. This is in accordance with the general observation that bulky organic groups tend to favour low degrees of association. The triethylmethoxide probably has a structure involving a four-membered Be_2O_2 skeleton, and that of the t-butoxide is discussed below.

Reactions of alkylberyllium alkoxides with bases.

Contrary to the above isothermal experiments, there were three instances in which preparations carried out in the presence of ether yielded mono- ether complexes, monomeric in benzene. One of these, $MeBeOCHPh_2.OEt_2$, has been described previously, together with the monomeric tetrahydrofuran (THF) complex, $MeBeOCHPh_2.THF$.[70] Their formation was attributed to the relatively large size of the diphenylmethoxy group. Another is the product from the reaction of dimethylberyllium and triphenylmethanol, in ether, $MeBeOCPh_3.OEt_2$, the dimer $(MeBeOCPh_3)_2$, being formed when the reaction is carried out in benzene. The third is the product of methanolysis of diphenylberyllium in ether/toluene mixture. This reaction had earlier been found [62] to yield a methoxide with an indefinite ether content, but further experiments have resulted in the formation of the complex $PhBeOMe.OEt_2$, which is monomeric in benzene. Methanolysis of di-isopropylberyllium and di-t-butylberyllium, however, yields products from which ether is readily separated, and which then dissolve in benzene as tetramers, $(Pr^iBeOMe)_4$ and $(Bu^tBeOMe)_4$, respectively. It would appear, therefore, that the formation of the ether complexes cannot wholly be explained by steric considerations. It may be that the phenyl group attached to beryllium in PhBeOMe acts as an electron-withdrawing group, thus making the metal atom more susceptible to nucleophilic attack by ether. In the case of the di-, and tri-, phenylmethoxy derivatives, the donor strength of the alkoxy-oxygen atoms may be reduced by the presence of the phenyl groups, thereby rendering the beryllium atom more 'electron-deficient' than in, say, Bu^tBeOMe. In the same way,[130] $(Me_2AlPPh_2)_2$ and $(Me_2AlAsPh_2)_2$ absorb trimethylamine reversibly, while $(Me_2AlPMe_2)_3$ does not.[32]

The reaction between phenol and dimethylberyllium, in ether solution, yielded a sparingly soluble mono-ether complex, $MeBeOPh.OEt_2$, but this differed from the above three ether complexes in being somewhat associated

($\underline{n}$ = 1.21 and 1.41 in 0.59 and 1.19 wt.-% solutions) in benzene. This result could be due to a monomer-dimer equilibrium or to formation of tetramer and free ether, or, more likely, to both equilibria obtaining at the same time.



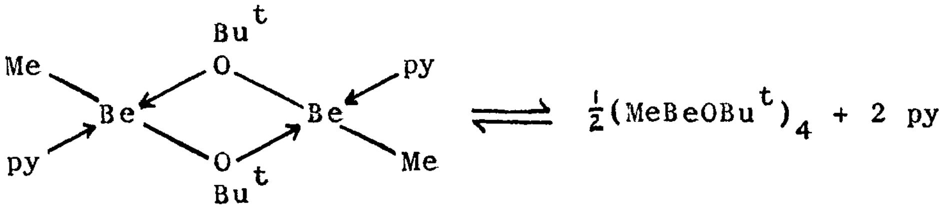
The presence of diethyl ether, amounting to about one-third of that originally present in the adduct, was found by examination of the p.m.r. spectrum of the condensate collected when 10c.c. of a 2.72 wt.-% solution of the adduct in benzene was evaporated to dryness at room temperature. Attempts to prepare ether-free MeBeOPh or EtBeOPh failed, on account of disproportionation to insoluble products containing little, or no, alkylberyllium.

$$2\ \mathrm{EtBeOPh} \rightleftharpoons \mathrm{Et_2Be} + \mathrm{Be(OPh)_2}$$

This disproportionation could also be aided by the weakened donor character of oxygen bound to phenyl, combined with the insolubility of $Be(OPh)_2$.

In contrast to methylzinc methoxide, which has yielded no pyridine complex,[83] methylberyllium methoxide gave a dipyridine complex, $Me(MeO)Be.py_2$, which is monomeric in benzene and analogous to $Me(Me_2N)Be.py_2$. But, whereas $MeBeNMe_2$ gave the dimer $(MepyBeNMe_2)_2$ on reaction with one mol. of pyridine per beryllium, and MeZnOMe yielded a 1:1 adduct with the more basic 4-dimethylaminopyridine,[82] treatment of methylberyllium methoxide with only one mol. pyridine per beryllium resulted in disproportionation to insoluble $(MeO)_2Be$ and soluble $Me_2Be.py_2$.

The t-butoxide, $(MeBeOBu^t)_4$, added four mols. pyridine, yielding a crystalline complex, $Me(Bu^tO)Be.py$, which was associated ($\underline{n}$ = 1.23, 1.41 in 0.35, 0.70 wt.-% solution) in benzene. It is likely that there is an equilibrium between the dimer containing coordinated pyridine, the tetramer, and free pyridine.



When a solution of the complex in benzene was evaporated to dryness at room temperature, about one-third of the pyridine was found in the condensate.

Reaction of Bu^tBeOBu^t with one mol. pyridine gave a pale yellow crystalline product whose composition was intermediate between those required for the mono- pyridine adduct and the disproportionation product, $Bu^t_2Be.py_2$. The p.m.r. spectrum of a solution of the product in benzene contained a resonance due to $\underline{Bu}^t$-Be (τ 8.72) about four times the intensity of that due to $\underline{Bu}^t$-O (τ 8.44), and very close to that due to $\underline{Bu}^t_2Be.py_2$ (τ 8.75 relative to benzene, 2.73), in a solution of the latter complex in benzene. A similar result was obtained from the reaction of Bu^tBeOBu^t with one mol. 4-dimethylaminopyridine. The failure of Bu^tBeOBu^t to add pyridine is, at first sight, surprising, as the complex must be formulated with three-coordinate beryllium, but construction of a molecular-model shows that steric interference between t-butyl groups bound to beryllium and to oxygen is so great, that addition of two mols. pyridine to the dimer, to give a complex of type $[Bu^t(Bu^tO)Be.py]_2$, probably would not be possible.

