The crystal structures of some coordination compounds of beryllium and indium

Twiss, J.

Twiss, J. (1969) *The crystal structures of some coordination compounds of beryllium and indium*, Durham theses, Durham University. Available at Durham E-Theses Online: http://etheses.dur.ac.uk/9685/

THE CRYSTAL STRUCTURES OF SOME COORDINATION COMPOUNDS OF BERYLLIUM AND INDIUM

by

J. TWISS, B.Sc.

Graduate Society, Durham

A Thesis Submitted for the Degree of

Doctor of Philosophy

September, 1969

PREFACE

This thesis describes research in chemical crystallography carried out in the Chemistry Department of the University of Durham between October 1966 and September 1969.

I extend my sincere thanks to Dr. H.M.M. Shearer, under whose direction the research was undertaken, for his example and invaluable guidance. I would also like to thank Mr. T. Caygill, Dr. P.T. Moseley and Dr. B.K. Wyatt for the provision of crystals.

In conclusion I gratefully acknowledge the award of a Science Research Council Studentship.

This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

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SUMMARY

X-ray diffraction techniques have been employed in the solution of the crystal structures of two alkoxides of beryllium and of an oxime complex of indium. The structures were determined by the heavy atom method, and refined by the method of least squares using three dimensional data.

The dimeric diethyl ether complex of t-butoxy beryllium bromide crystallises from ether in a monoclinic cell, with dimensions a = 9·035, b = 13·18, c = 9·805Å, β = 96° 22', and space group $P2_1/n$.

There are four units of ($Bu^tOBeBr.OEt_2$) in the unit cell,and the molecule is a dimer composed of two such units linked via a four membered Be_2O_2 ring. The beryllium-oxygen bond lengths in the ring are the same as that between the beryllium and the ether oxygen, and their mean of 1·63Å is in good agreement with quoted values.

The t-butoxy oxygen atoms and the ether oxygen atoms both have trigonal configurations and the structure is very similar to that of the magnesium analogue.

$Cl_2Be_3(OBu^t)_4$ is orthorhombic with a = 13·91, b = 12·19, c = 13·71Å, space group Cmcm. The unit cell contains four units of $Cl_2Be_3(OBu^t)_4$, arranged with two chlorine and three beryllium atoms on each of the intersections of the mirror planes at x = 0 and $\frac{1}{2}$, and z = $\frac{1}{4}$ and $\frac{3}{4}$. The bridging t-butoxy groups lie on the mirror planes.

The molecule has mm symmetry as dictated by the space group requirements, and the point group symmetry $\bar{4}2m$ holds for the chlorine, oxygen and beryllium atoms but not for the carbon atoms.

A shortening is observed in the lengths of the bonds involving the two terminal beryllium atoms, which seems to be indicative of dative π-bonding involving these atoms.

Dimethylindium pyridine-2-carbaldehyde oximate is recrystallised from benzene in the orthorhombic space group Pbcn, with cell dimensions a = 33·15, b = 9·54, c = 14·30Å. The unit cell contains eight dimeric units of $[C_5H_4NCH:NOInMe_2]_2$ together with four molecules of solvent C_6H_6.

The molecule is composed of five heterocyclic rings, the central one being InONInON. The indium atoms are five-coordinate and adopted a distorted trigonal bipyramidal arrangement. Corresponding bond lengths in the two halves of the dimer are in good agreement. The mean In-N distance in the central ring of 2·28Å contrasts with the mean In-N distance involving the pyridine nitrogens of 2·51Å.

Chapter One

Crystallographic Introduction

1.1. The Crystal Lattice

When ions or molecules crystallise to form a solid they arrange themselves regularly in three-dimensions, because a regular array has a lower potential energy than a random one. If an arbitrary point is chosen as origin then it is possible to find many further points in space with an identical environment. These points define a lattice which can be described in terms of three non-coplanar vectors $\underline{a}$, $\underline{b}$ and $\underline{c}$. The parallelepiped defined by $\underline{a}$, $\underline{b}$ and $\underline{c}$ is termed the 'unit cell' and the extended space lattice is constructed by translational operations on the unit cell. The contents of the unit cell are related by an array of symmetry elements called a 'space group', and there are in all 230 three-dimensional space groups. The unit cell is said to be primitive if it contains no interior lattice points.

A series of parallel planes passing through the lattice points and dividing $\underline{a}$ into h parts, $\underline{b}$ into k parts and $\underline{c}$ into l parts, is referred to as the (hkl) family of planes. These indices (hkl) are known as the Miller indices and are the reciprocals of the axial intercepts. For a plane to have a high density of lattice points, the Miller indices must be small. It is such planes which tend to form the faces of crystals and this is expressed in the Law of Rational Indices, which states that the ratio of the indices of a crystal face are rational and in general, small whole numbers.

1.2. The Reciprocal Lattice and the Diffraction of X-rays

The wave-like property of X-rays and their diffraction by a crystal lattice was first demonstrated by Friedrich and Knipping on a suggestion by von Laue. However it was W.L. Bragg who recognised and expressed the fact that the radiation diffracted by the crystal lattice, could be thought of as being reflected by the lattice planes. Bragg's Law, $n\lambda = 2d\sin\theta$, states that 'reflections' occur only at specific angles of incidence of the X-ray beam, which are functions of the interplanar spacings of the crystal.

As has been indicated, the orientation of a plane is specified by the Miller indices. It can also be specified by a vector perpendicular to the plane, where the orientation of the vector is described by the same three numbers as that of the plane. This concept is the basis for the reciprocal lattice.

The reciprocal lattice is constructed from the lattice in real space by drawing vectors from the origin perpendicular to the lattice planes and marking off along these lines, points at distances from the origin inversely proportional to the spacings of the lattice planes. The reciprocal lattice so formed consists of an array of points, each representing a plane in the crystal lattice. The unit cell of this lattice is defined by the vectors $\underline{a}^*$, $\underline{b}^*$ and $\underline{c}^*$. The construction is such that $\underline{a}^*$ is normal to the $\underline{b}\ \underline{c}$ plane and is inversely proportional to the spacing of the (100) planes. Mathematically

$$\underline{a}.\underline{a}^* = \underline{b}.\underline{b}^* = \underline{c}.\underline{c}^* = 1$$

$$\underline{a}^*.\underline{b} = \underline{a}^*.\underline{c} = \underline{b}^*.\underline{a} = \underline{b}^*.\underline{c} = \underline{c}^*.\underline{a} = \underline{c}^*.\underline{b} = 0$$

Each point in the lattice corresponds to a 'reflection' from the plane with Miller indices (hkl) and is at a distance $\frac{1}{d(hkl)}$ along a vector $\underline{R}$ in the direction normal to the planes (hkl) where

$$\underline{R} = h\ \underline{a}^* + k\ \underline{b}^* + l\ \underline{c}^*$$

1.3. The Structure Factor

In the simplest case the atoms of a crystal are all located with their mean positions at lattice points. However most crystals are more complicated than this and can only be represented by placing within each unit cell of the lattice a certain arrangement of atoms. Any one set of corresponding atoms in the different unit cells may still be regarded as lying upon a lattice, and a crystal with N atoms per unit cell can be regarded as based upon N identical interpenetrating lattices. X-rays scattered by the different lattices will differ in phase according to their separations. If there is a large number of atoms in the unit cell complicated relationships may be expected between the intensities of the various orders of diffraction.

Suppose the unit cell of the crystal contains N atoms situated at points x_n y_n z_n, where x_n y_n and z_n are expressed as fractions of the unit cell edges. The position of the nth atom, P, in the unit cell may be represented by the vector $\underline{r}_n$, where

$$\underline{r}_n = x_n\underline{a} + y_n\underline{b} + z_n\underline{c}$$

The path difference between the waves scattered by the atom at P and those that would be scattered by an atom at the origin is proportional to $\underline{r}_n$. The atom at P can be assumed to lie on a plane parallel to (hkl) and its perpendicular distance from the origin will be given by the projection of $\underline{r}_n$ on the vector $\underline{R}$ describing the normal to the plane (hkl).

Hence if ϕ_n is the phase of the wave scattered by the element of volume round P then

$$\begin{aligned} \frac{\phi_n}{2\pi} &= \underline{R}.\underline{r}_n \\ &= (h\underline{a}^* + k\underline{b}^* + l\underline{c}^*).(x_n\underline{a} + y_n\underline{b} + z_n\underline{c}) \\ &= hx_n + ky_n + lz_n \end{aligned}$$

and $$\phi_n = 2\pi(hx_n + ky_n + lz_n)$$

The expression for the complete wave scattered by the nth lattice is

$$f_n \exp 2\pi i(hx_n + ky_n + lz_n)$$

where f_n, the scattering factor for the nth atom represents the characteristic scattering power of that atom. Its value may be found from a knowledge of the distribution of the electrons about the atom. Since in atoms electrons occupy a finite volume, phase differences occur between waves scattered by different parts of the atom, hence the scattering factor decreases with increasing values of θ. The expression for the complete wave scattered by the crystal is given by

$$F(hkl) = \sum_{n=1}^{N} f_n . \exp 2\pi i(hx_n + ky_n + lz_n)$$

the summation being over all atoms in the unit cell.

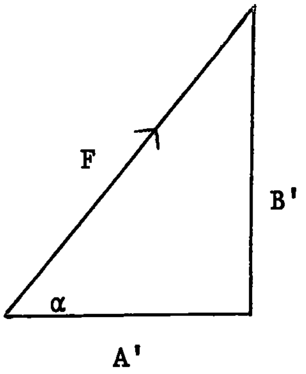
The quantity F is a function of h, k and l and is called the structure factor. Its modulus is called the structure amplitude and is defined as the ratio of the amplitude of the radiation scattered in the order h,k,l by the contents of one unit cell to that scattered by a single electron under the same conditions (Lonsdale, 1936).

The complex form of F indicates that the phase of the scattered wave is not simply related to that of the incident wave. The phase is however not an experimentally observed quantity only the intensity, proportional to $|F|^2$, can be observed. Since F is complex it can be expressed in terms of its real and imaginary components

$$F(hkl) = A'(hkl) + iB'(hkl)$$

where $$A'(hkl) = \sum_{n=1}^{N} f_n \cos 2\pi(hx_n + ky_n + lz_n)$$

and $$B'(hkl) = \sum_{n=1}^{N} f_n \sin 2\pi(hx_n + ky_n + lz_n)$$



The structure amplitude is given by $|F|^2 = (A'^2 + B'^2)$ and the phase constant $\alpha(hkl) = \tan^{-1}(B'/A')$.

When the space group has a higher symmetry than P1 the summation over all n atoms is usually split into a summation over symmetry related atoms followed by a summation over the members of the asymmetric unit N_A.

$$A' = \sum_{n=1}^{N_A} \sum_{r=1}^{S} f_n \cos 2\pi(hx_r + ky_r + lz_r)$$

$$B' = \sum_{n=1}^{N_A} \sum_{r=1}^{S} f_n \sin 2\pi(hx_r + ky_r + lz_r)$$

where S represents the number of equivalent positions. For computational purposes the following definitions are made

$$A = \sum_{r=1}^{S} \cos 2\pi(hx_r + ky_r + lz_r)$$

$$B = \sum_{r=1}^{S} \sin 2\pi(hx_r + ky_r + lz_r)$$

and simplified forms of A and B are obtained by 'summing' over all the equivalent positions in a particular space group (see Appendix I). For a space group with a centre of symmetry, the origin for coordinates is taken at the centre of symmetry and B, and therefore B' is zero, since for every set of coordinates x,y,z there is a set $\bar{x},\bar{y},\bar{z}$ and $\sin(\mathcal{f}(x,y,z)) = -\sin(\mathcal{f}(\bar{x},\bar{y},\bar{z}))$.

The reduction of a structure to a set of point atoms is essentially artificial and a more fundamental interpretation of the structure factor is possible by considering each volume element of the unit cell separately. If $\rho(x,y,z)$ is the electron density at the point (x,y,z) the amount of scattering matter in the volume element Vdxdydz is ρVdxdydz and the structure factor equation may be written

$$F(hkl) = \int_{x=o}^{1}\int_{y=o}^{1}\int_{z=o}^{1} V\rho(x,y,z)\exp 2\pi i(hx + ky + lz)dxdydz$$

1.4. The Temperature Factor

At all temperatures, atoms have a finite amplitude of oscillation. The frequency of this oscillation ($\sim 10^{13}$ per sec) is so much smaller than that of X-rays ($\sim 10^{18}$ per sec) that to a train of X-rays the atoms would appear stationary but displaced from their true mean positions in the lattice. In producing a given X-ray reflection atoms in neighbouring cells instead of scattering in phase will scatter slightly out of phase. The net effect will be an apparent reduction of the scattering of the atom by an amount which increases with angle. The thermal motions of the atoms must be taken into account and the scattering factor f_T for an atom undergoing thermal vibration is equated to f_o for the atom at rest multiplied by the transform q of the 'smearing' function t.

$$f_T(hkl) = f_o(hkl).q(hkl)$$

For the simple case in which the vibration is the same in all directions, isotropic vibration, the expression reduces to

$$f_T = f_o\exp[-B(\sin^2\theta/\lambda^2)]$$

where θ is the Bragg angle, and B, the Debye factor is given by $B = 8\pi^2\bar{u}^2$,

$\overline{u}^2$ being the mean square displacement of the atoms.

In general the thermal motions will be anisotropic and may be described in terms of an ellipsoidal distribution. In order to define an ellipsoid six quantities are required, and the quantities employed for this purpose are designated Uij, i = 1,3, j = 1,3. The transform of the smearing function for this case becomes

$$q(hkl) = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{31}lhc^*a^* + 2U_{12}hka^*b^*)]$$

and $f_T(hkl) = f_o(hkl).q(hkl)$

1.5. Fourier Series

Since a crystal is periodic in three dimensions it can be represented by a three-dimensional Fourier series:

$$\rho(x,y,z) = \sum_{h'}\sum_{k'}\sum_{l'=-\infty}^{\infty} C(h'k'l')\exp 2\pi i(h'x + k'y + l'z)$$

the Fourier coefficient C being allotted the three integral indices h'k'l'.

Inserting this expression for the electron density into the structure factor equation gives

$$F(hkl) = \int_0^1\int_0^1\int_0^1 \sum\sum\sum_{-\infty}^{\infty} C(h'k'l')\exp 2\pi i(h'x + k'y + l'z)\exp 2\pi i(hx + ky + lz).\, V dx dy dz$$

The exponential functions are both periodic and the integral of their product over a single complete period is in general zero. However if $h = -h'$, $k = -k'$, $l = -l'$ this periodicity disappears and the expression takes a non zero value, then

$$F(hkl) = \int_0^1\int_0^1\int_0^1 C(h'k'l') V dx dy dz$$

and therefore $F(hkl) = C(\bar{h}\,\bar{k}\,\bar{l})V$ i.e. the Fourier coefficients are directly related to the corresponding structure factors.

The three-dimensional Fourier series can now be written

$$\rho(x,y,z,) = \frac{1}{V}\sum_h\sum_k\sum_{l=-\infty}^{\infty} F(hkl)\exp[-2\pi i(hx + ky + lz)]$$

This expression is not suitable for quantitative evaluation since it contains complex quantities, but remembering that $F = A' + iB'$ and putting $\theta = 2\pi(hx + ky + lz)$ the expression can be reduced to

$$\rho(x,y,z) = \frac{1}{V}\sum_h\sum_k\sum_{l=-\infty}^{\infty} A'(hkl)\cos\theta + B'(hkl)\sin\theta$$

In view of the fact that $A'(hkl) = A'(\bar{h}\bar{k}\bar{l})$, $B'(hkl) = -B'(\bar{h}\bar{k}\bar{l})$ and taking into account that the term F(000) is its own conjugate further simplification, involving summing in h from only 0 to ∞, is possible

$$\rho(x,y,z) \;=\; \frac{1}{V}\left(F(000) + 2\sum_{h=o}^{\infty}\sum_{k}^{\infty}\sum_{l=-\infty}^{\infty} A'(hkl)\cos\theta + B'(hkl)\sin\theta\right)$$

or

$$\rho\,(x,y,z) \;=\; \frac{1}{V}\left(F(000) + 2\sum{}'\sum\sum|F(hkl)|\cos(\theta-\alpha(hkl))\right)\,.$$

where $\alpha(hkl)$ is the phase angle for the reflection hkl.

This is a general expression describing the electron density in all crystals. