Co-ordination chemiatiy of beryllium

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Co-ordination Chemistry
of
Beryllium

by

S. I. E. Green

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Memorandum

The work described in this thesis was carried out in the Durham Colleges in the University of Durham between September 1959 and May 1962. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

SUMMARY

The reactions of a number of ethers and thioethers with beryllium halides have been studied. The coordination compounds formed were of types already known for beryllium halides except for one of the complexes formed by dimethyl sulphide which appears to be di-μ-chlorodichlorobis(dimethyl sulphide)diberyllium, $(BeCl_2.Me_2S)_2$. These studies have shown that dimethyl sulphide, tetrahydrofuran, and 1,2-dimethoxyethane are all possibly useful solvents for reactions of beryllium chloride. Solutions of beryllium chloride in diethyl sulphide undergo some decomposition, particularly on slight warming when hydrogen chloride is liberated slowly.

A series of 2,2'-bipyridyl complexes of beryllium halides, alkyls, and aryls have been prepared which have the formula $bipyBeX_2$ (X=Cl,Br,I,Ph,Me, or Et) and which have unexpected colours. The visible and ultra-violet spectra of these compounds have been studied and on the basis of these spectra it has been suggested that their colours are due to an electron transfer from the Be-X bonds to the lowest unoccupied molecular orbital of bipyridyl.

By the reaction of bipyridyl lithium with beryllium chloride or the reaction of bipyridyl dilithium with dichloro(bipyridyl)beryllium the compound bis(bipyridyl)beryllium has been prepared. Its properties suggest that it is best regarded as a coordination compound of the bipyridyl anion with the Be(11) cation. Reaction with an excess of lithium metal affords the salt $LiBebipy_2$.

The reactions of ethylenediamine and certain N-methyl substituted ethylenediamines with dimethylberyllium have been studied. These containing one or more amino-hydrogen atoms gave methane on

reaction with dimethylberyllium giving either dimeric or polymeric products according to whether one or two mols. of methane were eliminated.

A 1:1 adduct of 1,2-dimethoxyethane and dimethylberyllium has been prepared. It is monomeric in benzene solution and can be sublimed unchanged in a vacuum.

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INTRODUCTION

INTRODUCTION

The work described in this thesis is concerned with the reactions of beryllium halides and, more particularly, organo-beryllium compounds with donor molecules. In this introduction beryllium chemistry relevant to these topics is reviewed. The preparation and properties of the beryllium halides and certain organo-beryllium compounds are covered first, then follows a review of the coordination compounds derived from these. A section on chelated oxygen complexes of beryllium is also included, since these are of great interest in beryllium coordination chemistry and because many chelating donors have been studied in this work.

Beryllium forms covalent compounds almost exclusively, this being due to the small size, and therefore high polarizing power of the atom. The atomic radius of beryllium is 0.89 Å and the calculated ionic radius of Be^{2+} is 0.34 Å. The first and second ionization potentials of beryllium are 215 and 420 kcal./mole respectively which suggests that the existence of free divalent ions of beryllium in its compounds is not to be expected. Thus beryllium fluoride, which might be expected to be the most ionic compound of beryllium, has been shown to be a poor conductor of electricity in the fused state,(1) and beryllium oxide has only about 40 per cent ionic character according to Pauling.

Compounds of beryllium have covalencies of two, three, or four for the metal atom. The coordination number of two arises from the use of Sp hybrid orbitals by the beryllium giving a linear molecule as is found in the case of beryllium chloride at very high temperatures, when it exists as a monomer.

Beryllium can also make use of Sp^2 orbitals giving a coordination number of three as in, for example, dimethylberyllium-trimethylamine.(2) However in the vast majority of its compounds beryllium is found to be 4-covalent, using Sp^3 orbitals to give tetrahedral bonding. It has an extremely strong tendency to form compounds with this maximum covalency of four. Thus the beryllium ion is more strongly hydrated than any other divalent cation as shown by heats of hydration and its salts always have four molecules of water of crystallization for each beryllium atom.

The phthalocyanine complex of beryllium is an exceptional case in that it has a square-planar configuration due to the shape of the phthalocyanine molecule.(2a)

Beryllium forms no known compounds with a coordination number greater than four since the atomic orbitals of principal quantum number three are of too high an energy to participate in bond formation and no hybrid orbitals involving d-orbitals can be expected for beryllium.

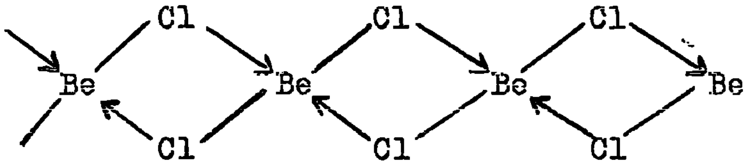
Beryllium Halides

Beryllium fluoride. Beryllium fluoride cannot be prepared from the hydroxide and hydrofluoric acid since the salt formed is hydrolysed on evaporating the solution. It can be prepared by heating the oxide in a stream of hydrogen fluoride gas or by the reaction between fluorine and beryllium. The simplest method of preparation is to heat ammonium tetrafluoroberyllate.(3) It is then obtained as a glassy residue which softens and begins to sublime at 800° and in the fused state is a poor conductor of electricity.(1) It is hygroscopic and very soluble in water.

Beryllium chloride. This is most conveniently prepared by heating beryllium in a stream of dry hydrogen chloride gas.(4,5) It can also be prepared by heating the metal in chlorine, by heating a mixture of the oxide and carbon in chlorine gas, or by heating the oxide in sulphur chloride vapour, phosgene, or carbon tetrachloride.(6) It forms white needles which melt at 405° and it boils at 488°; thus it can be easily purified by sublimation. At 564° it contains about 23% of Be_2Cl_4(7) but is completely monomeric at 745°.(4) It is a poor conductor in the fused state.

Beryllium chloride reacts vigorously with water forming some hydrogen chloride and fumes of beryllium hydroxide and dissolving in the water to a large extent. It can be crystallized out from the aqueous solution as $BeCl_2.4H_2O$. The anhydrous chloride is extremely soluble in several alcohols but again it probably reacts with the solvent since the viscous solutions formed smell of hydrogen chloride. It is also soluble in ether, acetone, and many amines and nitriles, but is insoluble in non-donor solvents such as benzene. With many donor solvents it forms coordination compounds, usually with the general formula $BeCl_2.2L$.(8,9)

The structure of anhydrous beryllium chloride in the solid state is shown below. The beryllium atoms achieve their covalency of four by coordination to the chlorine atoms so that a long chain polymer is produced.



Beryllium bromide. It is prepared in much the same way as is beryllium chloride.(5) It melts at 488° and sublimes at 473° and so it is more volatile than the chloride. Its structure is identical with that of the chloride.

It dissolves readily in water and from the solution the tetrahydrate can be obtained. Beryllium bromide forms many addition compounds similar to those of the chloride.

Beryllium iodide. Beryllium iodide is similar to the chloride and bromide but far less stable. It can be prepared by the action of hydrogen iodide on beryllium carbide at 700°. It melts at 480° and boils at 488°.

With water it reacts very violently giving hydrogen iodide. It dissolves in many organic solvents forming addition compounds.

Organo-Beryllium Compounds.

Beryllium dialkyls and diaryls can be prepared by the action of metallic beryllium on the alkyls or aryls of mercury. This method has been used for the preparation of dimethyl,(10) diphenyl,(11,12) and di-p-tolylberyllium(12) in small quantities. On a larger scale they are better prepared from beryllium chloride and a Grignard reagent (13) or alkyl or aryl lithium in ether:

$$BeCl_2.2Et_2O + 2RMgX \longrightarrow R_2Be + MgX_2 + MgCl_2$$

or

$$BeCl_2.2Et_2O + 2RLi \longrightarrow R_2Be + 2LiCl$$

When prepared by this method complete removal of last traces of ether from the beryllium compound is often difficult. This is especially true for dimethylberyllium.(13,14) These compounds must be prepared in an atmosphere of nitrogen with complete exclusion of oxygen, moisture, and carbon dioxide, all of which react rapidly with beryllium alkyls.

Certain alkyl- and aryl-beryllium halides(12,13) have been prepared by the reaction of beryllium with an alkyl or aryl halide in ether in the presence of a trace of mercuric chloride at about 100°;

$$CH_3I + Be \longrightarrow CH_3BeI,$$

though the existence of phenylberyllium bromide has recently been denied on the basis of non-exchange between Ph_2Be and $Be^{*}Br_2$.(14a)

<u>Dimethylberyllium</u>. This can be prepared by heating dimethylmercury with an excess of powdered beryllium metal at 100° for a day or so. The product can be sublimed from the mixture under a high vacuum but separation from mercury is rather difficult. Preparation by the Grignard method involves difficulties in separation from ether.(13)

When the Grignard reagent is prepared in dimethyl sulphide, and reacts with beryllium chloride in dimethyl sulphide,(15) separation of the product from the solvent is a simple matter since it has been shown that dimethyl sulphide does not coordinate to dimethylberyllium.(2)

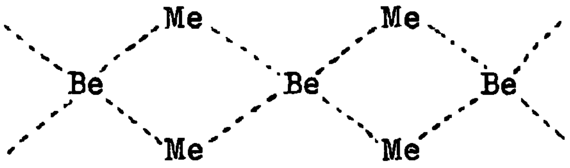
Dimethylberyllium forms colourless needles and the vapour pressure is given by the equations:(16)

$$100 - 150^{\circ}: \quad \log_{10} P(\text{mm.}) = 12.530 - 4771/T.$$

$$155 - 180^{\circ}: \quad \log_{10} P(\text{mm.}) = 13.292 - 5100/T.$$

By extrapolation the vapour pressure is 760 mm. at 217°. The latent heat of sublimation is 23.5 kcal./mole of monomer.

X-ray diffraction studies have shown its structure is a long chain polymer$^{(19)}$:

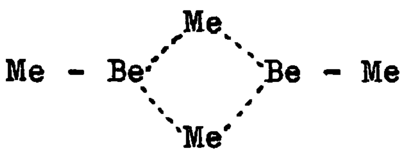


The Be - C distance is 1.92 Å and the Be - C - Be angle is 66°. Both beryllium and carbon atoms presumably use tetrahedral (Sp^3) atomic orbitals and it seems likely that three-centre molecular orbitals are formed to give the Be - C - Be bonds.

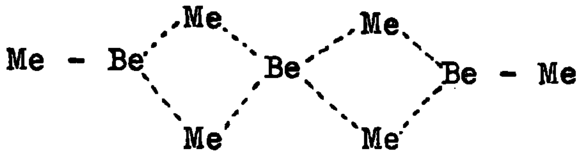
The vapour of dimethylberyllium consists of a mixture of monomer, dimer, and trimer molecules at low pressures. The likely structures for these molecules are shown below:

monomer: $\mathrm{Me - Be - Me}$

dimer:



trimer:



In these formulae dotted lines represent half-bonds.

Dimethylberyllium is extremely reactive. It takes fire in the air spontaneously, even in concentrated ethereal solution, and also catches fire in carbon dioxide. All the alkyls and aryls are quantitatively decomposed by water violently to give beryllium hydroxide and the hydrocarbon.

Dimethylberyllium reacts readily with diborane at 95^o giving trimethylborane and several unidentified products but further reaction with diborane gives methylberyllium borohydride,(10) $MeBeBH_4$, which is quite volatile. This will react with more diborane at about 60^o at just above atmospheric pressure forming the volatile beryllium borohydride, $Be(BH_4)_2$, m.p. 123^o, v.p. 760 mm. at 91.3^o, which is monomeric in the vapour.

When dimethylberyllium is treated with lithium aluminium hydride in ether a white precipitate of an etherate of beryllium hydride is formed.(17) It has been shown that this product is also contaminated with several per cent each of lithium hydride and aluminium hydride.(18) If it is treated with diborane it forms beryllium borohydride:

$$BeH_2 + B_2H_6 \longrightarrow Be(BH_4)_2$$

Diethylberyllium . This compound cannot be prepared from beryllium and diethylmercury.(13) It is conveniently prepared by the reaction of beryllium chloride with ethylmagnesium bromide in ether.(13,20,21) The product is concentrated by distillation in vacuo and finally by pumping for a long time at room temperature to avoid thermal decomposition. Diethylberyllium is thus obtained containing about 2% of ether, as a colourless liquid boiling at 63°/0.3 mm. and freezing to a glass at -80°. Its vapour pressure is given by the equation:

$$\log_{10} P(\text{mm.}) = 7.59 - 2200/T.$$

This gives an extrapolated boiling point of 194°. It is quite soluble in benzene, unlike dimethylberyllium. No molecular weight measurements have been reported.

At 85° it begins to decompose appreciably and at 190 - 200° this decomposition is rapid, forming ethane, ethylene, and butene with traces of certain other hydrocarbons. The residue is an ethylberyllium hydride of unknown constitution.

Like dimethylberyllium it takes fire in the air and it reacts explosively with water producing ethane.

Di-isopropylberyllium. This has been prepared by the reaction between isopropylmagnesium chloride and beryllium chloride in ether.(22) The ether can be separated from it by refluxing with continuous pumping for a long time. It is then obtained as a colourless, slightly viscous liquid freezing at - 9.5° and with an extrapolated boiling point of 280°. The vapour pressure at 20° is 0.17 mm. and at 40° is 0.53 mm. It is dimeric in benzene solution.

It fumes strongly on exposure to air, but does not take fire, and with water it reacts explosively.

Above 50° it slowly evolves propene, and this reaction goes fairly rapidly at 200° forming a viscous residue of *iso*propylberyllium hydride, $(C_3H_7BeH)_x$.

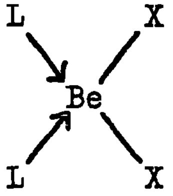
Di-tert-butylberyllium. This was prepared from beryllium chloride and *tert*.-butylmagnesium chloride in ether.(23) It decomposes slowly at room temperature giving *iso*butene and is best kept at a low temperature (-78°). It can be obtained free from ether by treatment with anhydrous beryllium chloride followed by distillation of the di-*tert*-butylberyllium.(18) It freezes at -16° and its vapour pressure is 35 mm. at 25° so that it seems probable that it is monomeric.

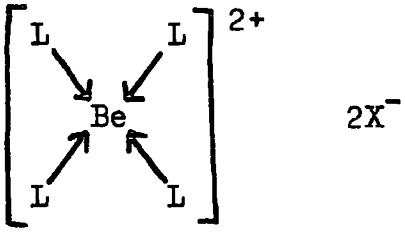
At 200° it decomposes rapidly forming nearly two moles of *iso*butene. The residue is beryllium hydride which still contains about one *tert*.-butyl group to every ten beryllium atoms, and which decomposes slowly at about 200° and quite rapidly at 220° giving off hydrogen. The beryllium hydride is almost inert to air and reacts slowly with water and rapidly with acids.

Diphenylberyllium(24,25) By heating a mixture of diphenylmercury and beryllium at 210° for 1 to 2 hours diphenylberyllium is obtained which can be recrystallized from benzene. It melts at 244 - 8° with decomposition. Although it is quite soluble in benzene no molecular weight measurements have been reported. It is more soluble in ethereal solvents forming the coordination compounds. Thus it dissolves in ether with formation of $Ph_2Be(OEt_2)_2$, m.p. 28-32°, which can be crystallized from the solution.(26) The ether complex loses ether in vacuo at 130°.

Coordination Complexes of Beryllium Halides

The beryllium halides form many complexes with amines, ketones, aldehydes, ethers, etc. of the general type $BeX_2.2L$. They also form stable compounds of the general formula $BeX_2.4L$ with ammonia and certain amines, and also with water. The difference in structure between these two types of coordination compounds is shown below:





In both cases beryllium achieves a covalency of four by the coordination. These types of compounds are reviewed below.

Ether complexes of beryllium halides. Diethyl ether reacts exothermically with anhydrous beryllium chloride forming two liquid layers. The lower layer is rather viscous and solidifies on standing or on cooling slightly giving crystals of $BeCl_2.2Et_2O$.(8,9) This compound dissolves readily in ether or benzene and many other complexes can be prepared from its solution, as the diethyl ether is easily displaced by certain other ethers, and by ketones, aldehydes, amines, etc.

The etherates of beryllium chloride and beryllium bromide can also be prepared by direct reaction of beryllium metal with the halogens or hydrogen halides in dry diethyl ether at room temperature.(27) The complex, $BeCl_2.2Et_2O$, has been found to melt at 43°, when freshly prepared, and begins to boil at 105-110°, with decomposition, at atmospheric pressure.(28) A compound $BeCl_2.3Et_2O$ has also been observed at low temperatures (-60 to -70°).(28)

A different type of complex containing diethyl ether has been prepared by passing hydrogen chloride gas into a suspension of beryllium hydroxide in diethyl ether containing a little water. Delicate needle-like crystals of $[Be(H_2O)_3.Et_2O]Cl_2$ separate out from the solution.(29) The complex liberates ether and hydrogen chloride when exposed to moist air. A bromide can be prepared similarly but this is even less stable than the chloride.

When a solution of beryllium chloride etherate in diethyl ether is treated with dioxan a colourless precipitate of $BeCl_2.C_4H_8O_2$ is produced.(30) The bromide, $BeBr_2.C_4H_8O_2$, was prepared similarly. Both deliquesce in air and the bromide fumes in moist air. Both tend to lose dioxan when placed over concentrated sulphuric acid and both are decomposed by water with elimination of hydrogen halide. They dissolve in ethanol and glycol, possibly with some reaction, but they are only sparingly soluble in diethyl ether, dioxan, and benzene.

By treating solid $BeCl_2.2Et_2O$ with excess boiling tetrahydrofuran and cooling, colourless needles of $BeCl_2.2T.H.F.$ are formed.(31) It melts with decomposition at 150° and is more stable in the air than $BeCl_2.2Et_2O$. It dissolves readily in benzene and toluene but is insoluble in aliphatic hydrocarbon solvents. Below -2° a compound $BeCl_2.3T.H.F.$ can be obtained.

Other oxygen complexes of beryllium halides. Addition compounds are not formed with alcohols and phenols, as occurs with magnesium and calcium halides. Beryllium chloride reacts exothermically with ethanol giving a viscous solution which smells strongly of hydrogen chloride indicating that some reaction has occurred.(33) It also reacts with phenol in boiling benzene forming hydrogen chloride and $Be(OPh)_2$ but again gives no coordination compound.(9,32)

However, aldehydes and ketones do add to beryllium halides readily, forming molecules of the type $BeX_2.2L$ (where L = donor and X = halogen). These can be prepared either by mixing beryllium chloride or bromide and the donor compound or, preferably, by mixing ether solutions of the two components.(34) Compounds of beryllium chloride with two molecules of acetone, benzophenone, benzaldehyde, and cinnamaldehyde have been prepared by the latter method. These compounds are mostly very slightly soluble in solvents which do not decompose them. The compound $BeCl_2.2MeCOMe$ is an exception since it is very soluble in benzene(9,34) and at 5° colourless crystals of $BeCl_2.2MeCOMe.4C_6H_6$ are produced. This compound melts at 40° and loses benzene very easily.

Nitrogen complexes of beryllium halides. The beryllium halides react with ammonia to form ammines.(35,36) Vapour pressure measurements on the halide and ammonia system show that all three halides studied give compounds with 4,6, and 12 molecules of ammonia. Only the tetrammines are stable at room temperature. The diammine $BeCl_2.2NH_3$, also appears to exist. The tetrammine is easily decomposed by water giving the compound $BeCl_2.4H_2O$.

Beryllium chloride forms complexes with a great number of amines of which only methylamine forms a tetrammine, the others forming diammines, $BeCl_2.2L$.(8,9,34,37,38,39) These complexes are usually prepared in ether. Complexes have been prepared with $L = Et_2NH$, $BuNH_2$, p-toluidine, o-toluidine, 2-lepidine, quinoline, pyridine. A complex $BeCl_2.2NH_3.4MeCOMe$ is formed in acetone(9) which loses acetone but not ammonia in dry air.

With ethylenediamine the salt $[Be(en)_2]Cl_2$ is formed,(38) which is quite insoluble in water.

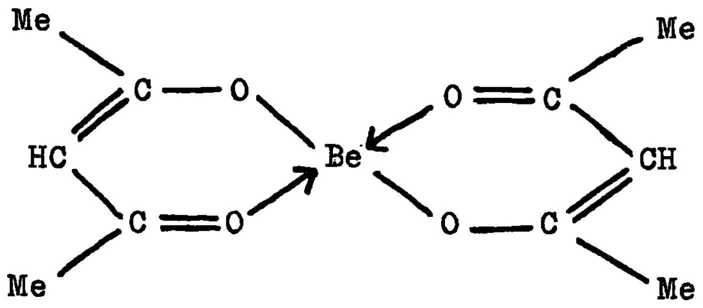
Beryllium chloride also reacts readily with nitriles.(8,37,39) It forms the compound $BeCl_2.4HCN$ with hydrogen cyanide, but with all the organic nitriles examined, seven in all, it gives only compounds of the type $BeCl_2.2RCN$. They are slightly soluble in organic solvents and are decomposed by water.

Chelated Oxygen Complexes of Beryllium

Beryllium forms many neutral compounds with chelate rings formed through oxygen atoms. There are two groups of these compounds; the derivatives of β-diketones and the series of covalent derivatives of the carboxylic acids of the general formula $Be_4O(O.CO.R)_6$.

Derivatives of β-diketones. Bis(acetylacetone)beryllium was the first compound of this type to be prepared.(40) It is a fairly volatile white crystalline solid which melts at 108° and boils at 270°. It is insoluble in cold water but is slowly hydrolysed by boiling water. It is soluble in organic solvents.

The structure of this compound is shown below:



A determination of the vapour density of this compound confirmed the atomic weight of beryllium.

Many other β-diketone derivatives have been prepared. The tetrahedral arrangement of bonds of 4-covalent beryllium was established by studies on certain of these compounds. Thus it was found that beryllium benzoyl-camphor shows mutarotation and later that the beryllium derivative of benzoylpyruvic acid can be resolved into optical isomers.(42) It has also been shown that bis(benzoylacetone)beryllium can be partially resolved.(43)

β-Ketoesters such as ethyl acetoacetate form similar types of complexes.

Basic carboxylic acid complexes. The carboxylic acids form beryllium derivatives of the composition $Be_4O(O.CO.R)_6$ which are covalent compounds, soluble in hydrocarbon solvents, and volatile.

The acetate, $Be_4O(O.CO.CH_3)_6$, was made by the reaction of acetic acid with beryllium hydroxide or carbonate.(44,45) It melts at 285-6° and boils at 330-1°. It is monomeric in the vapour, in benzene, and in acetic acid. It is insoluble in water and is hydrolysed by hot water and by dilute acids.

The structure of the basic acetate has been determined by x-ray diffraction.(46) It was found that it has an oxygen atom surrounded by four beryllium atoms tetrahedrally, with the six acetate groups across the edges of this tetrahedron. A basic beryllium nitrate which has been recently prepared may have a similar structure.(46a)

Coordination Complexes derived from Organo-beryllium Compounds.

Several types of coordination compounds of beryllium have been prepared by the reaction of donor molecules with organo-beryllium compounds or beryllium hydride. These compounds are discussed in the following sections under the headings of the beryllium compounds from which they have been derived.

Dimethylberyllium. Dimethylberyllium only coordinates with those molecules which are sufficiently strong donors to break down the polymeric structure of the dimethylberyllium.(2) It forms coordination compounds with trimethylamine, trimethylphosphine, and dimethyl and diethyl ether, but not with trimethylarsine or dimethyl sulphide. The properties of these indicate that the order of stability of the compounds is $N > P > O > As$, S.

Trimethylamine forms the compound $Me_2Be.NMe_3$ m.p. 36°, which is stable up to 180° and is monomeric in the vapour phase. Below 9-10° a compound $(Me_2Be)_2(NMe_3)_3$ can be obtained which begins to dissociate on warming.

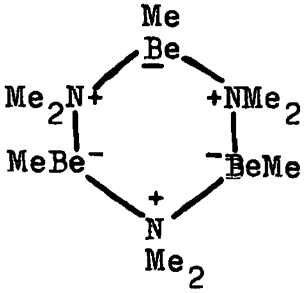
Reaction with trimethylphosphine is rather more complicated and a considerable range of compounds $(Me_2Be)_x(PMe_3)_y$

can be formed, each being stable in a certain range of temperature and pressure of trimethylphosphine. All the trimethylphosphine can be separated from them by pumping in a high vacuum at room temperature. These compounds range from $Me_2Be(PMe_3)_2$ to $(Me_2Be)_5(PMe_3)_2$ with four other intermediate compounds. One peculiarity is that two molecules of the phosphine can coordinate to dimethylberyllium, whereas the compound $Me_2Be(NMe_3)_2$ is unknown, although nitrogen is a stronger donor than phosphorus to beryllium as shown by dissociation pressures of these compounds.

With dimethyl ether the compounds $Me_2Be.OMe_2$, $(Me_2Be)_2(OMe_2)_3$, $(Me_2Be)_3(OMe_2)_2$ and $(Me_2Be)_2OMe_2$ have been observed but all are considerably less stable than the trimethylphosphine compounds.

With diethyl ether there is no indication of the formation of compounds of any definite composition.

Dimethylberyllium reacts with certain donor compounds containing reactive hydrogen atoms, forming methane and di-, tri or poly-meric products.$^{(47)}$ Dimethylamine forms the compound $Me_2Be.NHMe_2$ which melts at 44° with evolution of methane and the formation of $(MeBe.NMe_2)_3$ to which a cyclic structure has been assigned:



Methanol reacts with dimethylberyllium without forming an intermediate coordination compound, giving methane off immediately and forming $(MeBe.OMe)_2$ which probably has a cyclic structure. This compound readily disproportionates into dimethylberyllium and beryllium methoxide, $Be(OMe)_2$, above 120°.

Diethylberyllium Little study has been made of the coordination compounds of diethylberyllium. It has recently been shown that it reacts with trimethylamine forming a 1:1 coordination compound, $Et_2Be.NMe_3$.(57)

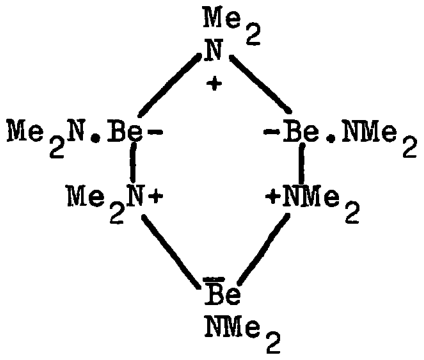
With diphenylamine it reacts rapidly evolving ethane and forming the polymeric compound $Be(NPh_2)_2$.(48)

Di-isopropylberyllium.(22) With trimethylamine it forms a liquid coordination compound, $i\text{-}Pr_2Be.NMe_3$, which is monomeric in benzene solution.

Di-isopropylberyllium reacts with methanol giving propane and $(i\text{-}PrBe.OMe)_x$, m.p. 133°.

With one mol. of dimethylamine, di-isopropylberyllium forms a mol. of propane and the liquid dimethylaminoisopropylberyllium, $(i\text{-}PrBe.NMe_2)_x$. The latter, on heating to over 100°, gives propene and dimethylaminoberyllium hydride which forms a glass at room temperature.

Addition of 2 mols. of dimethylamine to di-isopropylberyllium at just above room temperature affords bisdimethylaminoberyllium and propane. This compound is trimeric in benzene and in the vapour and its structure is probably that shown below:



It forms prisms melting at about 94°.

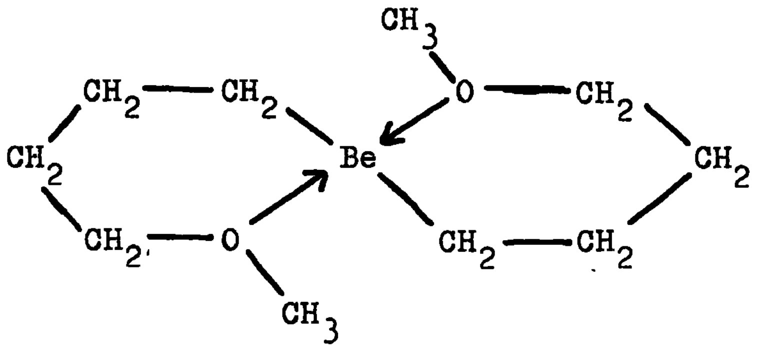
Di-tert.-butylberyllium.(23) With trimethylamine it forms a complex which melts at 42-47°, but this reaction product has not been well characterized.

No other coordination compounds of di-tert.-butylberyllium have been studied.

Beryllium hydride.(23) Beryllium hydride, prepared from di-tert.-butylberyllium by pyrolysis, reacts with dimethylamine at 160° forming hydrogen and bisdimethylaminoberyllium.

Organo-Beryllium Inner Complexes of the Spiran Type.(15)

Bis(4-methoxybutyl) beryllium



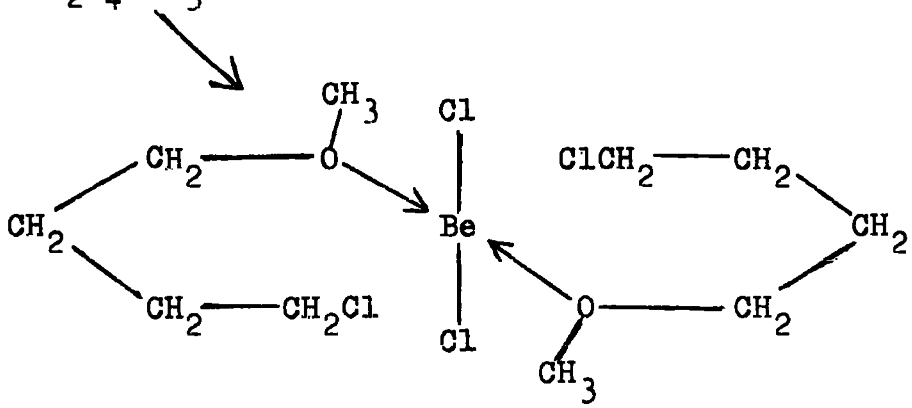
I

This compound can be prepared by two methods both of which start from 4-methoxybutyl chloride.

a) $CH_3O.(CH_2)_4Cl + Mg \longrightarrow CH_3O.(CH_2)_4MgCl$

$2CH_3O(CH_2)_4MgCl + BeCl_2 \longrightarrow (I) + 2MgCl_2$

b) $BeCl_2 + 2Cl(CH_2)_4OCH_3$



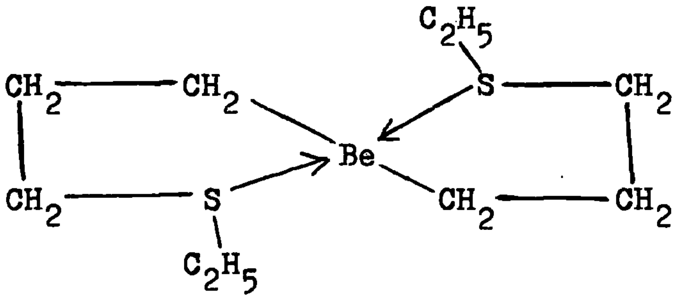
II

$(II) + 2Mg \longrightarrow (I) + 2MgCl_2$

Both reactions are done in diethyl ether. Reaction a) gives 45% of (I) and reaction b) gives only 22% yield.

The product, bis(4-methoxybutyl)beryllium, is a colourless liquid at room temperature, freezing at 7.6 - 7.8°.

Bis(3-ethylthiopropyl)beryllium



III

This compound was prepared by the following reaction:

$$2C_2H_5S(CH_2)_3MgCl + BeCl_2 \rightarrow (III) + 2MgCl_2$$

This reaction can be carried out in either dimethyl sulphide or diethyl ether.

The product is a colourless liquid freezing at 7-8°. This compound is of interest because it has been shown that dimethyl sulphide does not coordinate to dimethylberyllium.(2) The reason for this is that the energy required to break down the polymeric structure of dimethylberyllium is greater than the energy of coordination of sulphur to the organoberyllium compound. Such considerations do not apply in the case of the spiran type of compound.

EXPERIMENTAL

APPARATUS AND TECHNIQUES

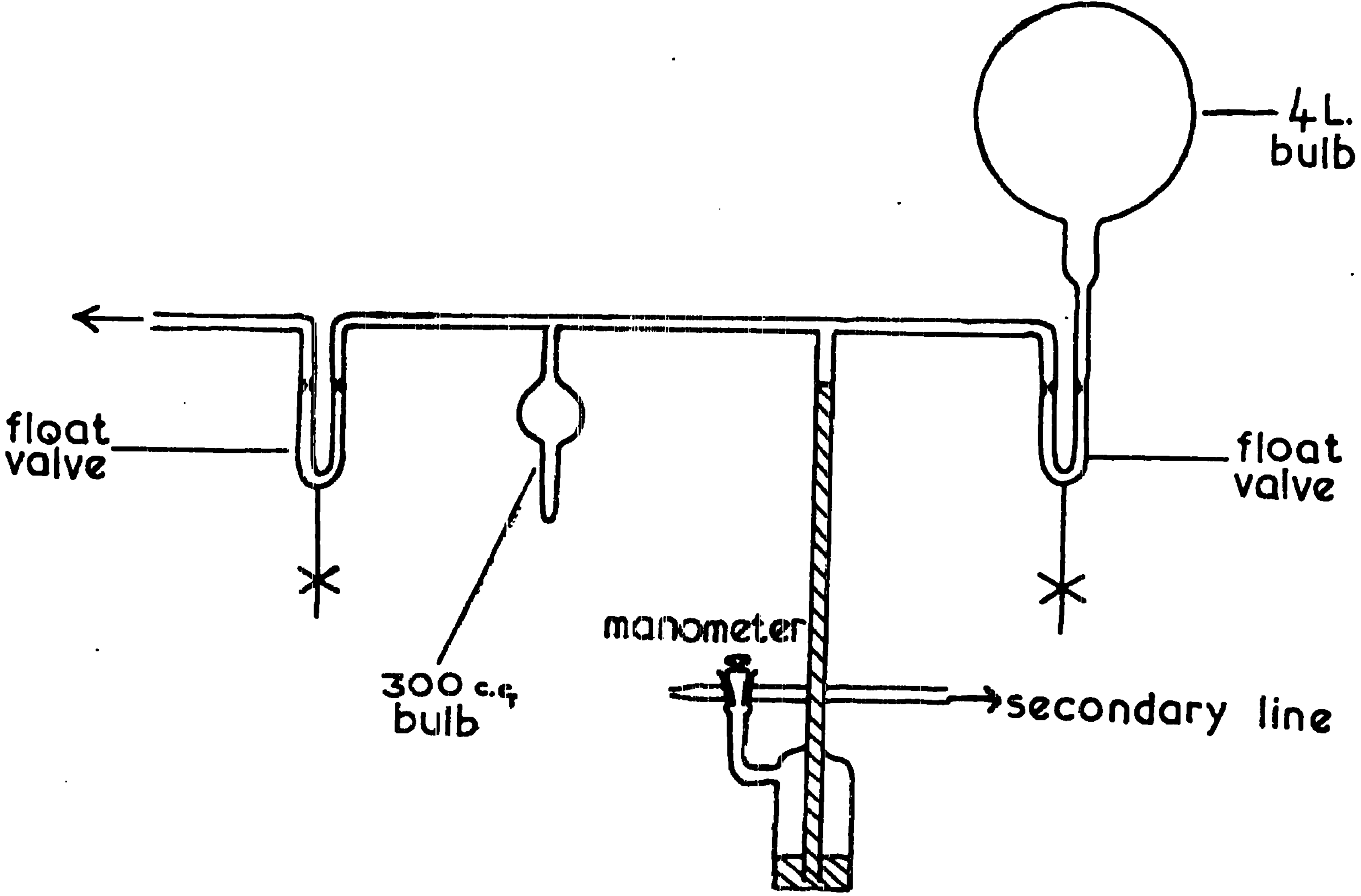
Nitrogen supply. Almost all the work undertaken was carried out in an atmosphere of dry nitrogen, since most of the compounds studied react with oxygen or with moisture.

For this purpose the nitrogen used was from a cylinder of "oxygen-free" nitrogen, but was additionally purified by passing it through a furnace at about 350° containing copper prepared by reducing copper oxide in a stream of hydrogen gas. It was then dried thoroughly by passing it through a column packed with a suitable molecular sieve.

Handling of beryllium compounds. Beryllium compounds must be handled with great care, particularly when they produce fumes of beryllium oxide on exposure to the atmosphere, since beryllium is extremely toxic. Many reactions, such as the preparation of beryllium chloride, were therefore carried out in fume chambers and transfer of solids was usually done in a glove box filled with dry nitrogen and fitted with a filter to prevent dusts passing out into the air. It was found that many starting materials, such as dimethyl- and diethylberyllium, were best stored in ether solution. They could then be kept in flasks fitted with a nitrogen lead and a serum cap so that the compounds could be transferred conveniently by means of a hypodermic syringe. In this way the stock of material had no risk of exposure to the air. Volatile compounds were usually handled on the vacuum apparatus.

Gas measurement bulbs.

Fig. 1.



Vacuum apparatus. Many of the reactions to be described were carried out on a vacuum apparatus which was also designed so that it could be used for gas analyses.

The apparatus had a section to which a reaction flask could be attached and this was connected to the rest of the line through a trap. A Töpler pump and gas burette were included in the apparatus to measure gas not condensed by liquid air (normally methane), and two measuring bulbs with a manometer were used for measuring condensable gases. The small bulb was used for volumes up to about 80 N-c.c. and both bulbs combined for volumes greater than this; (a normal c.c., written as N-c.c., is one c.c. at N.T.P.). The measuring bulbs were calibrated by using carbon dioxide gas, which was first measured accurately by using a bulb of known volume connected to a manometer.

The vacuum apparatus also contained a section from which gases could be fed into an infra-red spectrometer cell. This method was usually used to identify gases since it is rather more convenient than measuring vapour pressures, and is also more definite than the latter method.

The apparatus contained a lead through which certain parts of it could be let down to atmospheric pressure with nitrogen through a needle valve.

Ultra-violet spectrometry. The ultra-violet and visible absorption spectra were measured on an Optica CF.4DR double beam instrument. The cells used were one centimetre ones with a B.10 ground glass neck. They were fitted with the attachment shown in fig. 2 so that they could be evacuated, then filled with nitrogen, and loaded under nitrogen with a syringe. In this way the spectra of oxygen or moisture sensitive materials can be studied. Solutions of such materials must be prepared with very dry solvents therefore the ether and tetrahydrofuran used were distilled on to the compounds from lithium aluminium hydride.

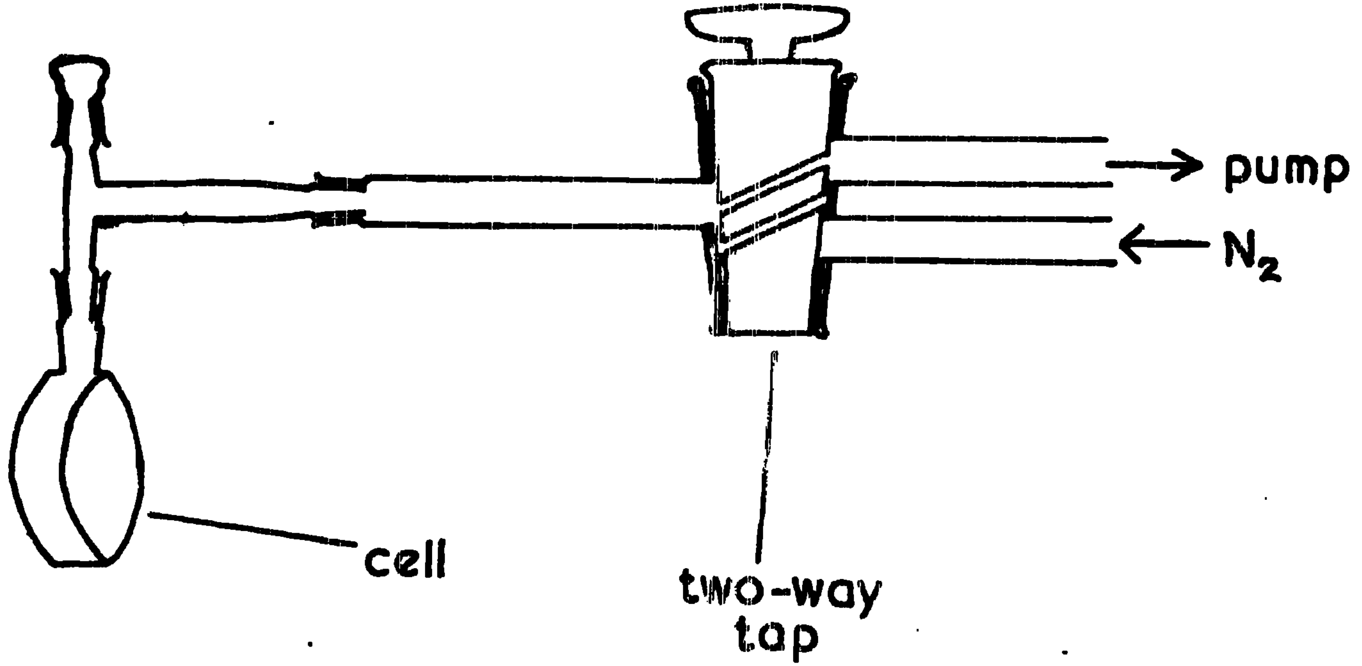
Analyses

Halogen analyses. Estimation of halogens was carried out by converting the halogen to halide ion in aqueous solution, acidifying with dilute nitric acid, and precipitating the silver halide by addition of silver nitrate solution. The silver halide was coagulated by warming to about 70° for a short time, then filtered into a sintered glass crucible, dried at 120°, and weighed.

Beryllium analyses. Beryllium was estimated by first converting it to the hydroxide in aqueous solution, by addition of ammonia, then igniting it to beryllium oxide, when mixed with pumice, and weighing the oxide obtained. The purpose of the pumice is to prevent loss of the very fine oxide from the crucible.

Gas analyses. Compounds which evolved gas on hydrolysis were usually analysed by hydrolysing a weighed sample of the

Fig. 2. Arrangement for filling spectrometer cells under nitrogen.



compound and measuring the gas liberated on the vacuum line. The gas was then identified by its infra-red spectrum.

Cryoscopic molecular weight measurements. These measurements were done in "Analar" benzene dried by sodium wire for several days. Cryoscopic constants for the benzene samples used were determined by using biphenyl which had been recrystallized from ethanol and dried.

PREPARATION AND PURIFICATION OF STARTING MATERIALS AND SOLVENTS

Diethyl Ether

Ether sold as "Anhydrous Methylated Ether" was dried thoroughly by standing for a few weeks over sodium wire before use.

Tetrahydrofuran

Commercial tetrahydrofuran was left standing for several weeks over sodium hydroxide pellets to remove the bulk of the moisture. It was then stirred under reflux in a nitrogen atmosphere with a little benzophenone and excess of potassium until it remained quite blue (a potassium ketyl). It was then distilled and treated a second time with potassium and benzophenone and then distilled again under nitrogen, collecting the fraction between 65° and 68°. It was stored under nitrogen and removed as required by draining from a storage bulb through a dried molecular sieve.

Ethylene Glycol Dimethyl Ether (Dimethoxyethane).

This was treated in exactly the same way as tetrahydrofuran.

Benzene

"Analar" benzene was allowed to stand over sodium wire to dry it before use.

Dimethyl Sulphide

Dimethyl sulphide was purified by a reflux distillation under nitrogen with copper powder (to remove mercaptans) and sodium wire (to remove water), followed by fractional distillation through a 10 inch column of glass helices collecting the 37.8-38.1° fraction.(49)

Diethyl Sulphide

This was refluxed over sodium for half an hour then fractionally distilled from sodium collecting between 91.2° and 92.2°.

Aliphatic Amines

Methylamine was prepared from methylamine hydrochloride. This salt usually contains some ammonium chloride and traces of dimethylamine hydrochloride and trimethylamine hydrochloride which must be removed.(58) The dimethylamine and trimethylamine salts were extracted with dry chloroform, from which the alcohol had been removed, by using a Sohxlet extractor. The methylamine hydrochloride was then extracted using dry n-butanol and was dried thoroughly. Methylamine was liberated by treatment with aqueous potassium hydroxide solution, dried with potassium hydroxide, then treated with sodium and distilled off into a storage vessel.

Trimethylamine was dried with phosphorus pentoxide and stored over this drying reagent. It was then distilled off as required.

Di-isopropylamine, N,N,N',N'-tetramethylethylenediamine, N,N,N'-trimethylethylenediamine, N,N'-dimethylethylenediamine,

ethylenediamine, and N,N-dimethylethylenediamine were all purified by refluxing over sodium (potassium for di-isopropylamine, b.p. 83.5°) and then fractionally distilling the amine from sodium under a nitrogen atmosphere.

Pyridine

The pyridine stood over potassium hydroxide pellets for several days. It was then fractionally distilled, collecting the fraction boiling between 113° and 116°. This fraction was then passed slowly through a well dried molecular sieve (Type 4A) and collected in the storage flask.

2,2'-Bipyridyl

This was prepared by the method of Badger and Sasse(50) by refluxing pyridine with specially prepared Raney nickel, causing dehydrogenation of the pyridine. The final purification of the bipyridyl was done by vacuum sublimation to obtain a product melting at about 70 - 71°, which is the reported value for pure bipyridyl.

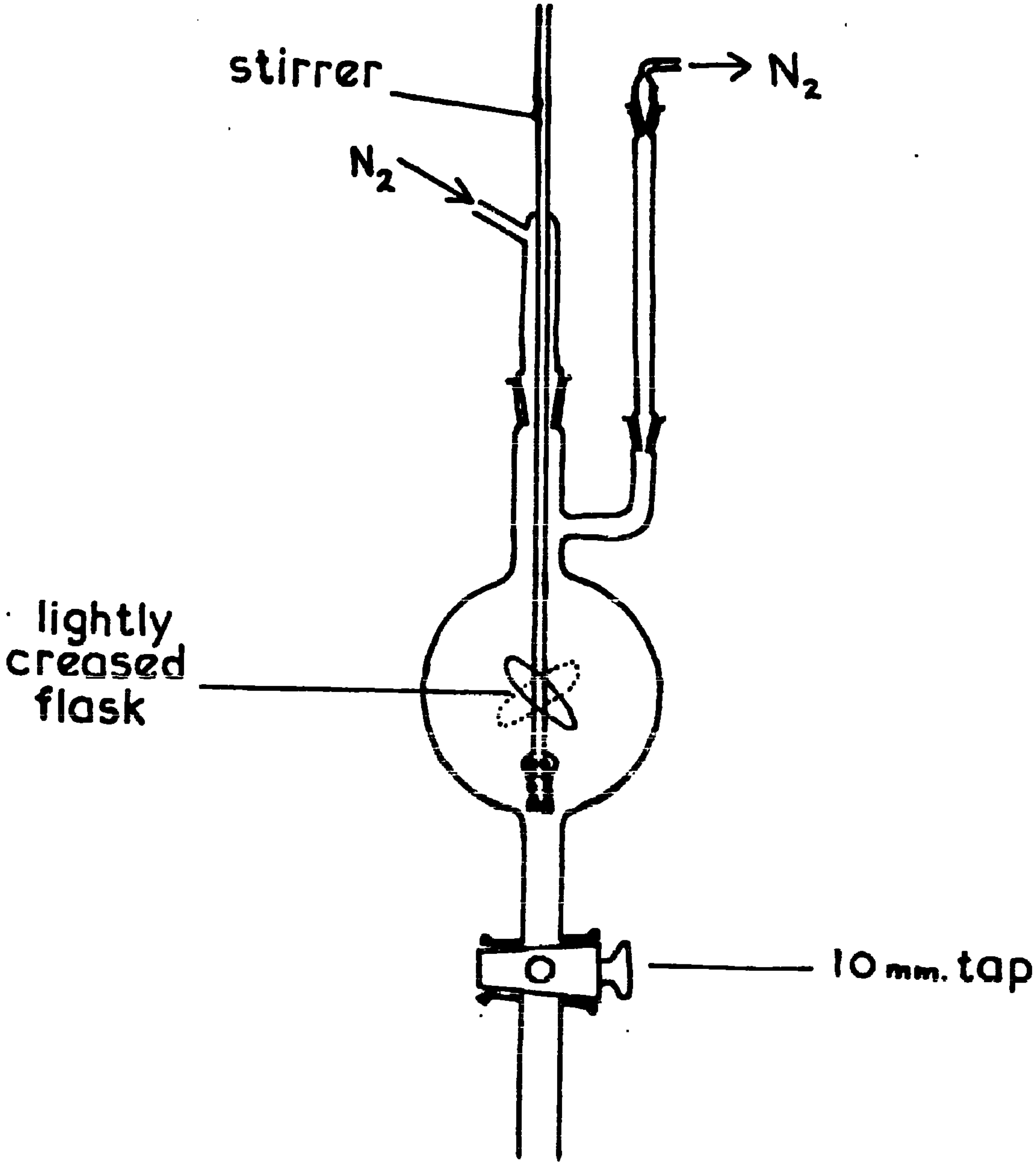
o-Phenanthroline

o-Phenanthroline monohydrate (m.p. 102°) was twice sublimed slowly under vacuum to obtain the anhydrous material (m.p. 118°).

Oil for Lithium Shot Preparation

A 200-240° petroleum fraction was washed with conc. sulphuric acid several times to remove unsaturated hydrocarbons then washed twice with water and dried over potassium hydroxide pellets. This was then distilled, collecting between 200° and

Fig. 3. Lithium shot apparatus.



240°.

Lithium Shot Preparation(51)

Lithium was made into a fine shot for its reactions by using the apparatus shown in fig.3. The apparatus is almost half-filled with the oil described above and the weighed quantity of lithium metal is placed on it in an atmosphere of dry nitrogen or preferably dry argon (molten lithium can react with nitrogen forming some lithium nitride). The oil is then heated by a small gas ring until it is refluxing well, when the lithium metal will have melted. The heating is now stopped and the stirrer is turned on to stir the mixture very vigorously and break down the lithium into tiny globules. The stirring is continued until the lithium has solidified. On cooling the oil is run out through the tap beneath the apparatus; the shot is washed with the solvent to be used in the reaction, and finally rinsed into the reaction flask.

Lithium reagents

These were prepared by reaction of the lithium shot, usually in ether, with the corresponding alkyl or aryl bromide or sometimes the chloride.

Thus methyl-lithium was prepared in 70-90% yield from methyl bromide and lithium in ether, ethyl-lithium in about 70% yield from ethyl bromide and lithium in ether at about -10°, *n*-butyl-lithium in 50% yield from *n*-butyl chloride and lithium in benzene, phenyl-lithium from bromobenzene and lithium in ether in 93% yield.

p-Dimethylaminophenyl-lithium was prepared by addition of a benzene solution of butyl-lithium to a solution of p-bromodimethylaniline in benzene.

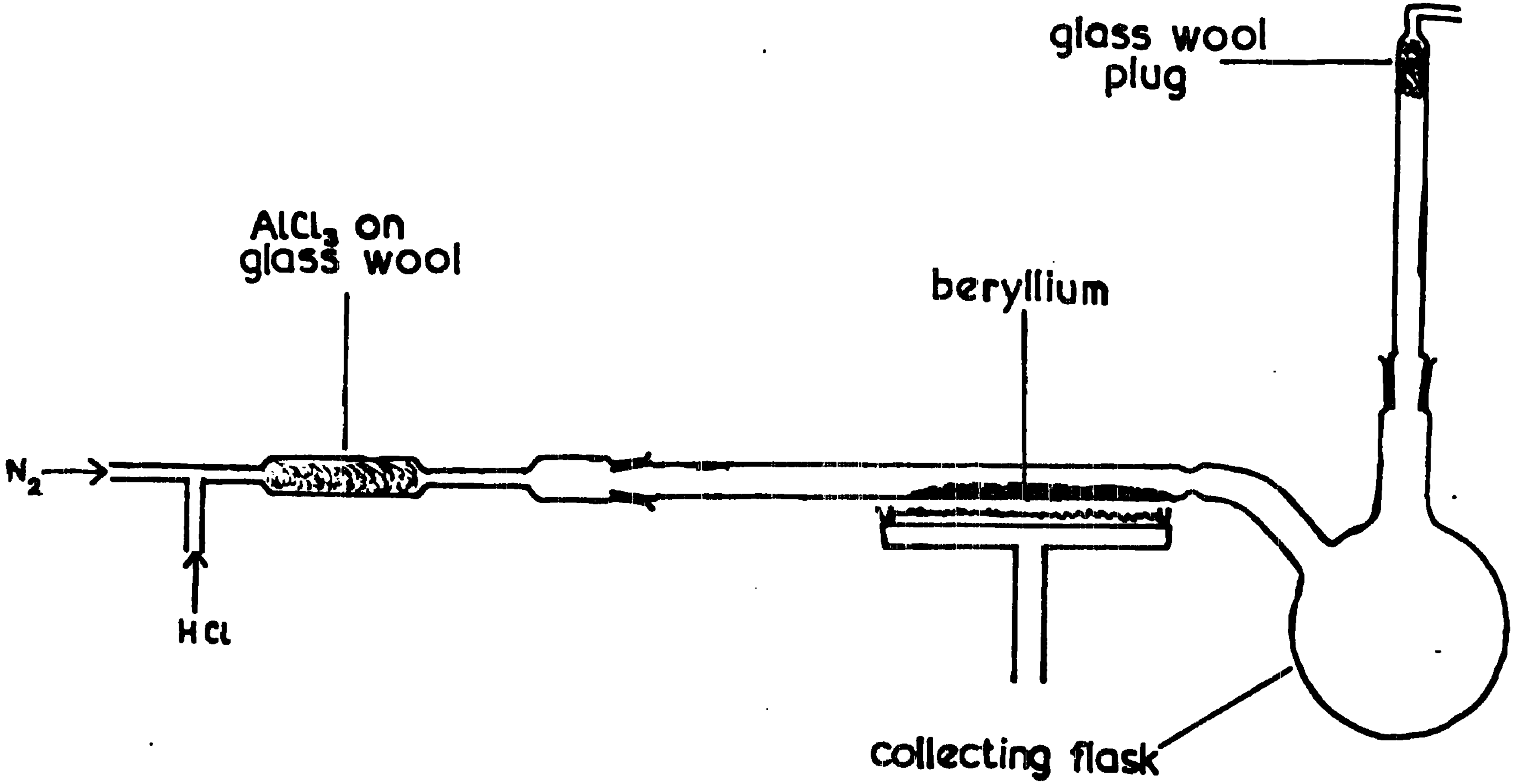
Beryllium Chloride

This was prepared by heating beryllium metal flakes in a stream of dry hydrogen chloride(4,5,20) in the apparatus shown in fig.4. The product was sublimed off and collected in the flask which was then sealed off from the reaction tube. The hydrogen chloride was supplied from a Kipp's apparatus containing ammonium chloride voltoids and conc. sulphuric acid and was passed through some glass wool on to which some aluminium chloride had been sublimed, to dry it completely. The beryllium chloride was obtained as white needles in 95% yield.

Beryllium Bromide

Beryllium bromide was prepared in the same type of apparatus as that used in the preparation of beryllium chloride. In this case the beryllium metal in the form of flakes was heated in a stream of gas consisting of dry nitrogen which had been passed through a bubbler containing bromine.(5) The preparation is done in this way because of the difficulty of obtaining dry hydrogen bromide in large quantities. The vapour pressure of bromine is 173 mm. of Hg at 20° therefore the nitrogen stream carries about 23% bromine which is sufficient

Fig. 4. Beryllium chloride apparatus.



for this reaction.

The beryllium bromide was obtained as fine white needles in about 97% yield.

Dimethylberyllium

The dimethylberyllium in ether solution was prepared by reaction of 2 mols. of methylmagnesium bromide with 1 mol. of beryllium chloride in ether. Most of the ether was pumped off and the solution filtered. The dimethylberyllium etherate was distilled over by a process of continuous ether distillation to separate it from magnesium bromide.(13).

Diethylberyllium

This was prepared by the addition of 2 mols. of ethyllithium to 1 mol. of beryllium chloride in diethyl ether. The clear solution was decanted from lithium chloride and most of the ether removed by pumping. The remaining solution was then decanted into a distillation apparatus and, after removing more ether, the diethylberyllium etherate was distilled under about 0.25 mm. of Hg at 60-65°. This was taken up in ether and the solution analysed by hydrolysis and measurement of ethane. The yield was 68%.

Diphenylberyllium

An ether solution of diphenylberyllium was prepared by the addition of 2 mols. of phenyl-lithium in diethyl ether to 1 mol. of beryllium chloride dissolved in ether. The solution was decanted from the precipitated lithium chloride and used directly for the preparation of 2,2'-bipyridyl-(diphenyl)beryllium, for which it was intended.

Di-isopropylberyllium(22)

Several samples of di-isopropylberyllium were available in this laboratory and one of these was opened under vacuum and dissolved up in diethyl ether which was condensed on it in the vacuum line. This solution was then used for a reaction with 2,2'-bipyridyl.

Isopropylberyllium hydride

This was prepared by the method described by G. E. Coates and F. Glockling.(22) Di-isopropylberyllium (0.55g.) was transferred from a storage tube to a small flask by vacuum distillation, where it was heated by an oil bath to about 180° and maintained at this temperature for about 7 hours, when all evolution of propene had ceased. This residue of isopropylberyllium hydride was a viscous colourless oil. It was dissolved in 10 ml. of dry diethyl ether for reaction with 2,2'-bipyridyl.

Di-n-butylberyllium

This was prepared from butyl-lithium and beryllium chloride etherate in benzene solution. 0.025 mole of butyl-lithium in benzene solution was added to a solution of 0.0125 mole of beryllium chloride etherate in benzene and the clear solution was filtered from the precipitated lithium chloride.

Bis(p-dimethylaminophenyl)beryllium

A benzene solution of bis(p-dimethylaminophenyl)beryllium was prepared by the addition of 0.016 mole of p-dimethylaminophenyllithium in 140 ml. of benzene to 0.008 mole of beryllium chloride etherate in 110 ml. of benzene. The pale yellow solution was filtered through a sintered glass disc to separate the lithium chloride which was precipitated in the reaction.

Diethylmagnesium(52)

This was prepared as a solution in diethyl ether by first preparing a solution of ethyl magnesium bromide from ethyl bromide and magnesium in ether, then precipitating magnesium bromide as its dioxan complex by adding dioxan and stirring for about 20 hours to complete the precipitation. The solution was then filtered and analysed for diethylmagnesium by hydrolysis of a sample and measurement of the ethane liberated.

Diphenylmagnesium(53)

Diphenylmagnesium in ether solution was prepared in a similar way to diethylmagnesium, by addition of dioxan to a solution of phenyl magnesium bromide, prepared from magnesium and bromobenzene in ether.

Dimethylcadmium

Hydrated cadmium chloride was heated on a boiling water bath under a water pump vacuum for about two hours to remove most of the water of crystallization, and was then dried in an air oven at 130° for several hours.

About 5.5g. (0.030 mole) of cadmium chloride were suspended in 150 ml. of dry ether and 25.2 ml. of 2.5M. methyl-lithium in ether were added slowly with stirring. Two-thirds of the ether was then removed by distillation and the remaining volatile material was then distilled off at room temperature under vacuum into a flask cooled in liquid air. Only ether and the dimethylcadmium are collected in this way.

2,2'-bipyridyl-lithium(54,55)

A slight excess of lithium metal shot was added to a solution of 2,2'-bipyridyl in diethyl ether and the mixture was stirred for several hours when all the 2,2'-bipyridyl would have reacted giving a deep purple-red solution of bipyLi.

2,2'-bipyridyl dilithium(54,55)

A mixture of about 2.5 mols. of lithium metal and 1 mol. of 2,2'-bipyridyl in tetrahydrofuran or dimethoxyethane was stirred for several hours when a purple-red solution of 2,2'-bipyridyl lithium was formed which slowly assumed the deep green colour of 2,2'-bipyridyl dilithium, bipyLi_2.

ETHER AND THIOETHER COMPLEXES OF BERYLLIUM HALIDES

A number of complexes of beryllium halides with certain ethers and thioethers were prepared either by direct reaction between the two compounds or by the displacement of diethyl ether from $BeX_2 2Et_2O$ in diethyl ether solution (X=Halogen). This work was carried out mainly with a view to finding useful solvents for beryllium chloride additional to the commonly used diethyl ether.

These complexes of beryllium halides are all extremely hygroscopic, often fuming slightly in moist air, therefore they were always prepared and handled in a dry atmosphere.

For the analyses of these compounds the halogen was determined gravimetrically as silver chloride or silver bromide, obtained by hydrolysing a weighed sample of the compound in a closed vessel, acidifying with dilute nitric acid, and precipitating the silver halide by the addition of an excess of silver nitrate solution.

Dichloro(bistetrahydrofuran)beryllium, $(C_4H_8O)_2BeCl_2$.

50 ml. of dry tetrahydrofuran were added slowly with stirring to about 4g. of beryllium chloride cooled to about -65°. Initially there was a vigorous exothermic reaction which quickly subsided and a white crystalline solid was produced. The mixture was allowed to warm to room temperature and the undissolved product left to settle. 5 ml. of the clear solution was pipetted out, hydrolysed by running into water, and then

analysed for chloride in order to estimate the solubility of the product in tetrahydrofuran at room temperature. It was found that at 18° 5.2g. of beryllium chloride dissolve in a litre of tetrahydrofuran (i.e. about 14g. of $(C_4H_8O)_2BeCl_2$ per litre). The product was found to be far more soluble in boiling tetrahydrofuran from which it was recrystallized as long colourless needles. Prolonged heating of the solution causes slight decomposition since the solution begins to turn brownish in colour. It appears therefore, that the tetrahydrofuran is very slowly attacked by beryllium chloride on heating. A similar darkening on heating was observed in solutions of beryllium chloride in diethyl sulphide but was much more rapid than that observed in tetrahydrofuran. If tetrahydrofuran is added slowly to beryllium chloride without cooling, extensive charring occurs. The product is moderately soluble in benzene and only very sparingly soluble in diethyl ether.

Found: Cl, 31.1, 31.6, 30.8, 31.2% $C_8H_{16}O_2BeCl_2$ requires Cl, 31.7%.

This compound, together with a complex, $BeCl_2.3C_4H_8O$, stable below -2°, has been reported fairly recently by A. V. Novoselova et al. (31)

<u>Dibromo(bistetrahydrofuran)beryllium</u>. $(C_4H_8O)_2BeBr_2$.

1g. of beryllium bromide was dissolved in about 100 ml. of diethyl ether and the solution was filtered. About 1g.

to tetrahydrofuran in 10 ml. of diethyl ether was added with vigorous stirring to this solution when a finely divided white crystalline solid was immediately precipitated. This was filtered, washed with a little ether, and dried in a vacuum. It was found to be soluble in tetrahydrofuran and can be recrystallized from a tetrahydrofuran-diethyl ether mixture.

Found: Br, 49.0%. $C_8H_{16}O_2BeBr_2$ requires 51.1%.

<u>1,2-Di(methoxy)ethane(dichloro)beryllium</u>. $C_2H_4(OMe)_2BeCl_2$

To about 4.5g. (0.056 mole) of beryllium chloride, cooled to -50°, was added 170 ml. of dry diethyl ether. The mixture was allowed to warm to room temperature with stirring and the solid slowly dissolved. This solution was filtered and about 6g.(0.06 mole) of ethylene glycol dimethyl ether in a small volume of diethyl ether was added slowly with vigorous stirring to it, when a white precipitate was immediately produced. This was filtered off, washed with diethyl ether, and dried in a vacuum. The absence of chloride in the filtrate as shown by testing with silver nitrate solution indicates that the product is insoluble in diethyl ether. It was also found to be insoluble in ethylene glycol dimethyl ether, benzene, carbon tetrachloride, and all the other common organic solvents with which it does not react. It dissolves extremely readily in ethanol forming a rather viscous solution from which it could not be crystallized, either by cooling or by removal of solvent in a vacuum, probably because reaction occurs with formation of ethoxyberyllium derivatives. m.p. (with decomposition): 237-244°.

Found: Cl, 41.5% $C_4H_{10}O_2BeCl_2$ requires Cl, 41.8%.

This compound, which has been reported,(59) is clearly very similar in properties to the beryllium chloride-dioxan complex which has been described recently.(30)

Dichloro(bisdimethyl sulphide)beryllium, $(Me_2S)_2BeCl_2$.

60 ml. of dimethyl sulphide were added to 4g. of beryllium chloride with stirring. The reaction was only slightly exothermic and the solid dissolved quite rapidly. The solution was filtered into one arm of a double Schlenk tube, where solvent was removed by pumping until crystals began to be deposited from the solution. The product was then crystallized from this solution by cooling and was filtered off rapidly and dried in a vacuum. It is extremely hygroscopic, fuming slightly in moist air, and reacts very vigorously with water. It smells strongly of dimethyl sulphide. When added to diethyl ether it dissolves with an exothermic reaction and the formation of two liquid layers which is characteristic of solutions of beryllium chloride etherate in diethyl ether. This displacement reaction is expected since oxygen is a stronger donor than sulphur to beryllium, as was observed by Coates and Huck in their study

of co-ordination compounds of dimethylberyllium.$^{(2)}$

On heating the compound melts to a straw-coloured liquid at 117 - 119°.

Found: Cl, 35.6, 36.4, 33.4% M, cryoscopic in benzene, 217, 209. $C_4H_{12}S_2Be\ Cl_2$ requires Cl, 34.8%; M, 204.

Di-μ-chloro-dichlorobis(dimethyl sulphide)diberyllium, $(Me_2S.BeCl_2)_2$.

2g. of dichloro(bisdimethyl sulphide)beryllium were dissolved in 40 ml. of dry toluene and the solvent was then removed by vacuum distillation at room temperature leaving a colourless crystalline solid which melts with slight decomposition at 135 - 140° and smells strongly of hydrogen chloride.

Found: Cl, 50.6, 49.6, 48.1%; M, cryoscopic in benzene, 261, 296. $C_4H_{12}S_2Be_2Cl_4$ requires Cl, 50.0%; M, 284.

1,2-Di(methylthio)ethane(dichloro)beryllium, $C_2H_4(SMe)_2BeCl_2$.

To 2g. (0.025 mole) of beryllium chloride was added a mixture of 3.1g. (0.025 mole) of 1,2-di(methylthio)ethane and about 40 ml. of dry benzene with vigorous stirring. A white crystalline product was formed which was filtered off, washed with a little dry pentane, in which it is insoluble, and dried in a vacuum. A further quantity of the product was obtained from the benzene filtrate, by addition of dry pentane, as colourless feathery needles. Thus the compound is moderately soluble in benzene.

Found: Cl, 34.4%. $C_4H_{10}S_2BeCl_2$ requires Cl, 35.1%.

<u>1,2-Di(ethylthio)ethane(dichloro)beryllium</u>, $C_2H_4(SEt)_2BeCl_2$.

To 2g. (0.025 mole) of beryllium chloride was added a mixture of about 4g. (0.027 mole) of 1,2-di(ethylthio)ethane and 30 ml. of dry benzene with stirring. An equal volume of pentane was added to the solution obtained, and on standing large colourless crystals slowly separated from the cloudy mixture produced. The product was found to be moderately soluble in benzene and in 1,2-di(ethylthio)ethane, and insoluble in dry pentane and hexane. Like the previous compound it fumes strongly in moist air.

Found: Cl, 29.8%. $C_6H_{14}S_2BeCl_2$ requires Cl, 30.9%.

<u>Beryllium chloride-diethyl sulphide system</u>.

Diethyl sulphide behaved very differently from dimethyl sulphide as a solvent for beryllium chloride. It was found that beryllium chloride is quite soluble in diethyl sulphide, about 12g. of beryllium chloride dissolving in 100 ml. of the thioether with a slightly exothermic reaction. However, some cleavage of the diethyl sulphide seems to occur in concentrated solutions, and quite extensively if the solution is heated under reflux when a considerable amount of hydrogen chloride is evolved. These solutions become quite viscous and turn orange-brown when solvent is removed by vacuum distillation and then on standing for a few days set to a solid brownish mass. If, however, the diethyl sulphide was removed by vacuum distillation at room temperature from a freshly prepared solution, a pale yellow syrupy liquid was obtained which could not be made to crystallize. Analysis of this liquid gave Cl, 31.9% ($BeCl_2.2Et_2S$ would require Cl, 27.3%) and the distillate was also found to contain an appreciable amount of chloride, probably carried over as hydrogen chloride. Thus, even when these solutions are not heated some decomposition seems to occur although to a much smaller extent.

2,2' - BIPYRIDYL COMPLEXES OF BERYLLIUM AND OTHER GROUP II METALS

Several 2,2' - bipyridyl complexes of beryllium halides, alkyls and aryls were prepared and studied. Since these showed remarkable stability it seemed possible that 2,2' - bipyridyl might form coordination compounds with the dialkyls of zinc which hitherto had been found to form only one stable coordination compound corresponding approximately to $2Me_2Zn.3C_4H_8O$,(56) involving dimethylzinc and tetrahydrofuran. As nitrogen is a stronger donor than oxygen to zinc, and 2,2' - bipyridyl is a bidentate ligand, it was perhaps not surprising that a co-ordination compound was in fact formed with both dimethyl- and diethylzinc. Even dimethylcadmium was found to react with 2,2'- bipyridyl but the complex (bipy $CdMe_2$) is relatively unstable and slowly decomposes into its components in vacuo at room temperature. Neither dimethyl-, diphenyl-, nor di(phenylethynyl)mercury form bipyridyl complexes.

The colours of the bipyridyl complexes, bipy BeX_2, vary markedly with the electronegativity of the group X, and a similar effect was also observed in the two zinc complexes prepared. The ultra-violet and visible absorption spectra of a series of the beryllium complexes have been studied.

Dimethyl(bipyridyl)beryllium, bipy $BeMe_2$.

3.80g. (0.0244 mole) of 2,2'- bipyridyl in 150 ml. of diethyl ether were added to 0.0244 mole of dimethylberyllium in about 10 ml. of ether. Immediately a bright yellow precipitate was produced which was filtered by suction on to a sintered glass disc and washed well with a little ether, in which it was observed to be only sparingly soluble, forming a pale yellow solution.

The product was only sparingly soluble in cold benzene giving a yellow solution, but was found to be more soluble in boiling benzene in which it formed a deep orange solution. Therefore the compound was crystallized by extraction with boiling benzene in a Sohxlet extractor when it was deposited slowly during the process as fine yellow needles.

It was found to be unaffected by dry oxygen and only very slowly hydrolysed by water with effervescence and thus it was only slowly affected by exposure to the air, turning white over about 15 minutes.

When heated in a sealed tube in vacuo it began to decompose at about 170° and charred rapidly to a black solid between 170° and 200° without any melting. It sublimes very slowly under a good vacuum (0.003 mm. Hg) in an oil bath at $135-140^{\circ}$, as a yellow microcrystalline solid, but some decomposition occurs if the temperature is raised to about 160°.

Found: Be, 4.60, 4.46%; 0.0536g. gave 11.8 N-c.c. of methane on hydrolysis with $2N.H_2SO_4$. $C_{10}H_8N_2Be(CH_3)_2$ requires Be, 4.61%; 12.3 N-c.c. of methane.

When hydrolysed with sodium hydroxide solution and extracted with light petroleum (b.p. $40-60^{\circ}$) about 96% of the expected amount of 2,2'-bipyridyl was recovered showing that the bipyridyl system is unchanged in the compound and in agreement with the above analysis.

Diethyl(bipyridyl)beryllium, bipy $BeEt_2$.

A solution of 3.70g. (0.0237 mole) of 2,2'-bipyridyl in 30 ml. of ether was added slowly to 0.0237 mole of diethylberyllium in 10 ml. of ether. Initially a red solution was produced but after addition of the first few ml. orange-red crystalline needles were precipitated as the solution was added. The product was filtered off and washed with a small quantity of ether then dried in a vacuum.

It is only moderately soluble in diethyl ether but more soluble in benzene. On standing in the air it turned white in about 10 minutes, forming 2,2'- bipyridyl and beryllium hydroxide, due to reaction with moisture as it was found to be unaffected by dry air at room temperature. With water it is slowly hydrolysed with effervescence.

When heated in a sealed tube decomposition to a white solid began at about 90° but this change was slow even at 125°. Under a pressure of about 0.0015 mm. Hg it sublimes very slowly, but with some decomposition, at about 100°.

Found: Be, 4.25, 3.98%; M, cryoscopic in benzene, 233, 220; 0.0681g. gave 14.0 N-c.c. of ethane on hydrolysis with ethanol and $2N.H_2SO_4$. $C_{10}H_8N_2Be(C_2H_5)_2$ requires Be, 4.04%; M, 223; 13.7 N-c.c. of ethane.

Diphenyl(bipyridyl)beryllium, bipy $BePh_2$

This was prepared by the addition of 2.93g. (0.0187 mole) of 2,2'- bipyridyl in 50 ml. of ether to a solution of 0.0187 mole of diphenylberyllium in 100 ml. of ether when it was precipitated immediately as a yellowish-cream solid which was filtered off, washed with ether, and pumped dry. It is sparingly soluble in ether and in benzene. Crystallization was effected by extraction with boiling benzene in a Sohxlet extractor when it was obtained as pale yellow needles.

The compound shows considerable stability to water, only hydrolysing very slowly in contact with water, and requiring warm 6N. sulphuric acid to effect reasonably rapid hydrolysis for the analysis for 2,2'- bipyridyl.

Found: Be, 2.78, 2.79%; C, 78.3, 78.0%; H, 5.88, 5.40%; bipy, 48.45%. $C_{10}H_8N_2Be(C_6H_5)_2$ requires Be, 2.82%; C, 82.8%; H, 5.64%; bipy, 48.9%.

The rather low analysis for carbon may be due to formation of some beryllium carbide on ignition.

Reaction of 2,2'- bipyridyl with certain other organo-beryllium compounds.

Addition of a solution of 2,2'- bipyridyl (0.0045 mole) in 15 ml. of ether to a solution of 0.0045 mole of di-isopropylberyllium in 30 ml. of ether gave a deep red coloured solution similar to that obtained with diethylberyllium, but it quickly took on a brownish tinge. On removing the ether under vacuum at room temperature a very viscous red-brown tar was obtained which turned dark brown within a few hours.

A very similar reaction occurred between 2,2'-bipyridyl and *iso*propylberyllium hydride, and also with di-*n*-butylberyllium, in both cases a deep red solution being obtained which turns brown slowly and from which only tarry products could be isolated. This decomposition was also observed when the reaction was done in benzene solution instead of diethyl ether.

When a solution of 1.25g. (0.008 mole) of 2,2'-bipyridyl in 20 ml. of benzene was added to a solution of 0.008 mole of bis(*p*-dimethylaminophenyl)beryllium in 250 ml. of benzene a deep orange-red coloured solution was obtained. After removal of the solvent at room temperature by vacuum distillation a dark orange-red solid was obtained which was slightly tarry. Extraction with a small quantity of benzene, and removal of the benzene from the solution obtained, gave a microcrystalline orange solid which slowly turns dark brown on standing and which rapidly decomposes on exposure to the air.

Dichloro(bipyridyl)beryllium, bipy $BeCl_2$

2.12g. (0.026 mole) of beryllium chloride were dissolved in 45 ml. of diethyl ether and a solution of 4.15g. (0.026 mole) of 2,2'-bipyridyl in 80 ml. of ether was added with vigorous stirring. A finely-divided white solid was immediately precipitated and this was filtered off, washed with ether, and dried under vacuum. The product was a white solid which was apparently amorphous and almost insoluble in diethyl ether, benzene and pyridine. It can be recrystallized from boiling nitrobenzene as colourless needles. On heating it begins to decompose extremely slowly above about 330° and does not melt up to 360°. It is slightly hygroscopic and has a very faint smell of hydrogen chloride.

Found: Be, 3.51, 3.64%; Cl, 30.0%. $C_{10}H_8N_2BeCl_2$ requires Be, 3.81%; Cl, 30.1%.

Dibromo(bipyridyl)beryllium, bipy $BeBr_2$

A solution of 1.5g. (0.01 mole) of 2,2'-bipyridyl in 10 ml. of ether was added with stirring to a solution of 1g. (0.006 mole) of beryllium bromide in 15 ml. of ether when a pale cream coloured precipitate was formed which was filtered off, washed with ether, and dried.

Found: Br, 48.9%. $C_{10}H_8N_2BeBr_2$ requires Br, 49.2%.

Diiodo(bipyridyl)beryllium, bipy BeI_2.

A solution of 5g. of iodine in 50 ml. of diethyl ether was added dropwise to a solution of 0.0072 mole of diethylberyllium in about 8 ml. of ether until a slight yellowish colouration persisted when the formation of beryllium iodide is complete:

$$(C_2H_5)_2Be + I_2 \longrightarrow 2C_2H_5I + BeI_2.$$

The solution was then filtered and 0.7g. (0.0045 mole) of 2,2'- bipyridyl in 10 ml. of ether was added with stirring. A yellow precipitate was produced which was filtered off, washed several times with small quantities of ether, and dried under vacuum.

The product, which is pale yellow when dry, is only very slightly soluble in diethyl ether and only a little more soluble in tetrahydrofuran. In carefully purified tetrahydrofuran it gives a very pale yellow solution, but if the tetrahydrofuran contains any traces of peroxide it produces a reddish-brown solution due to some oxidation of the compound giving iodine. The compound is rapidly hydrolysed by water.

Found: I, 60.3%. $C_{10}H_8N_2BeI_2$ requires I, 60.6%.

Reaction of 2,2'- bipyridyl with diethylmagnesium.

The addition of 2,2'- bipyridyl in ether to an ether solution of diethylmagnesium gave a deep red solution from which a dark red tar was obtained by removal of the ether. This turned brown within a few hours as was observed with the bipyridyl complexes of the higher alkyls of beryllium.

Reaction of 2,2'- bipyridyl with diphenylmagnesium

When a solution of 1.56g. (0.01 mole) of 2,2'-bipyridyl in 20 ml. of ether was added with stirring to a solution of 0.01 mole of diphenylmagnesium in 50 ml. of ether an orange-yellow precipitate was immediately produced. However the precipitate began to darken very rapidly and had turned a chocolate-brown colour within about ten minutes. This decomposition product was not investigated further.

Dimethyl(bipyridyl)zinc, bipy $ZnMe_2$.

820 N-c.c. (0.036 mole) of dimethylzinc were condensed into a flask containing 1.5614g. (0.0100 mole) of bipyridyl. The reaction flask was closed from the rest of the vacuum apparatus and allowed to warm up slowly to room temperature. As the dimethylzinc began to melt a bright yellow colour was produced on the bipyridyl. After leaving the reaction mixture for half an hour, to ensure complete reaction, the excess of dimethylzinc was taken off into the gas measurement bulbs. The excess was found to be 584 N-c.c., showing that 236 N-c.c. (0.0105 mole) of dimethylzinc had been reacted. Thus the bright yellow product is the 1:1 coordination compound.

This compound is remarkably stable, being only slightly hygroscopic and turning white when exposed to the atmosphere only after a few hours. It is only sparingly soluble in diethyl ether.

On heating it begins to darken at about 100^{o} becoming slowly charred.

Dimethyl(o-phenanthroline)zinc, o-phenan $ZnMe_2$

This preparation was carried out in the same way as the previous experiment with o-phenanthroline replacing 2,2'-bipyridyl. A yellow compound was again obtained from equimolar amounts of the reactants which has very similar properties to 2,2'- bipyridyl(dimethyl)zinc.

Diethyl(bipyridyl)zinc, bipy $ZnEt_2$.

1g. (0.0081 mole) of diethylzinc in about 15 ml. of ether was placed in one arm of a double Schlenk tube. A solution of 1.2g. (0.0077 mole) of 2,2'- bipyridyl in 10 ml. of ether was added when a red solution was produced. Most of the ether was pumped off and the product which had crystallized out was filtered from the remaining solution and dried in a vacuum. It was an orange-red crystalline solid (plates) which was rapidly decomposed on exposure to the atmosphere.

Found: 0.1670g. gave 26.4 N-c.c. of ethane on hydrolysis. $C_{10}H_8N_2Zn(C_2H_5)_2$ requires 26.8 N-c.c.

Dimethyl(bipyridyl)cadmium, bipy $CdMe_2$

When dimethylcadmium and ether were condensed on to about 2g. of 2,2'- bipyridyl a bright yellow compound was formed which is only sparingly soluble in ether. When the excess dimethylcadmium and the ether had been removed under vacuum it was found that the yellow colour began to turn gradually paler with pumping and the product slowly decreased in weight eventually giving pure bipyridyl again. Thus the yellow product, which is undoubtedly bipy $CdMe_2$, is relatively unstable and decomposes into dimethylcadmium and 2,2'- bipyridyl in vacuo at room temperature.

Addition of 2,2'- bipyridyl to dimethyl- and diphenylmercury.

0.60 ml. (about 0.008 mole) of dimethylmercury was added from a pipette to a solution of 1.56g. (0.01 mole) of 2,2'- bipyridyl in about 30 ml. of ether. No apparent change occurred and on pumping off about 20 ml. of the solvent, colourless crystals of 2,2'- bipyridyl (m.p. 69-70.5^{o}) were produced. The remaining ether was pumped off and the solid pumped dry. The weight of dry solid was 1.56g. therefore no reaction had occurred.

A saturated solution of diphenylmercury in ether was added to a concentrated solution of 2,2'- bipyridyl in ether. The solution remained colourless and no compound was precipitated, thus no apparent reaction occurred.

BIPYRIDYL ANION COMPLEXES OF BERYLLIUM

Bis(bipyridyl)beryllium, bipy$_2$ Be

When an ether solution of 2,2'- bipyridyllithium was added to beryllium chloride, also in ether, the deep red colour at once changed to an intense green and lithium chloride was precipitated:

$$2Li^+ \text{ bipy}^- + BeCl_2 \longrightarrow \underline{\text{bipy}}_2 \text{ Be} + 2LiCl$$

The same product was obtained when the dilithium derivative of bipyridyl was added to a suspension of dichloro(bipyridyl)-beryllium in tetrahydrofuran or in 1,2- dimethoxyethane. In this case there was no striking colour change but the very sparingly soluble bipy $BeCl_2$ dissolved readily when the bipy Li_2 was added:

$$\underline{\text{bipy}} \text{ } Li_2 + \underline{\text{bipy}} \text{ } BeCl_2 \longrightarrow \underline{\text{bipy}}_2 \text{ Be} + 2LiCl$$

A typical preparation is described below.

Lithium in excess (about 1g.) was added to bipyridyl (1.2g.) in 50 ml. of 1,2- dimethoxyethane. The solution quickly became purple-red and then gradually turned deep green; it was left to stand for 24 hours to ensure complete formation of the dilithium adduct, and was then filtered and added to a suspension of bipy $BeCl_2$ obtained by addition of 1.28g. of bipyridyl in 10 ml. of ether to 0.65g. of beryllium chloride in 50 ml. of 1,2- dimethoxyethane contained in a double Schlenk tube. The bipy $BeCl_2$ dissolved giving a deep green solution, which was evaporated to dryness by pumping at room temperature. The black residue was extracted with 40 ml. of dry benzene, and the extract twice filtered through sintered glass discs (porosity 3) to separate lithium chloride and the slight excess of bipy $BeCl_2$. Benzene was then pumped off, the residue finally being heated to 35° for 2 hours in a vacuum. The black product was broken to a finely crystalline glistening powder, and washed with two 10 ml. portions of ether to remove any traces of free bipyridyl. The complex has not been observed to melt but it sublimes very slowly at 180° (about 10^{-4}mm.), with some decomposition since a small amount of bipyridyl was deposited on the cooler parts of the condenser.

Found: Be, 2.6, 2.9%; bipy, 95.1%. $C_{20}H_{16}BeN_4$ requires Be, 2.8%; bipy, 97.2%. Halogen could not be detected in the product.

The complex is sparingly soluble in diethyl ether, more readily so in tetrahydrofuran or in 1,2-dimethoxyethane; in these solvents the colour is deep green. It is also moderately soluble in benzene, but the solution is then of a brownish olive green colour.

Addition of bromine (1 mol.) in ether to a solution of the complex in diethyl ether immediately discharged the green colour, and the pale cream bipy $BeBr_2$ was precipitated.

Professor R. S. Nyholm and Dr. C. S. Pande of University College, London, kindly measured the magnetic susceptibility of this compound and found values of 2.05 and 2.15 B.M. for the room temperature susceptibilities of two specimens after diamagnetic corrections had been made.

Lithium bis(bipyridyl)beryllate, Li [bipy$_2$ Be]

0.0075 mole of dichloro(bipyridyl)beryllium was precipitated by adding 2.34g. (0.015 mole) of bipyridyl in 50 ml. of ether to 0.60g. (0.0075 mole)of beryllium chloride in 50 ml. of ether. After addition of 0.25g. of lithium the mixture was stirred. A green colour, bipy$_2$ Be, soon developed and after an hour all the suspended bipy BeCl$_2$ had dissolved. With continued stirring the colour changed through brown to deep violet-blue. The solution was filtered from lithium chloride and excess lithium, introduced into a double Schlenk tube and solvent removed by pumping. The residue was extracted with dry benzene, in which it dissolved with a brown-violet colour, and filtered into the other limb of the double Schlenk tube. Removal of benzene by pumping yielded the lithium salt as a black microcrystalline glistening powder.

Found: Li, 2.24%; Be, 2.58%. $C_{20}H_{16}BeLiN_4$ requires Li, 2.14%; Be, 2.74%.

Like the previous compound it is rapidly decomposed, with fuming, on exposure to air.

Addition of bromine in ether to a solution of the lithium salt in the same solvent resulted in a colour change from violet to green, followed by precipitation of pale cream bipy BeBr$_2$.

PYRIDINE COMPLEXES OF BERYLLIUM ALKYLS

The complexes of pyridine with dimethylberyllium and diethylberyllium were prepared for two main reasons. Firstly, to see if the stability of the 2,2'- bipyridyl complexes of beryllium towards oxygen is due to chelation of the donor or to the aromatic properties of the donor, or to a combination of both these factors. Secondly, to see if they were coloured, as are the 2,2'- bipyridyl complexes.

Bis(pyridine)dimethylberyllium py_2BeMe_2.

About 0.01 mole of dimethylberyllium in 10 ml. of ether was placed in one arm of a double Schlenk tube and 1.9g. (0.024 mole) of pyridine in 2 ml. of ether was added. The reaction was slightly exothermic and a very pale yellow solution was produced which was immediately filtered. Long white needles began to crystallize out quite rapidly on standing. The product was filtered on to the sintered glass disc and pumped dry.

It effervesces very vigorously with water and fumes strongly with air.

On heating in a sealed tube under vacuum it melts to a yellow liquid at 91-2°.

Found: 0.4399g. gave 100.9 N-c.c. of methane on hydrolysis with propanol and then $2N.H_2SO_4$. $(C_5H_5N)_2Be(CH_3)_2$ requires 100.1 N-c.c. of methane.

Bis(pyridine)diethylberyllium, py_2BeEt_2.

To a solution of 0.0118 mole of diethylberyllium in 15 ml. of ether was added 1.88g. (0.0237 mole) of pyridine in 25 ml. of ether when a golden-yellow solution was produced. The solution was filtered and the product was crystallized from it by pumping off ether. The product was an orange-yellow crystalline solid which was slightly sensitive to light, darkening to a brown colour when exposed to the light for several days. It fumes vigorously, but does not take fire, when exposed to the air, and is hydrolysed by water with vigorous effervescence.

On heating in an atmosphere of nitrogen it began to darken slowly at about 90-100° and rapidly above 140° becoming dark brown and finally black.

Found: 0.0379g. gave 7.3 N-c.c. of ethane on hydrolysis; M, cryoscopic in benzene, 232, 192. $(C_5H_5N)_2Be(C_2H_5)_2$ requires 7.5 N-c.c. of ethane; M, 225.

ULTRA-VIOLET AND VISIBLE ABSORPTION SPECTRA OF 2,2'-BIPYRIDYL COMPLEXES

The colours of the complexes, bipy BeX_2, are remarkable. When X = Et, i-Pr, n-Bu, the complexes are red, X = p-$C_6H_4.NMe_2$, orange, X = Ph, Me, or I, yellow, X = Br, cream, and when X = Cl, white. The colour changes can be seen to be in the order of the electronegativities of the group X which suggests that the light absorption involves an electron transfer to the 2,2'- bipyridyl from the other part of the molecule. To investigate this effect more closely the ultra-violet and visible absorption spectra of 2,2'- bipyridyl and six of these complexes have been studied in either diethyl ether or tetrahydrofuran solutions. The concentrations of the solutions used for the spectra of the complexes were estimated by taking a known volume of the solution, removing the solvent, and adding a buffered solution of ferrous sulphate in just sufficient quantity to convert the 2,2'- bipyridyl present into $(Fe\ bipy_3)^{2+}$. This solution was made up to a measured volume in a graduated flask and the concentration of the ferrous-bipyridyl complex ion estimated colorimetrically using the absorption maximum at 522 mμ., with $\epsilon = 8660$. From this the concentration of bipy BeX_2 in the original solution could then be calculated.

Descriptions of the methods used in each case are given below together with the values of the molecular extinction coefficient at the absorption maxima:

2,2'- Bipyridyl

0.0651g. of 2,2'- bipyridyl was dissolved in 100 ml. of diethyl ether and this solution was diluted 100 times giving a solution of 0.00651g. per litre (4.17 x 10^{-5} moles per litre). The spectrum obtained on this solution is shown in figure 5.

λmax	ϵ
237.5 mµ	22000
283	30000

Diethyl(bipyridyl)beryllium

Since very dilute ether solutions of this complex are readily decolourised by slight traces of moisture the spectra were measured on dilute solutions of the complex in 0.005 molar diethylberyllium in ether with the same diethylberyllium solution in the reference cell.

λmax	ϵ
241 mµ	-
297.5	29600
365	3440
461.5	3700

Dimethyl(bipyridyl)beryllium

The spectra of this complex were done on solutions of the compound in about 0.01 M. dimethylberyllium in diethyl ether,

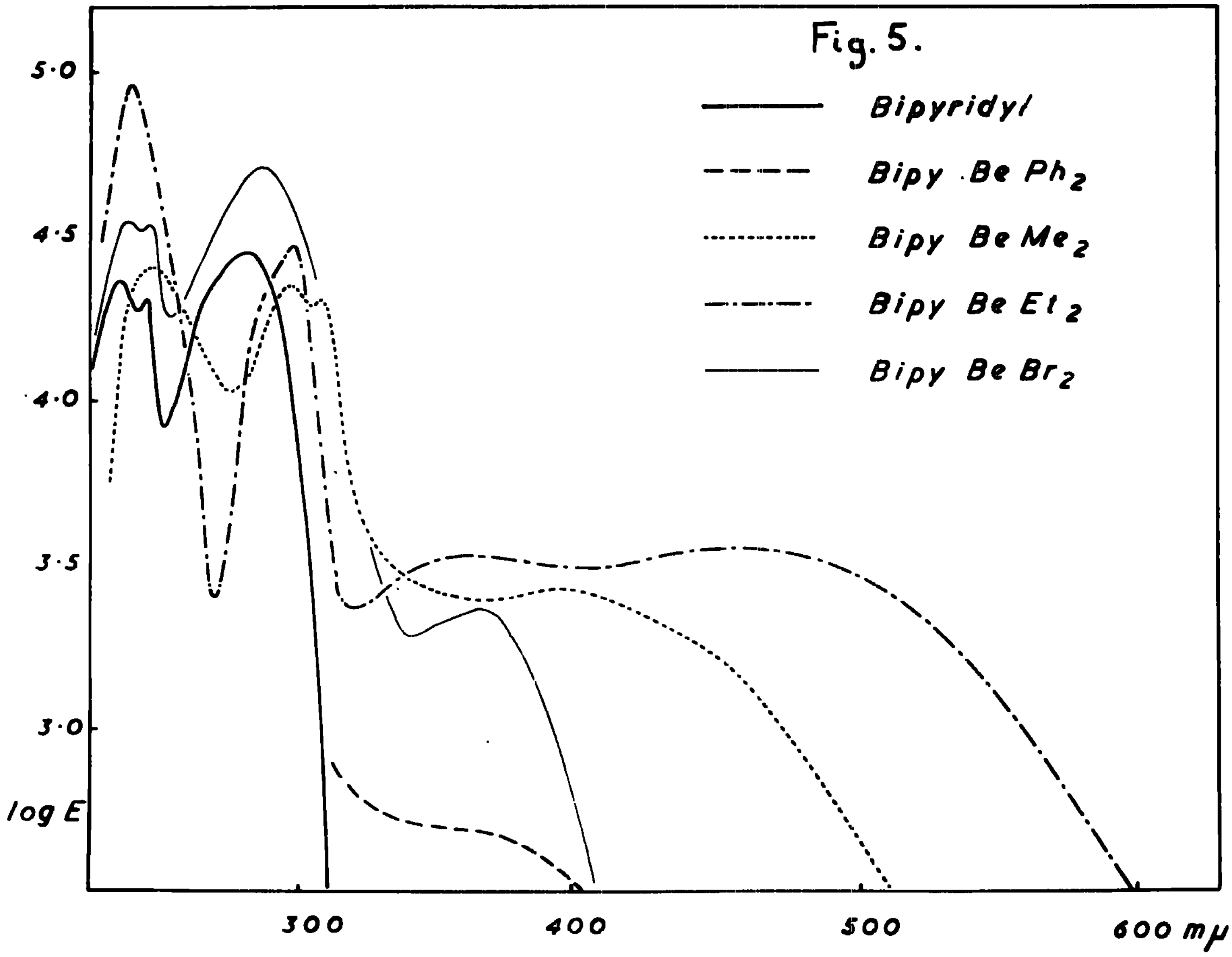


Fig. 5.

5·0
4·5
4·0
3·5
3·0
log E
300
400
500
600 mμ
Bipyridyl
Bipy .Be Ph2
Bipy Be Me2
Bipy Be Et2
Bipy Be Br2

λ max	ϵ
247 mμ	25000
298	22000
395	2700

Diphenyl(bipyridyl)beryllium

Spectrum was done on a saturated solution of the complex in diethyl ether.

The point of inflexion is at about 353 mμ. with ϵ = 501.

Dichloro(bipyridyl)beryllium

This complex is insoluble in diethyl ether therefore the spectrum was done on a saturated solution of the complex in tetrahydrofuran diluted with an equal volume of the solvent.

λ max	ϵ
239.5 mμ	33000
285.5	38000
309 (inflexion)	13000
352 (inflexion)	1200

Dibromo(bipyridyl)beryllium

Spectra were done on a saturated solution in tetrahydrofuran, and on this solution diluted five times.

λ max	ϵ
239 mμ	35300
286.5	50500
364.5	2360

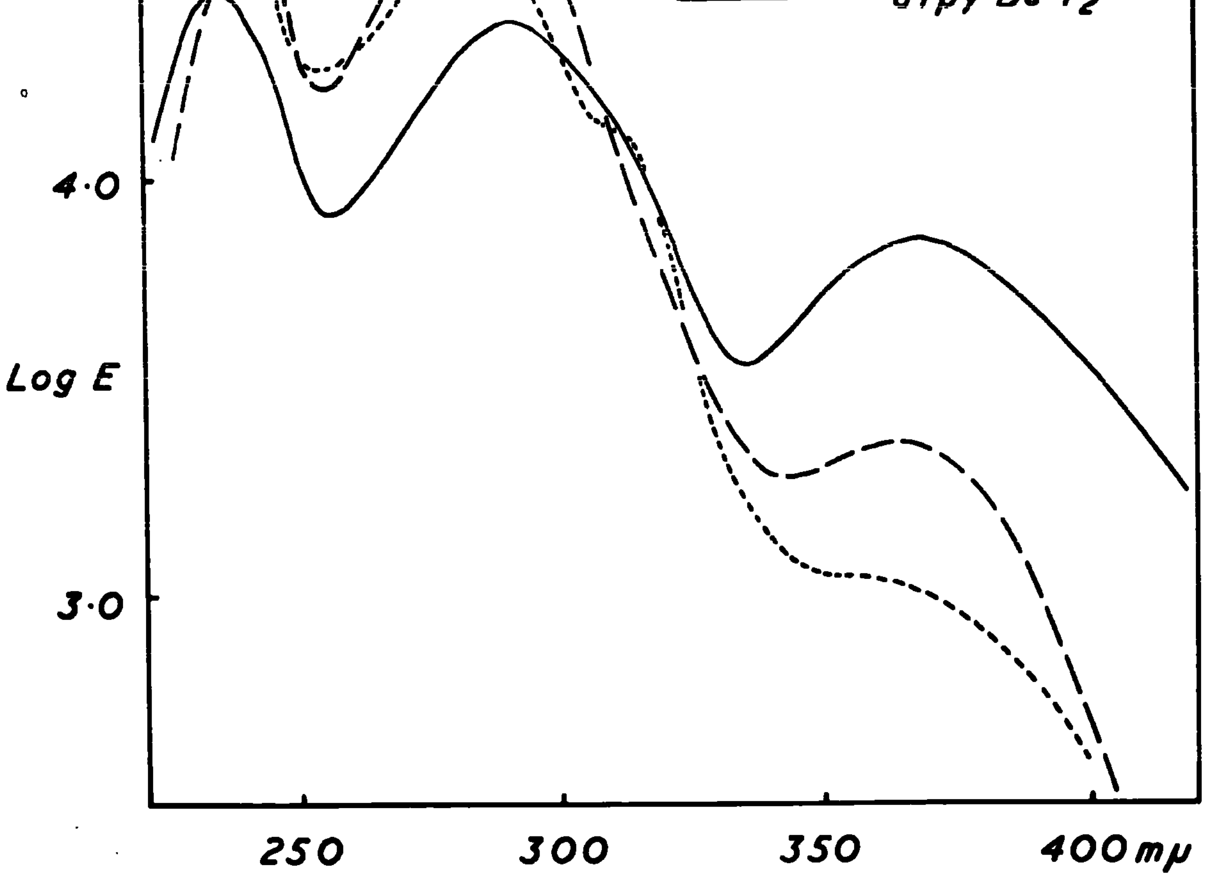
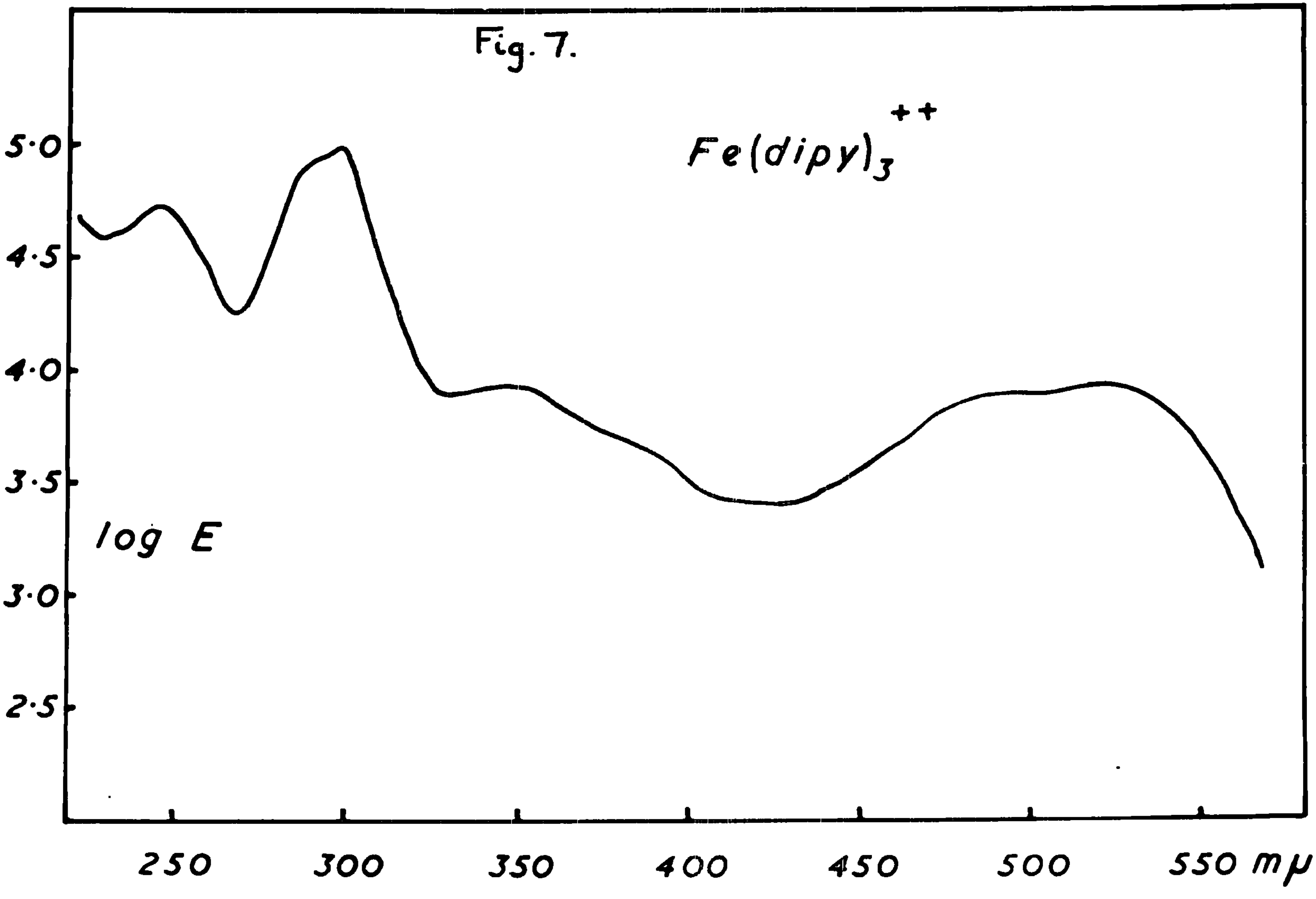


Fig. 6.
5·0
4·0
3·0
Log E
dipy Be Cl_2
dipy Be Br_2
dipy Be I_2
250
300
350
400 mμ

Fig. 7.



Diiodo(bipyridyl)beryllium

Spectra were done on a saturated solution in tetrahydrofuran, and on this solution diluted five times.

λmax	ϵ
235 mμ	30000
290	24000
368	7000

Tris(2,2'- bipyridyl)ferrous ion, $(\mathrm{Fe\ bipy}_3)^{2+}$.

The solution was prepared from 2,2'-bipyridyl with a very slight excess of ferrous sulphate in water.

λmax	ϵ
246.5 mμ	51200
298.5	96800
347.5	8650
522	8660

The spectrum of bis(bipyridyl)beryllium in benzene solution was also examined and found to have broad absorption bands with maxima at 801 and 899 mμ. accounting for its deep green colour in solution.

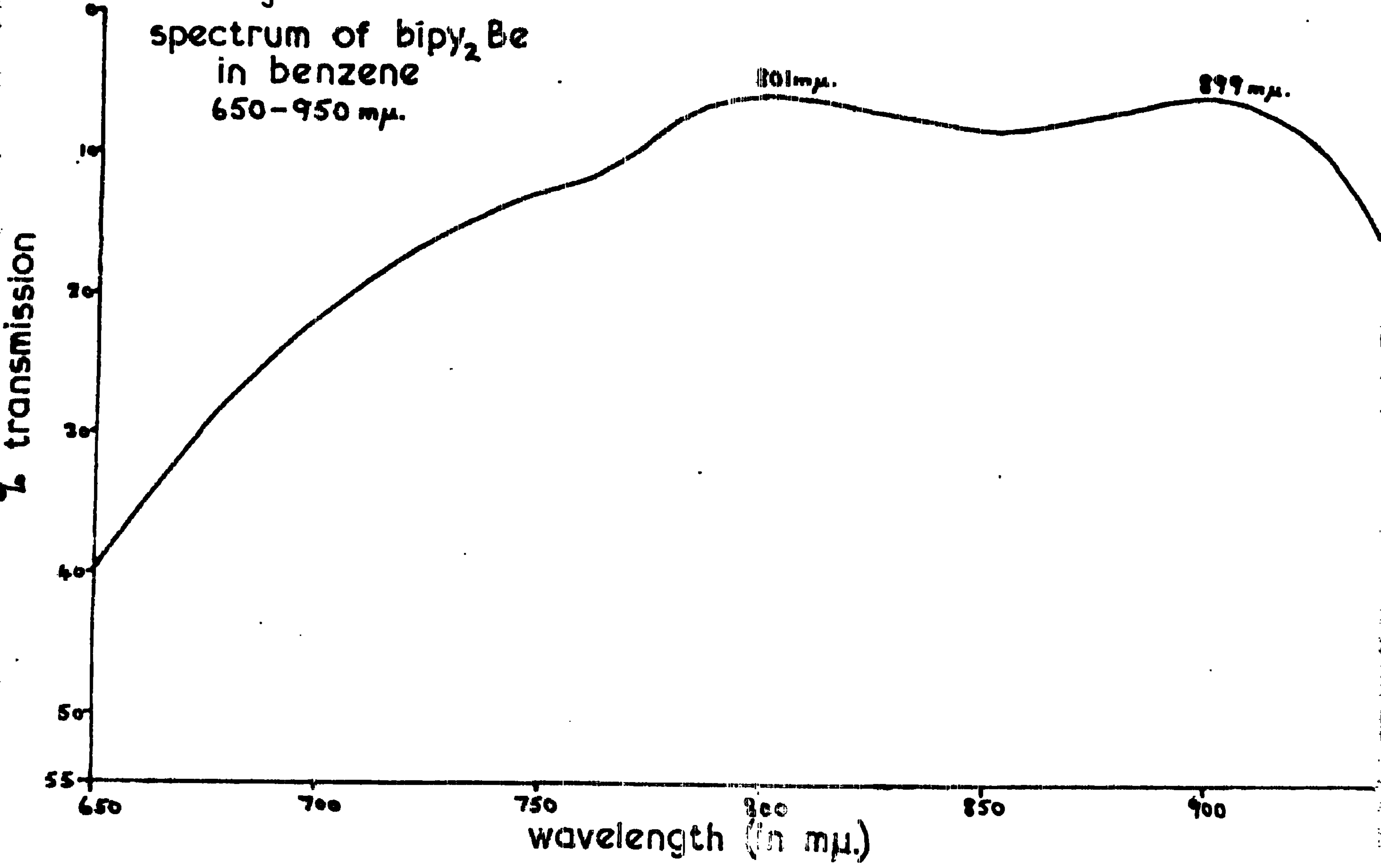


Fig. 8.
spectrum of bipy$_2$Be
in benzene
650–950 mμ.

COMPLEXES OF CERTAIN ETHYLENEDIAMINE DERIVATIVES WITH DIMETHYLBERYLLIUM

The reactions of ethylenediamine and N-methyl substituted ethylenediamines with dimethylberyllium have been studied. In four of these amines there are one or more reactive hydrogen atoms (i.e. they contain primary or secondary amine groups), which can be eliminated with a methyl group from the dimethylberyllium as methane gas.

Dimethyl(N,N,N',N',-tetramethylethylenediamine)beryllium, $Me_2N.CH_2CH_2.NMe_2.BeMe_2$.

About 0.01 mole of dimethylberyllium in 10 ml. of ether was placed in a double Schlenk tube. 0.012 mole of N,N,N',N',-tetramethylethylenediamine (1.4g.) was added in 2 ml. of ether when a slightly exothermic reaction occurred giving a colourless solution from which ether was removed until sufficient product had crystallized out. The white crystals were then filtered off and pumped dry.

On heating in a sealed tube under vacuum the product melts at 81.2°. It fumes strongly when exposed to the atmosphere for a short time, but without taking fire, and it reacts vigorously with water with effervescence.

Found: Be, 5.5%; 0.2315g. gave 67.9 N-c.c. of methane on hydrolysis; M, cryoscopic in benzene, 176, 170, in 0.29, 0.64 wt.% solutions. $C_2H_4(NMe_2)_2.BeMe_2$ requires Be, 5.8%; 66.9 N-c.c. of methane; M, 155.

The molecular weight measurements correspond to degrees of association of 1.13 and 1.10 respectively.

Reaction of N,N,N',-trimethylethylenediamine with dimethylberyllium.

About 52 N-c.c. of dimethylberyllium in 0.8 ml. of ether solution were cooled in liquid air in a reaction bulb on the vacuum line and about 56 N-c.c. of N,N,N',-trimethylethylenediamine were condensed on it. The reaction bulb was then isolated from the rest of the vacuum line and allowed to warm up slowly. A product soluble in the ether was formed, then at about room temperature (18°) vigorous effervescence occurred with the formation of a white crystalline solid (needles), and a gas.

The ether and excess diamine were condensed out in a trap cooled in liquid air and the non-condensable gas was measured. It was found that 49.6 N-c.c. of gas, identified as methane by its infra-red spectrum, was formed in the reaction. The product was then hydrolysed by water vapour and the liberated methane measured. 56.7 N-c.c. of methane were obtained from the hydrolysis.

In a second reaction using a large excess of the diamine 59 N-c.c. of dimethylberyllium in 0.9 ml. of ether was mixed with about 270 N-c.c. of N,N,N',-trimethylethylenediamine and after effervescence had finished at room temperature, the mixture was heated in an oil bath at 60° for about 30 minutes but no further evolution of gas occurred. The methane was measured and found to be 57.4 N-c.c.

The product was then prepared on a larger scale in order to investigate its properties. 0.0058 mole of dimethylberyllium in about 2 ml. of ether was placed in one arm of a double Schlenk tube and cooled in liquid air. 0.7g. (0.0068 mole) of N,N,N',-trimethylethylenediamine in about 10 ml. of ether was added and the mixture allowed to warm up slowly with occasional shaking to mix the reactants thoroughly on melting. At about 0° a steady evolution of methane began. When the reaction was complete the solution was filtered into the other arm of the apparatus and most of the ether was pumped off. On cooling the solution, white needles crystallized out and were filtered off and pumped dry for 2 hours.

The product was very soluble in benzene. It reacts vigorously with water liberating methane and fumes of beryllium hydroxide but when exposed to the atmosphere it is slowly hydrolysed without fuming.

On heating in a sealed tube under vacuum it melts at 116-8°.

Found: 0.2076g. gave, on hydrolysis, 34.8 N-c.c. of methane; M, cryoscopic in benzene, 255, 241, in 0.77 and 1.16 wt.% solutions. $C_5H_{13}N_2.BeCH_3$ requires 37 N-c.c. of methane; M, 125.

Thus for $C_5H_{13}N_2.BeCH_3$ the degree of association is 2.04 and 1.93 in the two solutions measured.

Reaction of N,N',-dimethylethylenediamine with dimethylberyllium

90 N-c.c. of N,N',-dimethylethylenediamine were condensed on to 0.75 ml. of an ether solution containing 49 N-c.c. of dimethylberyllium cooled in liquid air. On allowing the reaction bulb to warm up slowly vigorous effervescence occurred as soon as the diamine melted. On reaching room temperature the bulb contained a white solid and the excess diamine and ether, plus a considerable quantity of a non-condensable gas which was measured. The excess diamine and the ether were pumped off leaving a white crystalline product as tiny needles. The gas, which was shown to be methane by its infra-red spectrum, measured 48.2 N-c.c.

The solid product was heated at 60° for an hour with no apparent change. It was then heated under vacuum with an oil bath when it began to sublime very slowly at about 90°. At 145° sudden vigorous decomposition occurred with fuming, producing an amorphous white solid and a gas. The gas was measured (39.1 N-c.c.) and shown by its infra-red spectrum to be methane. The solid, which is insoluble in benzene, gave no more methane even on heating to the temperature at which it began to char slowly. Thus approximately 80% of the expected methane was eliminated by heating.

The compound obtained after the elimination of the first mol. of methane was prepared on a larger scale by the addition of 1.15g. (0.0132 mole) of N,N'-dimethylethylenediamine in 20 ml. of ether to a solution of 0.0117 mole of dimethylberyllium in 4 ml. of ether cooled in liquid air, the mixture then being allowed to warm up slowly. At about -30° gas began to be evolved slowly from the solution which was immediately filtered. As the gas was evolved colourless needles began to crystallize out from the solution. When the reaction had ceased about two-thirds of the ether was distilled off under vacuum and then the mixture was cooled and filtered, and the product was pumped until completely dry. It was found to be soluble in benzene and the molecular weight was therefore determined cryoscopically in benzene solution.

Found: M, 222, 217 in 0.81, 1.41 wt.% solutions. For $C_4H_{11}N_2.BeCH_3$ (formula weight: 111) these correspond to degrees of association of 2.00 and 1.96 respectively.

The compound is little affected by short exposure to the atmosphere, but reacts with water evolving methane.

A more complete elimination of methane from this compound was effected by heating its solution in tetralin. The tetralin used for this was purified by shaking with ferrous sulphate solution to remove peroxides, drying over calcium chloride, refluxing over sodium, and finally distilling from sodium at 206-8°.

0.029 mole of dimethylberyllium in 40 ml. of ether was allowed to react with 3g. (0.034 mole) of N,N',-dimethylethylenediamine in 35 ml. of ether by mixing the two solutions, cooled below - 100°, and leaving the mixture to warm up to room temperature. When evolution of methane had ceased the ether and excess diamine were distilled off under vacuum and 120 ml. of the tetralin were added to the product which partly dissolved. On heating up slowly all the solid dissolved in the tetralin amd at about 140-150° evolution of methane began. After heating for about 2 hours no more methane was being evolved and the solution had formed a clear pale yellowish gel. By vacuum distillation at 80-100° the tetralin was removed from the gel quite readily leaving a cream-coloured solid which was washed once with 30 ml. of dry ether and dried in a vacuum.

A sample of this solid was hydrolysed with dilute sulphuric acid followed by concentrated hydrochloric acid when a pale yellowish solution was formed but no gas was evolved. The hydrolysate was found to smell strongly of tetralin.

A weighed sample of the solid was hydrolysed with strong hydrochloric acid then carefully made strongly alkaline with concentrated sodium hydroxide solution. The water and the diamine were pumped off into a cooled trap and the diamine was titrated with normal hydrochloric acid using methyl red as indicator. An analysis for beryllium was also carried out on the product.

Found: Be, 8.1%; $MeN.C_2H_4.NMe$, 76.5%. The ratio of Be to $MeN.C_2H_4.NMe$ is therefore 0.106. The ratio of the atomic weight of beryllium to the molecular weight of the group, $MeN.C_2H_4.NMe$, is 0.105. The remaining 15.4% of the product is tetralin which can be slowly removed between 150 and 200° under a good vacuum.

The product was found to be insoluble in all the common organic solvents. It reacts readily with water liberating the diamine with an exothermic reaction.

Reaction of N,N,-dimethylethylenediamine with dimethylberyllium.

In a preliminary reaction 73 N-c.c. of N,N,-dimethylethylenediamine were condensed on about 59 N-c.c. of dimethylberyllium in about 0.90 ml. of ether solution, cooled in liquid air in a reaction bulb on the vacuum line. The bulb was then allowed to warm up slowly and as soon as the diamine melted a white crystalline solid was formed which dissolved as the temperature increased. Vigorous effervescence began just below room temperature with a highly exothermic reaction and a white crystalline solid was produced. The methane evolved was measured and found to be 60.9 N-c.c.

In a second reaction about 150 N-c.c. of the N,N,-dimethylethylenediamine were reacted with 65 N-c.c. of dimethylberyllium giving the white product and 64 N-c.c. of methane together with about 85 N-c.c. of excess diamine. The product, on hydrolysis with 2N.sulphuric acid, gave a further 60 N-c.c. of methane.

A larger quantity of the product was prepared from 0.012 mole of dimethylberyllium and a slight excess of N,N,-dimethylethylenediamine in diethyl ether. The white compound obtained was found to be quite soluble in benzene and its molecular weight was therefore determined cryoscopically in benzene solution. This gave M, 224, 222 in 0.70, 0.47 wt.% solutions, corresponding to degrees of association of 2.02, 2.00 for $C_4H_{11}N_2.BeCH_3$.

A sample of 0.2810g. of the compound was heated under a high vacuum in a reaction bulb. At about 115° it began to sublime slowly on the cooler parts of the bulb, then began to evolve methane slowly at about 138°. At 170° it melted with vigorous evolution of gas forming some colourless needles which melted again almost immediately with further effervescence giving a viscous liquid. This continued to evolve gas slowly for a further 1½ hours at 170°. The total quantity of methane produced was found to be 54.2 N-c.c. The expected amount of methane from 0.2810g. of $(Me_2N.C_2H_4.NH.BeMe)_2$ is 56.6 N-c.c., therefore 95.7% of the expected amount was evolved. The viscous residue produced set to a glassy solid, on cooling to room temperature, which is only sparingly soluble in benzene.

Reaction of ethylenediamine with dimethylberyllium.

54 N-c.c. of dimethylberyllium were cooled in liquid air in a reaction bulb on the vacuum apparatus and about 200 N-c.c. of ethylenediamine were condensed on it. The bulb was shut off from the rest of the apparatus then allowed to warm up gradually. Vigorous effervescence occurred at about -20°. The product was left at room temperature for about one hour then the methane evolved was measured. It was found that 90.6 N-c.c. of methane had been liberated at this stage. However, on heating the reaction bulb to 45° for half an hour a further 10.9 N-c.c. of methane were collected making a total of 101.5 N-c.c. of methane, or 94% of the expected quantity if 2 mols. were to be eliminated from each mol. of dimethylberyllium. The white amorphous residue obtained was found to be only sparingly soluble in benzene. On hydrolysis with water it gave 7.5 N-c.c. of methane.

A CHELATED OXYGEN COMPLEX OF DIMETHYLBERYLLIUM

Dimethyl(1,2-dimethoxyethane)beryllium, $MeOC_2H_4OMe.BeMe_2$.

Prepared from 1,2-dimethoxyethane and dimethylberyllium in ether solution, this was precipitated as colourless feathery needles which were separated, pumped dry, and recrystallized from ether. The complex, m.p. 100-101°, sublimes at 60-70° (0.06 mm.) and condenses as colourless glistening prisms.

Found: CH_3, by hydrolysis, 23.1%, M, cryoscopically in 0.37, 0.73 wt.% benzene solutions, 123, 125. $C_6H_{16}BeO_2$ requires hydrolyzable CH_3, 23.2%; M, 129.

The complex soon inflames when exposed to the air (not immediately like dimethylberyllium).

DISCUSSION

DISCUSSION

Complexes of Beryllium Chloride with Ethers and Thioethers.

One purpose of this investigation was to find possibly useful solvents for beryllium chloride. Two of the compounds studied appear to be useful in this respect, one being dimethyl sulphide which has already been suggested as a solvent in the preparation of dimethylberyllium,(15) due to the fact that it is a much weaker donor than diethyl ether, and the other being tetrahydrofuran which has found use in these investigations as a solvent in the preparation of bis(bipyridyl)beryllium. Although 1,2-dimethoxyethane does not dissolve beryllium chloride it has been used in the place of tetrahydrofuran as the reaction medium for the preparation of bis(bipyridyl)beryllium.

Both dichloro(bistetrahydrofuran)beryllium(31) and 1,2-di(methoxy)ethane(dichloro)beryllium(59) have been reported while this work was in progress. However, the latter complex was described as $Cl_2Be(MeOC_2H_4OMe)_2$, although the analysis given for the compound corresponds to $Cl_2Be(MeOC_2H_4OMe)$.

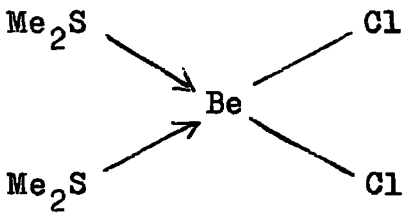
The complexes formed by dimethyl sulphide are of some interest. It is known that dimethyl sulphide does not coordinate to dimethylberyllium(2) and it has been suggested that this is because the energy required to break down the polymeric structure of dimethylberyllium is greater than the energy of coordination of this ligand to monomeric dimethylberyllium

Although the energy required to break down the polymeric structure of beryllium chloride is probably higher than that for dimethylberyllium, the energy of coordination of dimethyl sulphide to monomeric beryllium chloride will certainly be much greater than that to dimethylberyllium due to the greater electronegativity of the chlorine atoms over methyl groups, which makes the beryllium atom a stronger acceptor in beryllium chloride. The fact that dichloro(bisdimethyl sulphide)beryllium could be prepared shows that the stronger acceptor properties of beryllium in beryllium chloride outweigh the greater energy of polymerisation of beryllium chloride over dimethylberyllium. However, it is clear that the sulphur is not very strongly coordinated to the beryllium atom even in this compound, since one molecule of dimethyl sulphide can be removed at room temperature to form di-μ-chloro-dichloro-bis(dimethyl sulphide)diberyllium, $(Me_2S.BeCl_2)_2$. The preparation of this coordination compound from a toluene solution of dichloro(bisdimethyl sulphide) beryllium by vacuum distillation at room temperature would appear to indicate that the equilibrium shown below exists in solution:

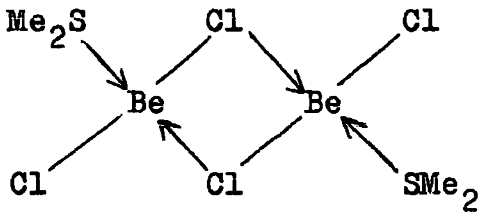
$$2(Me_2S)_2BeCl_2 \rightleftharpoons (Me_2S.BeCl_2)_2 + 2Me_2S$$

On pumping the solution the more volatile dimethyl sulphide would be removed more rapidly than the toluene so that the equilibrium would be continuously displaced to the right hand side finally giving as the product di-μ-chloro-dichlorobis(dimethyl sulphide)diberyllium.

Dichloro(bisdimethyl sulphide)beryllium was shown to be monomeric in benzene solution and its structure must therefore be similar to that of the diethyl ether coordination compound of beryllium chloride. The other dimethyl sulphide complex was found to be dimeric in benzene solution and the most likely structure for this is one with the beryllium atoms joined through two chlorine bridges, as in beryllium chloride itself, thus giving beryllium a covalency of four:



Dichloro(bisdimethyl sulphide)beryllium



Di-µ-chloro-dichlorobis(bimethyl sulphide)diberyllium

2,2'-Bipyridyl Complexes

Complexes were prepared from bipyridyl and various beryllium compounds which had unexpected colours. Those compounds on which ultra-violet and visible absorption spectra have been studied are listed in the table below:

X in Bipy Be X_2	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

In the table only the long wavelength absorption band/is listed. All the complexes do have high-intensity bands in the 220-300 mμ. region, similar to those of free bipyridyl (see Figures 5 and 6). Considering the absorption bands causing visible colour, Figure 6 shows a small decrease in λmax. and a marked decrease in the molar extinction coefficient in passing from the less to the more electronegative halogen. In the case of the organo-complexes studied (Figure 5) both λmax. and the molar extinction coefficients decrease as the electronegative character of the organic group increases. The bipyridyl complexes of di-n-butylberyllium, di-iso-propylberyllium, and bis(p-dimethylaminophenyl) beryllium also appeared to fit into this sequence from their colours, but they were far too unstable to be isolated so that their ultra-violet and visible absorption spectra have not been studied.

It can be seen from Figure 7 that there is some similarity between the spectra of these beryllium complexes and the spectrum of the bipyridyl complex of the ferrous ion, $(\mathrm{Fe\ bipy}_3)^{2+}$ The colour of this complex ion is regarded as being produced by electron transfer from the 3d-orbitals of the iron atom to the lowest unoccupied molecular orbital of the bipyridyl molecule.

The observations on the beryllium complexes are probably best explained by assuming that the colours are due to an electron transfer. However, since there are no d-electrons on the beryllium atom, it seems that an electron transfer must occur from one of the Be-X bonds to the lowest unoccupied molecular orbital of the bipyridyl. In the excited state of the complex the Be-X bonds would thus be acting as electron donors, and their donor character would clearly be greater if the electrons in the bonds were relatively loosely held, as is probable in the Be-alkyl bond, than if the bonding were strong, as it probably is in the Be-Cl bond. A decrease in the electronegativity of X should increase the molar extinction coefficient, as was observed, since it would increase the size of the beryllium orbitals and hence the extent of their overlap with the π-orbitals of the bipyridyl. This effect is essentially similar to the back-donation of electrons well known in carbonyl, phosphine, as well as bipyridyl complexes of transition metals, only in the case of the beryllium complexes the absorption of a quantum of visible light (about 64-80 kcal. mole^{-1}) is necessary for such an electron transfer to occur. Assuming that in the excited state a beryllium-carbon bond has become a one-electron bond or half bond, chemical decomposition would not necessarily result since beryllium-carbon half bonds can have some stability. In the dimethylberyllium polymer all the beryllium-carbon bonds are represented as half bonds in the generally accepted explanati of its structure.(16)

It is possible that in the halide complexes the electron source is one of the non-bonding atomic orbitals of the halogen atom, but in the organo-complexes the Be-C bond seems to be the only likely electron source. For example, in the dimethyl complex the only other electrons are those in the orbitals forming the C-H bonds of the methyl groups.

Similar electronic transitions have been suggested as the origin of the colours of a number of decaborane derivatives. For example, the introduction of electron attracting substituents in the pyridine rings of $B_{10}H_{12}py_2$ complexes deepens their colours.(60)

Diethylberyllium forms a bispyridine complex, py_2BeEt_2, orange-yellow in colour and monomeric in benzene solution like its red bipyridyl analogue, but the bispyridine complex of dimethylberyllium is white in colour, therefore it seems likely that a similar effect operates in these complexes causing a colour change with variation of electronegativity of the group on the beryllium and probably involving the same type of electron transfer, in this case to the lowest unoccupied molecular orbital of pyridine instead of bipyridyl.

Pyridine appears to act as a stronger donor than trimethylamine towards dimethylberyllium and diethylberyllium, since trimethylamine forms only mono-amine complexes, $(Me_3N)BeMe_2$(2) and $(Me_3N)BeEt_2$(57), as the only stable complexes at room temperature. In fact for diethylberyllium the mono-amine complex is the only stable complex above -40°.

Coloured complexes were formed with bipyridyl by several organic derivatives of Group II elements. With diethylmagnesium a deep red solution was obtained in ether when bipyridyl was added to it, but the complex was too unstable to be isolated, and formed a red-brown tarry material when attempts were made to isolate the complex. Bipyridyl and diphenylmagnesium gave an immediate orange-yellow precipitate, which turned chocolate brown in about ten minutes at room temperature. These decompositions may involve attack of the bipyridyl at the C-N double bond since organomagnesium compounds are highly reactive, and Grignard reagents add to pyridine in this way giving, for example, 2-arylpyridines by addition at the C-N bond.

The less reactive dimethyl derivatives of the Group II B elements form an interesting sequence in their behaviour with bipyridyl. Dimethylzinc gave a bright yellow complex, bipy Zn Me_2, from which the dimethylzinc cannot be removed by pumping at room temperature. Dimethylcadmium formed an unstable yellow complex, which has an appreciable dissociation pressure at room temperature since prolonged pumping leaves only colourless bipyridyl. Dimethylmercury dissolves in a solution of bipyridyl in ether without colour change and the dimethylmercury can rapidly be removed by pumping at room temperature which seems to show that no complex is formed.

As expected by analogy with the beryllium compounds, bipy Zn Et_2 has a deeper colour (orange-red) than the dimethyl complex; it is also much more rapidly decomposed in the air, a marked difference which was not apparent in the beryllium compounds. The only dialkylzinc complexes previously described are the unstable tetrahydrofuran complex(56), corresponding approximately to $2Me_2Zn.3C_4H_8O$, and the anionic complexes exemplified by $Li_2ZnMe_4.Et_2O$(61).

Bipyridyl Anion Complexes

The lithium salt of the bipyridyl anion, Li bipy, and the green dilithium derivative, Li_2 bipy, have been used in the preparation of bipyridyl compounds of transition metals in low valency states, such as the compounds of titanium(0) and titanium(-I)(55), viz. $bipy_3Ti$ and $Li[bipy_3Ti]$. By the reaction between lithium-bipyridyl and beryllium chloride in diethyl ether, or the reaction between the dilithium derivative of bipyridyl and a suspension of dichloro(bipyridyl)beryllium in tetrahydrofuran or in 1,2-dimethoxyethane, the deep green bis(bipyridyl)beryllium is formed in solution.

The compound $bipy_2Be$, whose colour is due to the tail of a very intense broad absorption band (λ_{max} = 801 mμ.; there is another band with a maximum at 899 mμ.), could be formulated as a bipyridyl complex of beryllium(0) in which the beryllium would presumably have two electrons in the 2s level, or as a bis(bipyridyl$^-$) complex of the beryllium(II) cation. The values of 2.05 and 2.15 B.M. for the room temperature susceptibilities of two specimens of this compound, after diamagnetic corrections had been made, were found. Though the formulation as $(bipy^-)_2Be^{2+}$ would imply a magnetic moment of 2.8 - 2.9 B.M., the rather lower observed paramagnetism excludes the formulation as a beryllium(0) complex since this should be diamagnetic. The difference between the observed magnetic moment and that expected for a complex containing two bipyridyl anions, each with a single unpaired electron, could be due to at least two possible effects. In the first place some decomposition into diamagnetic products could have occurred in the interval between the preparation of the compound and the magnetic measurements being carried out at University College, London. Alternatively there may be an equilibrium with the diamagnetic complex $[(\text{bipy}^{2-})(\text{bipy}^{0})\text{Be}^{2+}]$. To try to eliminate the first possibility the specimens were cooled to -78° immediately after they were prepared and sealed in the Gouy tubes, and kept at this temperature until immediately before their magnetic susceptibilities were measured. Further, there was insignificant change in the measured values of 2.05 and 2.15 B.M. after the specimens had remained at room temperature for two weeks.

An equilibrium such as:

$$(\text{bipy}^{-})_2\text{Be}^{2+} \rightleftharpoons [(\text{bipy}^{2-})(\text{bipy}^{0})\text{Be}^{2+}]$$

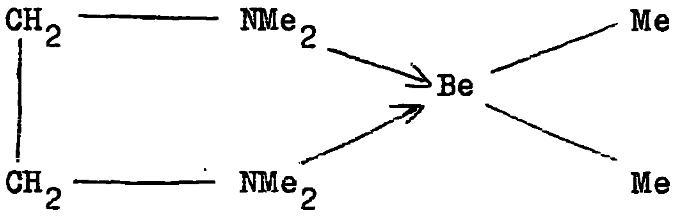
would very probably be temperature-dependent, but the variation of magnetic susceptibility with temperature was not investigated.

By reaction with lithium, bis(bipyridyl)beryllium gave a very deep violet solution in ether from which the black product, $\text{Li}[\text{bipy}_2\text{Be}]$, was isolated. The properties of this compound have not been studied in detail, but Professor Nyholm and Dr. Pande report that it is weakly paramagnetic.

These beryllium complexes evidently differ from the bipyridyl complexes of transition metals in low valency states. The transition metal compounds are regarded as complexes of neutral bipyridyl with the metals in their zero oxidation level in order to explain, for example, the diamagnetism of $bipy_3Ti$(62). The different formulation of the beryllium compounds as derivatives of the bipyridyl anion is supported not only by magnetic evidence but also by their very intense colours; their colours are as intense as those of hydrocarbon anions (e.g. in sodium-naphthalene), unlike the transition metal compounds which have distinctly weaker colours.

Complexes of Beryllium with Aliphatic Chelate Donor Groups

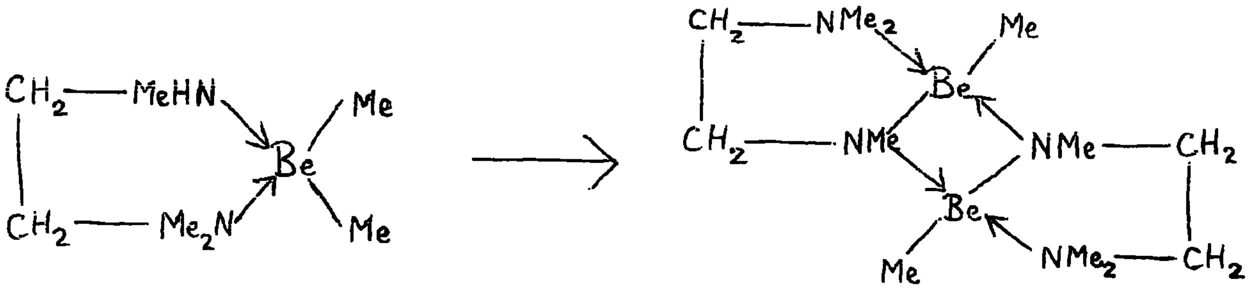
Dimethylberyllium forms with trimethylamine a 1:1 complex which does not noticeably dissociate up to 180°, and an unstable 2:3 complex, $(Me_2Be)_2(NMe_3)_3$, which readily loses a mol. of trimethylamine(2). The failure to prepare a bisamine complex $Me_2Be(NMe_3)_2$ is surprising, particularly since an unstable bisphosphine complex, $Me_2Be(PMe_3)_2$ was obtained. The non-formation of $Me_2Be(NMe_3)_2$ must be due to an entropy rather than a steric effect since we have been able to prepare a 1:1 complex with N,N,N',N'-tetramethylethylenediamine:



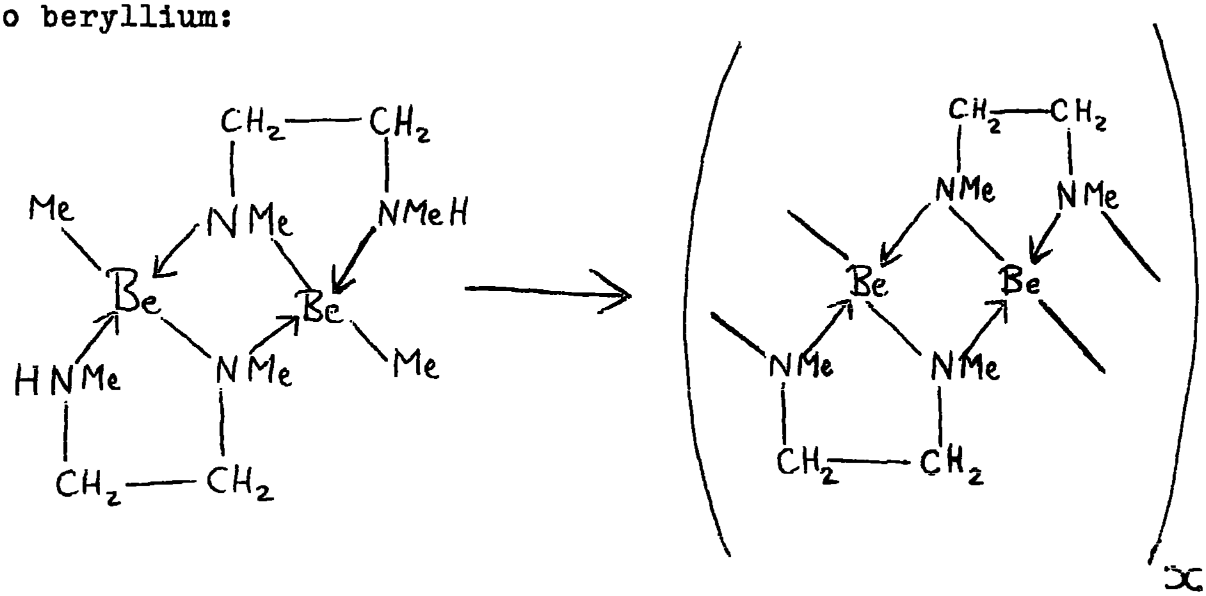
This compound is about 10% associated in benzene solution; some association would be expected since this compound no doubt has a large dipole moment.

In contrast to dimethyl- and diethyl-ether, which form unstable complexes with high dissociation pressures at room temperature(2), the chelating diether 1,2-dimethoxyethane forms a well defined complex, $Me_2Be(MeOC_2H_4OMe)$, which may be crystallized from diethyl ether. It is, however, more reactive to the atmosphere than the diamine complex. It is monomeric in benzene and its dissociation pressure must be very small since it sublimes unchanged at 60-70° at 0.06 mm. pressure.

Since the dimethylamine complex, $Me_2Be.NHMe_2$, loses a mol. of methane when it is melted (44°) and forms a trimer(47) $(MeBeNMe_2)_3$, the dimethylberyllium complexes of ethylenediamines containing reactive amino-hydrogen atoms were studied to observe the association or polymerisation by which the co-ordinative unsaturation of the beryllium is relieved in these types of compounds when methane is eliminated. N,N,N'-trimethylethylenediamine forms a complex, which is probably that shown below, which loses a mol. of methane just below room temperature forming a dimer:



Ethylenediamines with two or more amino-hydrogen atoms give polymeric products by elimination of two mols. of methane, but intermediates which were dimeric were isolated in reactions with both symmetrical and unsymmetrical dimethylethylenediamine after elimination of only one mol. of methane. Thus methane (1 mol.) is evolved from a frozen mixture of N,N'-dimethylethylenediamine and dimethylberyllium in ether, as soon as the reactants melt. The product sublimes slowly in a vacuum at 90°, and at 145° suddenly decomposes with evolution as methane of four-fifths of the remaining methyl bound to beryllium:



Freezing of the resulting polymer could account for a proportion of Me-Be groups not reacting with NH groups, since it was found that all the Me-Be groups were eliminated by heating a solution of the dimer in tetralin to 150°. The polymer is insoluble in all the common organic solvents but reacts rapidly and exothermically with water to form beryllium hydroxide and the diamine.

The unsymmetrical diamine, $Me_2NC_2H_4NH_2$, reacted with dimethylberyllium evolving one mol. of methane and forming a dimeric product which is probably similar to those already described. On heating the dimer for some time at 170° this evolved almost one mol. of methane and on cooling gave a glassy solid which is probably polymeric.

Ethylenediamine itself liberated about 80% of the total methyl from dimethylberyllium at room temperature with formation of a white amorphous evidently polymeric material. About 6% of the methyl groups were retained even after heating at 45° for some time, and are released on hydrolysis with water or aqueous acids.

APPENDIX

APPENDIX

1. Studies on Dimethylberyllium-trimethylamine

Introduction. Dimethylberyllium-trimethylamine was previously prepared on a small scale by the direct reaction of dimethylberyllium and trimethylamine(2). It forms colourless rhombic crystals, m.p. 36°, and reacts vigorously with air and moisture. Measurements of its vapour pressure have been made in the range 26° - 140°, and molecular weights have been calculated from measurements of the temperature and pressure of a known weight of its vapour in a high-temperature bulb. The molecular weights corresponded to degrees of association of 1.073, 1.065, 1.056, 1.040, and 1.024 at 150°, 155°, 160°, 170°, and 180° respectively. These measurements led to the suggestion that the compound is probably associated in the solid and liquid states. In order to examine this possibility further, molecular weights in benzene solution have been measured in this work.

The reaction of dimethylberyllium-trimethylamine with methylamine has been investigated, since there seemed to be the interesting possibility that if two mols. of methane could be eliminated a compound $(Me_3N^+.Be^-NMe)_x$ might be obtained, which could have a structure analogous to the borazoles or to the tetrameric borazynes(63). In fact it was found that trimethylamine is lost on reaction, therefore the reaction between dimethylberyllium-pyridine and aniline was studied, since pyridine is a stronger donor than trimethylamine to dimethylberyllium and may be lost less easily.

Preparation of Dimethylberyllium-trimethylamine

A 2.1 M. solution of methyl-lithium was prepared by reaction of methyl bromide and lithium shot in diethyl ether (91.7% yield).

202 ml. of this solution containing 0.424 mole of methyl-lithium were added slowly with stirring to 17.05g. of beryllium chloride (0.212 mole) dissolved in 210 ml. of diethyl ether. The reaction was slightly exothermic and the rate of addition was adjusted so that the ether refluxed gently. The white precipitate of lithium chloride was allowed to settle, then the clear solution of dimethylberyllium was decanted off. About 140 ml. of ether were distilled off to reduce the volume of solution, then the solution was cooled to -60° and 20.4g. of trimethylamine (0.345 mole) in 60 ml. of ether were added. The excess trimethylamine and about two-thirds of the ether were pumped off at room temperature, then the remaining ether was pumped off through a flask cooled to -35° to collect any of the product which came over. Finally the product was distilled under vacuum at 40° into a flask cooled in liquid air. The last traces of ether were removed by pumping the product for a few minutes at 30°.

The dimethylberyllium-trimethylamine was obtained as colourless rhombic crystals melting at 36°. (Yield: 65%).

Molecular Weight Measurements

0.5130g. of dimethylberyllium-trimethylamine was dissolved in 25 ml. of benzene and samples of this solution, diluted with benzene, were used to measure its molecular weight cryoscopically.

Found: M, 117.0, 115.5, 114.9 in 2.05, 1.03, 0.51 wt. % solutions. These values correspond to degrees of association of 1.19, 1.18, 1.17 for $Me_2Be.NMe_3$.

Reaction of Dimethylberyllium-trimethylamine with Methylamine

In a preliminary experiment 0.110g. of dimethylberyllium-trimethylamine (0.00112 mole) was sublimed into a reaction tube and 22.95 N-c.c. of methylamine (0.00102 mole) were condensed on it. The tube was sealed off and on warming up the methylamine melted (-95°) and began to react with the dimethylberyllium-trimethylamine immediately. The reaction became more vigorous and at about room temperature very vigorous evolution of gas occurred. The reaction tube was then heated to 70° when only very slight effervescence was observed and on heating to 100° for thirty minutes no further change was apparent.

The tube was opened on the vacuum apparatus and the non-condensable gas, identified by its infra-red spectrum as methane, was measured and found to be 24.3 N-c.c. A condensable gas present was measured (17.4 N-c.c.), and its infra-red spectrum showed it was trimethylamine containing no methylamine. A trace of unreacted dimethylberyllium-trimethylamine was sublimed out of the tube.

The amorphous involatile white product was hydrolysed with water giving 17.0 N-c.c. of methane.

A similar reaction was then carried out in a flask attached to the vacuum apparatus. 0.5454g. (125 N-c.c.) of dimethylberyllium-trimethylamine was placed in the flask, and 125 N-c.c. of methylamine were condensed into the flask cooled in liquid air. On allowing it to warm up, slight effervescence began soon after the methylamine had melted. This became more vigorous and the reaction was controlled by cooling the flask occasionally. When no further reaction occurred at room temperature (20°)the methane produced was measured and found to be 127.5 N-c.c. The condensable gas present was transferred to the measuring bulbs and found to be 95 N-c.c. of trimethylamine, identified by its infra-red spectrum. Finally 0.1052g. (24.1 N-c.c.) of unreacted dimethylberyllium-trimethylamine was sublimed from the product into a weighed trap.

The product was an involatile white solid which gave 73.5 N-c.c. of methane on hydrolysis with water. Therefore the 100.9 N-c.c. of dimethylberyllium-trimethylamine which had reacted gave a total of 201.0 N-c.c. of methane from the reaction with methylamine and the hydrolysis of the final product.

This reaction with methylamine was repeated to obtain and study the white solid product of the reaction. It was found that over half of this product was soluble in toluene, and it was therefore extracted with this solvent. The molecular weight of the toluene soluble part was determined cryoscopically in benzene solution, and it was analysed for hydrolysable methyl groups by hydrolysis with 2N. sulphuric acid and measurement of the methane produced.

Found: M, 323, 346, 318, in 0.64, 0.64 0.32 wt. % solutions; 0.0642g. gave 23.0 N-c.c. of methane on hydrolysis. Me.Be.NHMe would require M, 54; 26.6 N-c.c. of methane.

The product which was insoluble in toluene gave only slight effervescence when hydrolysed with 2N. sulphuric acid.

Reaction of Dimethylberyllium-pyridine with Aniline

Aniline was used in this reaction instead of methylamine since it probably reacts more readily than the latter to give methane in this type of reaction.

To a solution of 0.0175 mole (391.8 N-c.c.) of dimethylberyllium in 6 ml. of ether was added 1.38g. (0.0175 mole) of pyridine in 15 ml. of ether. 1.63g. (0.0175 mole) of aniline in 15 ml. of ether was then added dropwise when methane was evolved readily. As the gas was produced a white amorphous precipitate began to appear. When the reaction had ceased about 540 N-c.c. of methane had been evolved. The product was filtered off and dried (Yield: 1.75g.).

A weighed sample of this product (0.1900g.) was heated in a flask on the vacuum apparatus to 180° until evolution of gas had ceased. It was found that 5.7 N-c.c. of methane had been collected, and a trace of pyridine had distilled off (identified by its infra-red spectrum). The white residue (0.1482g.) appeared to contain no pyridine from its infra-red spectrum, and it was insoluble in benzene.

Discussion

The molecular weights found for dimethylberyllium-trimethylamine in benzene solution show it to be slightly more associated than it is in the vapour in the 150-180° region, and this appreciable association supports the suggestion that it may be dimeric in the solid and liquid states.(2)

In its reaction with methylamine it is evident that the trimethylamine is very readily displaced, therefore the reaction is very similar to the direct reaction between dimethylberyllium and methylamine.(47) However, in the latter reaction only one mol.of methane is eliminated readily, whereas in the reaction involving dimethylberyllium-trimethylamine about 1.26 mols. of methane were evolved at room temperature. The analysis of the toluene soluble part of the product shows that it does not quite correspond to Me.Be.NHMe, and it is likely that the insoluble part of the reaction product is a more polymeric material in which there are more Be-N bonds, since it gives very little methane on hydrolysis.

The reaction between dimethylberyllium-pyridine and aniline appears to follow a similar course, in that most of the pyridine is easily displaced together with about 1.4 mols. of methane. The reaction product is probably polymeric since it is involatile, and insoluble in both ether and benzene.

2. The Reaction of Dimethylberyllium with Diisopropylamine

Introduction. This reaction has been studied in order to investigate the coordination compound formed, and in order to try to prepare bis(di*iso*propylamino)beryllium. The latter compound would be of some interest since it has recently been found that the corresponding aluminium compound, tris(di*iso*propylamino)aluminium, is monomeric in benzene solution, presumably because the *iso*propyl groups sterically hinder any association(64).

Experimental

106 N-c.c. of di*iso*propylamine were condensed on 44 N-c.c. of dimethylberyllium cooled in liquid air. On allowing the mixture to warm up to room temperature the di*iso*propylamine melted and dissolved the dimethylberyllium giving a colourless solution, with no evolution of methane. The excess di*iso*propylamine was distilled off at room temperature and measured (60 N-c.c.). The liquid product, which freezes at about 13-14°, is therefore the 1:1 coordination compound. This was prepared on a larger scale and its molecular weight was determined cryoscopically in benzene solution.

Found: M, 156, 152, in 0.98, 0.49 wt. % solutions. These correspond to degrees of association of 1.11, 1.09, for $Me_2Be.NHi\text{-}Pr_2$.

The compound fumes strongly in air and is hydrolysed vigorously by water giving methane. On heating to 100° for thirty minutes with excess di*iso*propylamine it gives only about one-eighth of the expected methane. For example, 104 N-c.c. of dimethylberyllium with about 310 N-c.c. of di*iso*propylamine gave, on heating for thirty minutes at about 100°, 25.5 N-c.c. of methane. Hydrolysis of the remaining solution gave 182 N-c.c. of methane, as expected.

In order to carry this elimination of methane as far as possible a solution of 455 N-c.c. of dimethylberyllium in 50 ml. of di*iso*propylamine was refluxed for a long time. For about six days very slow evolution of methane was observed, then for a further three days no gas was produced and the solution became pale brown in colour. Excess di*iso*propylamine was pumped off until the volume of solution was 15 ml., then a 1.8 ml. sample was removed and hydrolysed with 2N sulphuric acid giving 31.0 N-c.c. of methane. Thus the whole of the product would give about 240 N-c.c. of methane on hydrolysis, which shows that only about 1.5 mols. of methane have been eliminated by heating with di*iso*propylamine.

Discussion

This reaction is another example showing that dimethylberyllium tends to form a stable coordination compound with only one molecule of an alkylamine as was found also with both trimethylamine(2) and dimethylamine.(47)

The difficulty of removing methyl groups as methane in this reaction is probably due to the fact that the amino-hydrogen atom in di*iso*propylamine is not sufficiently "acidic" because of the small electron withdrawing effect of *iso*propyl groups compared, for example, to the methyl groups in dimethylamine, (dimethylberyllium-dimethylamine loses one mol. of methane very rapidly at 44°). If the elimination of methane in this type of reaction is inter-molecular it may also be sterically hindered by the *iso*propyl groups. In view of this difficulty it seems that the preparation of bis(di*iso*propylamino)beryllium would be better attempted by the reaction of lithium di*iso*propylamide with beryllium chloride.

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