The fact that disproportionation processes often hinder these reactions with pyridine, may be due, in part, as in the case of the amino-derivatives, to the solubility of the various components in equilibria such as:

$$RBeOR'.py \rightleftharpoons \tfrac{1}{2} R_2Be.py_2 + \tfrac{1}{2} (R'O)_2Be$$

Except where the above ether complexes are concerned, ether can be removed without difficulty from these alkoxy compounds.

Though beryllium t-butoxide must react to some extent with 2,2'-bipyridyl in ether, since the colourless reactants yield a yellow solution, this coordination cannot be very strong, since only the reactants can be isolated by crystallization.

Infrared and proton magnetic resonance spectra.

The infrared spectra of several methylberyllium complexes have been examined[53], and the symmetric $Be-CH_3$ deformation identified as being in the range $1186-1206 cm.^{-1}$ Similar assignments can be made in respect of these alkoxy compounds, (see Table VI), but it must be borne in mind that these assignments are only tentative, as, in most cases, other absorptions occur not very far out of the above range, and these may equally well be due to $\delta_{sym.}(Be-CH_3)$.

The proton magnetic resonance spectra of some of these compounds contain, in certain instances, doublets when singlets would be expected on the basis of a symmetrical structure like that of crystalline methylzinc methoxide. The spectrum of methylberyllium methoxide in

Table VI.

Symmetric Be-CH_3 deformations in alkylberyllium alkoxides.

Compound.	$\delta_{sym.}$	Compound.	$\delta_{sym.}$
$(MeBeOMe)_4$	1208m	$(MeBeOCPh_3)_2$	1205m
$(MeBeOEt)_4$	1170m	$MeBeOPh.OEt_2$	1193m
$(MeBeOPr^n)_4$	1211m	$MeBeOCPh_3.OEt_2$	1201w
$(MeBeOPr^i)_4$	1210m	$MeBeOMe.py_2$	1212m
$(MeBeOBu^t)_4$	1200s	$MeBeOBu^t.py$	1208m
$(MeBeOCHPh_2)_2$	1198m		

benzene consists of a singlet at +7.88p.p.m. relative to benzene (or τ 10.61 relative to benzene τ 2.73), clearly due to $\underline{CH_3}$-Be, and a doublet at τ 6.50 and 6.76, due to $\underline{CH_3}$-O, the area of the singlet being equal to that of the doublet. No temperature-dependence could be detected using d_8-toluene as solvent (TMS as reference), the methylberyllium resonance at τ 10.76 remaining unchanged at -90°. Similarly, the methoxy doublet stayed the same at +33, +70 and +100, the components being of about equal intensity in all the spectra. The structure of the molecules present in solution cannot be as symmetrical as that of crystalline methylzinc methoxide, and it is likely that methoxy groups are present in at least two environments. Methylberyllium groups could also be present in different environments, if exchange between them is fast at -90°; exchange between methoxy groups is less likely. The spectrum of methylzinc methoxide,[83] above, shows a similar splitting at room temperature, but disproportionation into free dimethylzinc and methoxy-rich species occurs here,[85] and this must be ruled out for the beryllium analogue, as dimethylberyllium is insoluble in hydrocarbons. Disproportionation into species such as $Me_2Be_4(OMe)_6$ and $Me_6Be_4(OMe)_2$ cannot be eliminated, since these might be soluble.

In view of the observation [85] that zinc methoxide dissolves in a solution of dimethylzinc in benzene until the methoxy to methylzinc ratio is 4:3, the solubility of beryllium methoxide in a solution of dimethylberyllium in diethyl ether was investigated. The methoxide, which is insoluble in ether alone, dissolved until the methoxy to methylberyllium ratio was 1:1; evaporation of ether from the filtrate then yielded methylberyllium methoxide, identical with that prepared from dimethylberyllium and methanol. Beryllium methoxide did not dissolve at all in a boiling solution of methylberyllium methoxide in hexane.

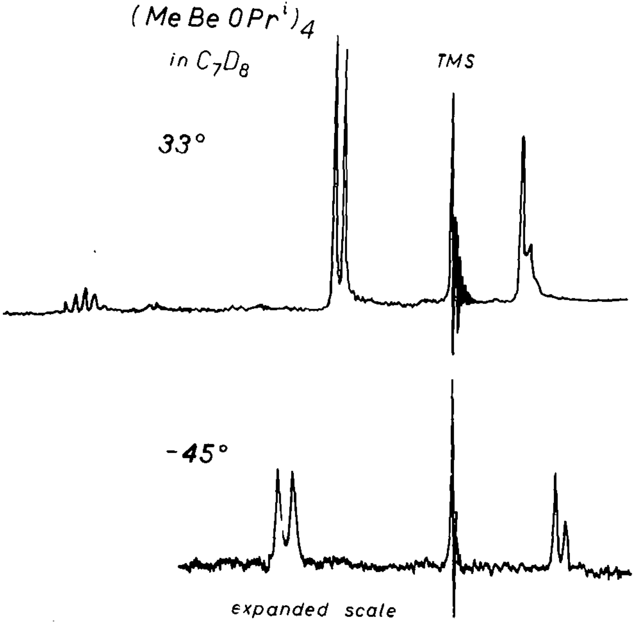
The p.m.r. spectra of methylberyllium t-butoxide are more peculiar than those of the methoxide. In benzene, the spectrum consists of two singlets (in ratio 3:1) due, respectively to t-butoxy and methylberyllium protons. These were not detectably changed by dilution, or on heating from 33^{o} to 50^{o} and to 65^{o}. In C_7D_{14}, however, these resonances were split into approximately equal doublets; examination at 10^{o} intervals from $60-100^{o}$, showed negligible change in chemical shifts or in relative intensities, nor were these affected by halving the concentration at 33^{o} and at 70^{o}. The shifts are all given in the experimental results section. Dimethylberyllium dissolved in a solution of beryllium t-butoxide in toluene until the t-butoxy to methylberyllium ratio was 1:1, evaporation of solvent leaving methylberyllium t-butoxide, identical in properties to that prepared by other methods.

In this case, disproportionation into free dimethylberyllium and t-butoxy-rich species can be ruled out, not only because of the insolubility of dimethylberyllium in hydrocarbons, but also because of the conclusion[86] that methylzinc t-butoxide must exist in solution largely as a genuine alkylmetal alkoxide, $(MeZnOBu^t)_n$.

Slow intramolecular exchange of alkoxy groups, as proposed to explain the splittings of signals in the p.m.r. spectrum of aluminium isopropoxide,[156] and extended to include some alkylzinc alkoxides,[93] can probably be ruled out in the case of beryllium, as it involves an intermediate containing five-coordinate metal. However, exchange processes must be considered as a possible reason for the observed splittings, and if they did take place, they might account for the splitting of the Bu^t-O signal in $(MeBeOBu^t)_4$, as the bulky Bu^t-O group would exchange relatively slowly. The splitting of the Me-O resonance in $(MeBeOMe)_4$ would then be anomalous, as this is the smallest alkoxy group used, and there is no splitting pattern other than that normally expected for the alkoxy resonances in $(MeBeOEt)_4$, $(MeBeOPr^n)_4$ or $(MeBeOPr^i)_4$. The latter was recorded at temperatures down to -45°, [see (39), below].

The size of the alkoxy group might also be expected to affect the speed of exchange of the methyl group. The observations that the Me-Be resonance is a doublet at room temperature in $(MeBeOBu^t)_4$, develops a shoulder at -5° in $(MeBeOPr^i)_4$, [see (39)], and is a singlet at -90° in $(MeBeOMe)_4$, are in accordance with this.

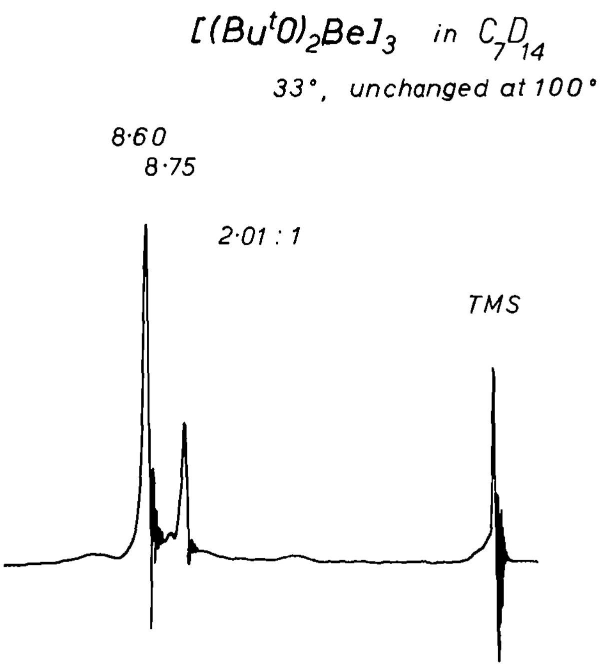
The possibility of solvation by benzene, to account for the lack of splitting of methylberyllium and t-butoxy signals when this was used as solvent for methylberyllium



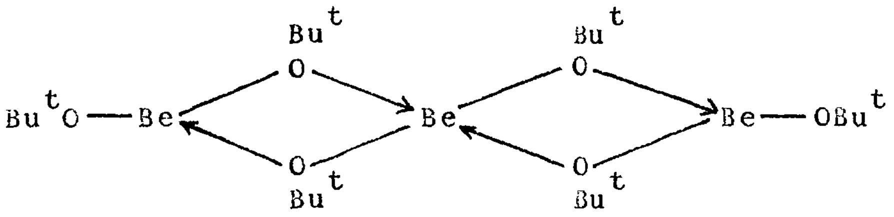
(39)

t-butoxide and beryllium t-butoxide (see below), was eliminated by heating a sample of the former to 50^o and to 65^o. No splitting, which might be expected to occur if de-solvation were taking place on heating, was observed.

As can be seen from the data given in the experimental results section, the p.m.r. spectra of the beryllium t-butoxide trimer show a similar solvent effect to those of methylberyllium t-butoxide. The spectra in aliphatic solvents, (40), below, containing two t-butoxy resonances in the ratio 2:1, suggest a structure based on a linear Be-Be-Be chain, with four bridging, and two terminal, t-butoxy groups (41). A similar structure, for the trimeric form of bis(dimethylamino)beryllium, was proposed by Fetter and Peters.[64] In this case, however, the larger signal, due, presumably, to the bridging dimethylamino groups, is upfield of the smaller one, due to terminal dimethylamino. Unless the electron pairs on the terminal NMe_2 groups are back-donating significantly to beryllium,[158] these should be the other way round, as is observed for the t-butoxy groups in beryllium t-butoxide.



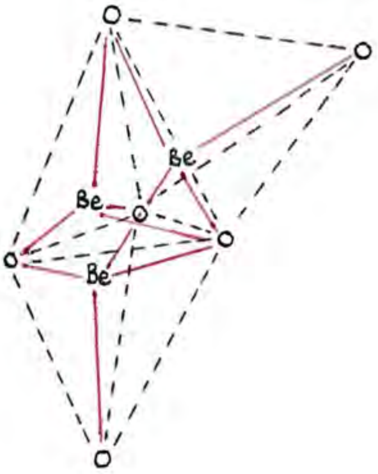
(40)



(41)

An alternative structure, consisting of three fused tetrahedra, two faces being shared, (42), would conform to the principle forwarded by Bradley,[157] which is that a covalent alkoxide undergoes the minimum degree of polymerization consistent with the attainment of the maximum covalency of the metal. This takes no account of the possibility, very unlikely in this case, of coordination numbers of greater than four for beryllium.

In this structure, there would be two two-, two three, and two four- coordinate oxygen atoms, that is the



Black, dotted lines
- edges of tetrahedra.
Red, unbroken lines
- Be-O bonds.
t-Butyl groups
omitted.

(42)

possibility of three different kinds of t-butoxy group, but a greater objection is that the Be-Be distance is only 0.67 times the Be-O distance, or about 1.0-1.1 Å.

A six-membered, puckered, Be_3O_3 ring, would be inconsistent with the p.m.r. spectra in aliphatic solvents.

Finally, reference should be made to the observation that the magnetic resonance (in benzene or d_6-benzene) of methyl protons bound to three-coordinate beryllium is normally at higher field than that of methyl protons bound to beryllium in tetramers, and thus, very probably, four-coordinate. Thus, for the tetramers, $(MeBeOR)_4$, R = Me, Et, Pr^n, Pr^i, Bu^t, the Be-$\underline{CH}_3$ resonances are at τ 10.61, 10.71, 10.77, 10.77, 10.46 (relative to benzene, τ 2.73 or TMS). For the methylberyllium complexes that can hardly contain other than three-coordinate metal, $(MeBeOCHPh_2)_2$, $(MeBeOCPh_3)_2$, $(MeBeOCPh_3.OEt_2)$ and $(MeBeOCHPh_2.OEt_2)$,[70] the Be-$\underline{CH}_3$ resonances are at τ 11.06, 11.43, 11.53 and 10.82 (TMS as reference). On this basis, the relatively low-field resonances, τ 10.48 and 10.26 of

Be-$\underline{CH}_3$ in [MeBeOPh.OEt_2] and [MeBeOBu^t.py], in C_6D_6, TMS as reference, suggest that most of the beryllium present in these equilibrium mixtures (see above) is in a four-coordinate state.

Other reactions producing alkoxy compounds.

Some of the alkoxides described above were also prepared by addition of the dialkylberyllium compound across the C=O bond of an aldehyde or a ketone.

In the three instances studied, no alkane evolution could be detected, so there was negligible side-reaction due to enolization. This contrasts with the observation[93] that dimethylzinc and acetone evolve methane slowly at room temperature and quantitatively on heating to 90°.

Diethylmagnesium adds to diethyl ketone, in ether solution, to give $EtMgOCEt_3.OEt_2$. As in the beryllium case, there is no detectable evolution of ethane.[17]

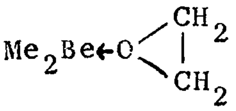
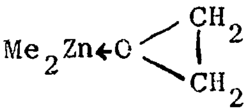
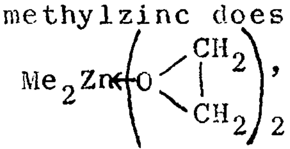
Ethylberyllium triethylmethoxide was obtained from diethylberyllium and diethyl ketone, in ether, but, unlike the magnesium analogue, it can be readily separated from ether. Thus, the explanation that the above etherate is formed because of steric hindrance set up by the triethylmethoxy group, cannot be extended to the beryllium analogue, as there should be even greater steric crowding round the smaller beryllium atom. It may be, though, that steric interaction between the ethyl and triethylmethoxy groups is so great that an ether molecule cannot approach closely enough for coordination to take place.

By analogous reactions, the methylberyllium isopropoxide and methylberyllium t-butoxide tetramers were obtained from dimethylberyllium and acetaldehyde and acetone respectively.

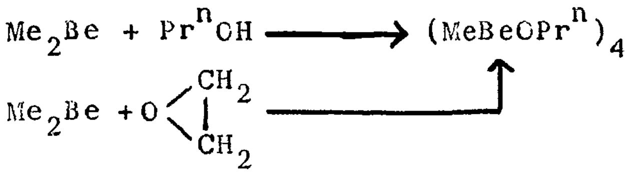
Reaction of a second mole of acetone with methylberyllium t-butoxide yields beryllium t-butoxide.

Alkyl and aryl peroxides, RO.OR and ArO.OAr, are readily, and sometimes violently, cleaved, with formation of free radicals. Dimethylberyllium reacted with the relatively stable di-t-butyl peroxide, $Bu^tO.OBu^t$, to form methylberyllium t-butoxide and methyl t-butyl ether. This alkoxide has now been prepared by four different routes, viz.

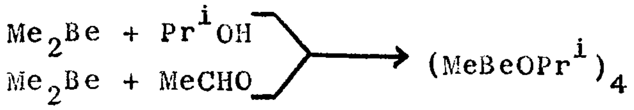
$$\left.\begin{array}{l} Me_2Be + Bu^tOH \\ Me_2Be + Me_2CO \\ Me_2Be + Bu^tO.OBu^t \end{array}\right\} \longrightarrow (MeBeOBu^t)_4 \underset{Me_2Be}{\overset{Me_2CO}{\rightleftharpoons}} [(Bu^tO)_2Be]_3$$

Methylberyllium n-propoxide is formed, not only by the method described above, but also by addition of ethylene oxide to dimethylberyllium. Presumably, an adduct,  is formed at first, as in the case[159] of dimethylzinc, but, unlike , the dimethylberyllium adduct rearranges quickly and exothermically at room temperature to yield the n-propoxide. A second mole of ethylene oxide could not be added, at least under the conditions used. Although no attempt was made to use forcing conditions, e.g., sealed tube under pressure, it is clear that there is a large difference between the rate of addition to the first and second methylberyllium groups, especially when, as in this case, the process involves ring opening. In point of fact, dimethylzinc does not form a 2:1 coordination complex, , so the possibility of the same situation arising with dimethylberyllium was avoided by first preparing $(MeBeOPr^n)_4$, then condensing on a further mole of ethylene oxide.

The two methods of preparing methylberyllium n-propoxide can be summarised thus:



and those by which methylberyllium isopropoxide tetramer can be arrived at, thus,



Reactions with thiols and thiophenol.

Prior to this investigation, no alkylberyllium alkylsulphides, RBeSR', were known, the only attempt at the preparation of such a compound being the reaction of dimethylberyllium with methanethiol,[63] referred to above.

Four of these derivatives were prepared in the course of this study. They are all tetrameric in benzene solution (cryoscopically) and are listed in Table VII.

Table VII.

Alkylberyllium Alkylsulphide Tetramers.

$(MeBeSBu^t)_4$	$(EtBeSEt)_4$
$(EtBeSBu^t)_4$	$(EtBeSPr^i)_4$

Of the four tetramers, all of which are presumed to have the cubic structure, $(EtBeSEt)_4$ and $(EtBeSPr^i)_4$ appear to be the most stable with respect to disproportionation. Addition of ether does not cause them to disproportionate (as happens in the case of EtBeSMe, see below), nor could crystalline pyridine complexes be isolated. Evidence of coordination (i.e. yellow solutions) was apparent, but the unchanged alkylsulphides could be recovered by exposure to a vacuum. This is in contrast to the two tetrameric alkoxides, $(MeBeOMe)_4$ and $(MeBeOBu^t)_4$, both of which form pyridine complexes, and is not in accord with the generally believed idea that oxygen is a better donor to beryllium than is sulphur.

The tetramers $(MeBeSBu^t)_4$ and $(EtBeSBu^t)_4$, on the other hand, disproportionate more readily. Benzene solutions of the former slowly deposit dimethylberyllium identified by formation of its dipyridine complex, and, presumably, $(Bu^tS)_2Be$, and $(EtBeSBu^t)_4$ itself becomes wet (liquid Et_2Be) on mild heating (ca. 40°) under vacuum. A hexane solution of this compound began to deposit $(Bu^tS)_2Be$ on heating to ca. 50°.

The difference between the t-butylthio compounds and those containing EtS or Pr^iS groups can be explained in terms of slow dissociation, prompted by greater steric hindrance, into dimeric species which, unlike the tetramers, will contain three-coordinate beryllium and sulphur, and which, therefore, would be very likely to add further base.

It is also believed that the order of strength of alkyl bridges in, for example, R_2Be or R_3Al is $Me > Et > Pr^i$ and so on. Thus it can be seen that the relative bridging properties of the group R in RBeSR' may in fluence the disproportionation process, for, if methyl groups, in particular, can compete successfully with R'S groups for bridging positions, then disproportionation, with formation of dimethylberyllium, will be favoured. The same argument applies, to a lesser extent, in the case of $(EtBeSBu^t)_4$.

In fact, no methylberyllium alkylsulphide, other than $(MeBeSBu^t)_4$, has yet been formed, and this is believed to be a reflection of the good bridging properties of the methyl group. An attempt to prepare MeBeSMe (from Me_2Be and MeSH), some years ago[63], failed because dimethylberyllium was formed, presumably by disproportionation, when the product was heated. Similar processes may prevent the formation of $MeBeSPr^i$. The product from the reaction of dimethylberyllium amd isopropylthiol, in ether, contained coordinated ether and was not investigated further, but the product from the same reaction in benzene, which, when formed, was soluble in this solvent, gave, on exposure to a good vacuum, a viscous solid which did not completely redissolve. Integrated proton magnetic resonance spectra on the benzene-soluble extract, after five minutes and after sixteen hours, indicated that disproportionation was occurring in solution and, surprisingly, that the product containing Pr^i-S- bound to beryllium was, to some extent at least, soluble in benzene. As beryllium isopropylsulphide is, by analogy with $[Be(SEt)_2]_x$ and $[Be(SBu^t)_2]_x$, very likely to be polymeric and insoluble in hydrocarbons, the possibility of soluble disproportionation species, such as $Me_2Be_4(SPr^i)_6$, must be considered. The insoluble product was shown to contain dimethylberyllium by isolation of the dipyridine complex, $Me_2Be.py_2$.

Reaction of diethylberyllium and methanethiol, in equal amounts, gave an insoluble product whose hydrolysable ethyl and beryllium contents were a little lower than those required by pure EtBeSMe. That this was due, also, to disproportionation,

$$2\ EtBeSMe \rightleftharpoons Et_2Be + Be(SMe)_2$$

was concluded from the fact that the soluble material in the filtrate contained free diethylberyllium. The possibility of a very fast reaction, giving some $(MeS)_2Be$ at once, and leaving an excess of Et_2Be, cannot be completely ruled out, but is unlikely as the disproportionation can be increased by addition of ether which, presumably, solvates the diethylberyllium. The product, EtBeSMe, was never isolated in a pure form, but is presumed polymeric as the ether-insoluble material contains a high percentage of ethyl groups bound to beryllium.

Attempts to prepare the sterically-hindered alkylsulphides Pr^iBeSPr^i and Pr^iBeSBu^t failed, again due to disproportionation. In the first instance, nothing could be crystallized from the clear solution obtained when Pr^i_2Be and Pr^iSH (in equimolar amounts) had reacted together, and removal of solvent left a gluey substance, suggestive of free di-isopropylberyllium. The 'Pr^iBeSBu^t' disproportionated completely to give $[(Bu^tS)_2Be]_x$ and Pr^i_2Be (positively identified by isolation of its pyridine complex).

Beryllium ethylsulphide, $[Be(SEt)_2]_x$, prepared from diethylberyllium and ethanethiol (1:2 molar ratio), and its t-butylsulphide analogue, are presumed to be polymeric, as they are insoluble in ether and do not melt on heating up to 360^o. The ethylsulphide, however, reacts, in the cold, with a deficiency of diethylberyllium, in ether, to give $(EtBeSEt)_4$ and unreacted, excess, sulphide. This reaction is analogous to that of beryllium methoxide and dimethylberyllium, giving methylberyllium methoxide.

The formation of $(MeBeOBu^t)_4$ from dimethylberyllium and di-t-butyl peroxide prompted an investigation into the reaction of diethylberyllium with diethyl disulphide, EtS.SEt. The reaction proceeds readily, below room temperature, to yield $(EtBeSEt)_4$, identified by comparison of its i.r. and p.m.r. spectra with those of an authentic sample. A sample of diethylsulphide was isolated, after fractionation from ether on the vacuum line, and identified by i.r. spectroscopy.

The three routes to the ethylberyllium ethylsulphide tetramer can thus be summarised as follows:

$$\left.\begin{array}{l} Et_2Be + EtSH \\ Et_2Be + (EtS)_2Be \\ Et_2Be + EtS.SEt \end{array}\right\rangle \longrightarrow (EtBeSEt)_4$$

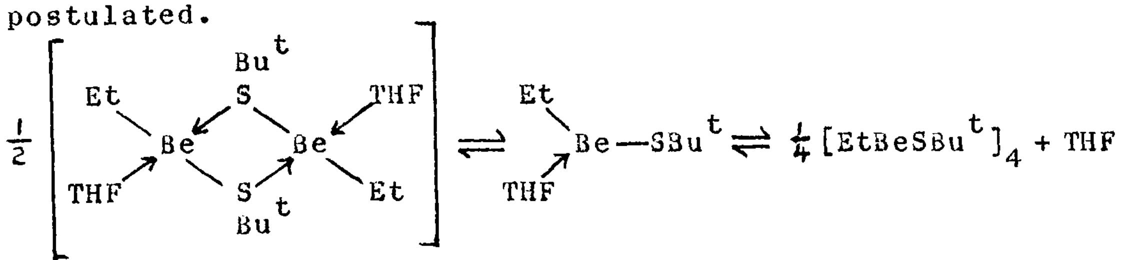
It was reported some years ago[63] that methanol reacts much more quickly with dimethylberyllium than does methanethiol, although the latter is the more acidic in hydroxylic solvents. This was explained in terms of relative donor strengths which favour the initial formation of a complex between dimethylberyllium and methanol over one with methanethiol. In the course of this study, similar observations were made. Phenol reacts faster than thiophenol, isopropanol faster than isopropylthiol and t-butanol faster than t-butylthiol.

Reactions of alkylberyllium alkylsulphides with bases.

The fact that some of the above alkylberyllium alkylsulphides are prone to disproportionation, suggests that, in solution, species containing three-coordinate beryllium may exist, and these, on addition of a donor molecule, should form crystalline complexes in which the metal will become four-coordinate. Several such complexes have been isolated.

The proposed slow dissociation of $(EtBeSBu^t)_4$ into dimers has already been discussed, and is further substantiated by the fact that, unlike $(EtBeSEt)_4$ and $(EtBeSPr^i)_4$, this compound readily forms complexes with tetrahydrofuran, pyridine and 2,2'-bipyridyl.

With excess tetrahydrofuran, the complex $[Et(THF)BeSBu^t]_n$ (n = 1.06, 1.04 in 0.67, 1.00 wt.-% benzene, cryoscopically) is formed. This is not believed to be a genuine monomer, as free tetrahydrofuran can be removed by pumping from a benzene solution of the complex. Equilibria (below), similar to those obtaining in the case of $MeBeOPh.OEt_2$, giving rise to some free base, are postulated.



Reaction with pyridine yields two products, depending on the reactant ratios. With one molar proportion of the base, the complex $[Et(py)BeSBu^t]_n$, (n = 1.73, 1.80 in 0.65, 1.30 wt.-% benzene, cryoscopically), is isolated. Similar dissociation processes probably account for the observed degrees of association. The greater donor strength of pyridine is illustrated by the observation that, unlike tetrahydrofuran, it breaks down the Bu^t-S bridge to yield a 2:1 complex, $Etpy_2.BeSBu^t$, when it reacts, in excess, with $(EtBeSBu^t)_4$. This complex is the expected monomer in benzene solution.

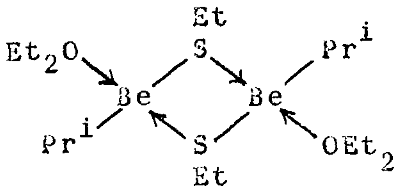
The formation of $Etpy_2.BeSBu^t$ is in contrast to the reactions of $(MeBeOBu^t)_4$ with pyridine, which yield only the monopyridine derivative, even with excess base. This may, in part, be due to the larger size of the sulphur atom which would neccessitate the t-butyl groups being in positions where they are further removed from the beryllium atoms and less likely to interfere with the approach of a pyridine molecule. A similar explanation was forwarded[62] for the fact that $Ph_2Be.(PMe_3)_2$ is stable at 0^o, but $Ph_2Be.(NMe_3)_2$ has a dissociation pressure of 0.8 mm. at this temperature.

2,2'-Bipyridyl displaces tetrahydrofuran from $Et(THF)BeSBu^t$, in ether, to give a red solution from

Photograph 2. Et(bipy)BeSBu^t

which the insoluble, presumably monomeric, bipyridyl adduct, $\mathrm{Et(bipy)BeSBu^t}$, crystallizes. This complex is orange in colour (see Photograph 2) and, like other bipyridyl adducts, it is relatively stable to atmospheric oxidation, owing to shielding of the beryllium atom by the bulky groups present. A sample placed in the air was not noticeably oxidised (change of colour) for two hours, and became white only after three hours' exposure.

The reaction of di-isopropylberyllium with ethanethiol in diethyl ether, yields not $\mathrm{(Pr^iBeSEt)_4}$, as may have been expected, but a crystalline monoether complex, which is dimeric in benzene and probably has structure (43).



(43)

Thus, it appears that the steric effect of the isopropyl group is greater around the smaller beryllium atom than the larger sulphur atom, as $\mathrm{(EtBeSPr^i)_4}$, in which the positions of the ethyl and isopropyl groups are reversed, does not interact strongly with ether or pyridine. Pyridine, in the ratio one mole per g. atom of beryllium, displaces ether smoothly to yield the yellow, crystalline monopyridine complex, $\mathrm{(Pr^ipy.BeSEt)_2}$, also dimeric, and with structure, in all likelihood, analogous to (43).

A hexane solution of the viscous product from the reaction of di-isopropylberyllium with isopropylthiol reacted with excess pyridine to form yellow, monomeric

$Pr^{i}py_{2}BeSPr^{i}$.

In a manner very similar to the formation of $MeBeOPh.OEt_2$, in diethyl ether solution, dimethylberyllium reacts with thiophenol, in ether, to yield dimeric (in benzene) $(MeBeSPh.OEt_2)_2$. That this is undissociated in solution is probably due to the poorer donor strength of a bridging sulphur atom (as compared to oxygen), resulting in a more tightly bound ether molecule.

Unlike beryllium t-butoxide, to which 2,2'-bipyridyl does not coordinate strongly, beryllium t-butylsulphide forms crystalline complexes, $(Bu^{t}S)_{2}Be.py_{2}$, with excess pyridine, and $(Bu^{t}S)_{2}Be.bipy$, with an equimolar amount of bipyridyl. These reactions were carried out in boiling toluene, circumstances under which the products are at least partially soluble. They crystallized on cooling. The formation of these complexes is a further reflection of the strength of the bonds formed by a bridging R'S group, which must be considerably less than the strength of those formed by a bridging R'O group. The dipyridine complex is highly dissociated in benzene solution (n = 0.59, 0.64 in 0.24, 0.42 wt.-% solutions), presumably because four such bulky groups cannot be accommodated around the beryllium atom. The bipyridyl complex is too insoluble to permit cryoscopic molecular-weight determinations in benzene, but is very likely to be monomeric in the solid phase. It is hydrolysed relatively slowly by water.

These observations enable certain generalizations to be made. They are:

1. In contrast to the alkylberyllium alkoxides, several of which are dimeric and have to be formulated with three-coordinate beryllium, no alkylberyllium

alkylsulphides have been prepared other than tetramers.

2. Disproportionation of RBeSR' into R_2Be and $Be(SR')_2$ seems to interfere to a greater extent with the preparation of alkylberyllium alkylsulphides than do the analogous processes in the case of alkylberyllium alkoxides.

3. Disproportionation of RBeSR' appears to occur more readily when R' is Bu^t than when it is Pr^i or Et, and when R is Me rather than Et. The former is attributed to the bulky Bu^t group facilitating dissociation into the presumed labile dimers, $(RBeSBu^t)_2$, and the latter to the good bridging properties of Me-Be compared with Et-Be.

An investigation into the reactions of dialkylmagnesium compounds with thiols has revealed similar trends.[16] For example, the reaction of dimethylmagnesium with t-butylthiol, in diethyl ether, results in disproportionation to insoluble $(Bu^tS)_2Mg$ and Me_2Mg due to successful competition for bridging positions by the methyl group. From tetrahydrofuran, however, $[Me(THF)MgSBu^t]_2$ can be isolated. This base is a stronger donor than ether, so results in the formation of a complex which, like the beryllium ones, contains four-coordinate metal. As yet, the only compound RMgSR' isolated is $EtMgSBu^t$ which, apparently, has a degree of association, in benzene, of between five and six.

Infrared and proton magnetic resonance spectra.

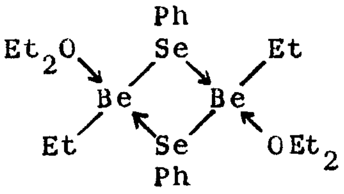
The shifts observed for the methyl protons in $(MeBeSBu^t)_4$ (τ 10.23) and $(MeBeSPh.OEt_2)_2$ (τ 10.38) are in the low-field range observed for the tetrameric methylberyllium alkoxides (presumably containing four-coordinate metal). The spectrum of $(MeBeSBu^t)_4$ (benzene solution; TMS reference) also contained a singlet due to

$\underline{Bu}^t$-S protons (τ 8.46). An attempt to see if the use of d_{14}-methylcyclohexane as solvent would produce splittings of the type observed for $(MeBeOBu^t)_4$ was frustrated on account of insufficient solubility at room temperature, and deposition of solid material, leading to a poor quality spectrum, at higher temperatures. The spectra of other compounds, RBeSR', and their complexes with donor molecules, containing, as they do, ethyl or isopropyl groups bound to beryllium, were complex, but no splitting, other than the normal pattern for these groups, was observed. The details are listed in the experimental results section.

As in the cases of the compounds MeBeOR', methylberyllium symmetric deformations can be tentatively assigned in the infrared spectra of $(MeBeSBu^t)_4$ (1172 cm.$^{-1}$) and $(MeBeSPh.OEt_2)_2$ (1179 cm.$^{-1}$).

Reactions with selenophenol.

In view of the formation of the complexes $MeBeOPh.OEt_2$, which is dissociated in benzene solution, and $(MeBeSPh.OEt_2)_2$, dimer, the isolation of $(EtBeSePh.OEt_2)_2$, dimer, from the reaction of diethylberyllium and selenophenol, in diethyl ether, was expected. It probably has structure (44).



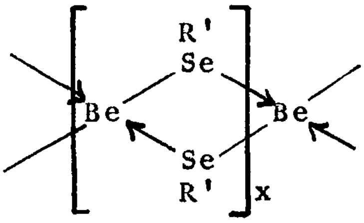
(44)

The reaction of diethylberyllium with two molar proportions of selenophenol yielded, not the expected polymer, $[Be(SePh)_2]_x$, but a product containing 12.97% by weight of diethyl ether, that is to say, of empirical formula, $(PhSe)_2Be.0.65\ OEt_2$. Though it is perhaps premature to speculate about the existence of a compound of type $[Be(SeR')_2]_x$ until a further attempt to prepare $[Be(SePh)_2]_x$, e.g., by heating of the ether complex under vacuum has been made, three factors may still be considered.

1. The order of decreasing donor strength towards dimethylberyllium [4] is $N>P>O>S$, and towards trimethylaluminium [32] $N>P>O>S>Se$. Thus, selenium might be expected to be a weaker donor than either sulphur or oxygen towards beryllium. Diethyl ether, therefore, should coordinate strongly enough to break down the (presumed) polymeric $[Be(SePh)_2]_x$, giving less associated species.

2. If phenylselenide acts as an electron-withdrawing group, its presence will aid the coordination of ether, by making the beryllium atoms more 'electron-deficient'.

3. Though it can be seen, from the construction of molecular models, that there will be some steric interaction between adjacent selenium atoms in a polymeric selenide, $[Be(SeR')_2]_x$, (45),



(45)

nevertheless, inspection of the covalent radius of beryllium (1.06 Å) and that of selenium (1.14 Å),[163] indicates that such an arrangement, with the selenium atoms tetrahedrally disposed round the beryllium atoms, should be possible. In fact, it does occur in beryllium selenide, which has the zinc blende structure,[164] and it can be calculated that the Se-Se distance in such an arrangement is 3.59 Å, which is 1.31 Å greater than twice the covalent radius of selenium, and only 0.41 Å less than twice its Van der Waal's radius (2.0 Å) which, in any case, might be expected to be directed away from the straight line joining adjacent selenium atoms.

It is concluded that a balance between these three factors accounts for the formation of the ether complex, which reacts with one mol. of 2,2'-bipyridyl to give the complex, $(PhSe)_2Be.bipy$, presumed to be monomeric.

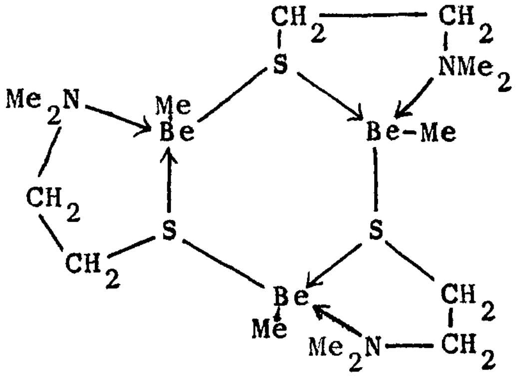
Reactions with molecules which contain a chelate group.

These three reactions are considered together, as the presence of a chelating group has an effect on the degree of association, dependent on its nature, and sometimes different from the effects discussed above.

Methylberyllium 2-methoxyethoxide has already been shown[73] to be tetrameric in benzene solution. The ethylberyllium analogue, $(EtBeO.CH_2.CH_2.OMe)_4$, is here found to be a tetramer also. Thus, presumably, the molecules have a cubic structure, like the simpler alkylberyllium alkoxides, with the ether oxygens not taking part in the internal coordination. This is in accord with Hoffmann's observations[8] that $(Et_2AlO.CH_2CH_2OEt)_2$ is dimeric (above) and is supported by the degree of association of $(MeZnO.CH_2.CH_2.OMe)_4$, which is also a tetramer.[83]

The more basic dimethylamino groups in methylberyllium 2-dimethylaminoethoxide and methylberyllium 2-dimethylaminoethylsulphide, however, may compete successfully with the alkoxy- oxygen and sulphide- sulphur atoms for coordination positions about the beryllium atom. If they do so, then tetramers will not be formed, but instead the products will be more or less associated, depending on whether some, or all, of the dimethylamino is coordinated. In fact, successful competition is quite likely, as the dimethylamino group would be competing with the fourth valency of the relatively rarely encountered four-coordinate oxygen.

Trimeric $(MeBeS.CH_2.CH_2.NMe_2)_3$ therefore, can reasonably be supposed to have the cyclic structure (46), containing coordinated nitrogen.



(46)

It is high melting (194° with decomposition) and crystallizes well, facts which support the above structure, containing four fused rings, but, as yet, no attempt to form a methiodide has been made.

The more highly associated ($n = 6.7 \rightarrow 7.1$ in $1.33 \rightarrow 2.00$ wt.-% solutions) complex, $(\mathrm{MeBeO.CH_2.CH_2.NMe_2})_n$, may, in solution, have some uncoordinated $\mathrm{Me_2N}$ which cross-links with other trimeric units. However, why this $\mathrm{Me_2N}$ should dissociate when the oxygen atom occupies less space than the sulphur atom in (46), is perplexing. In the solid state this compound, like $(\mathrm{MeBeS.CH_2.CH_2NMe_2})_3$, has properties (high crystallinity and melting point) which indicate the presence of four-coordinate metal. It is not hydrolysed by water, which would certainly be surprising if the complex contained three-coordinate metal. Its p.m.r. spectrum (in benzene) contains a $\underline{\mathrm{CH_3}}$-Be resonance in the high-field range (τ 10.83 relative to benzene 2.73) associated with three-coordinate beryllium, whereas that of (46) is at τ 10.62, indicative of four-coordinate beryllium. The possibility, therefore, of the ethoxide having a structure analogous to (46) in the solid phase, but being more associated in solution, must be considered.

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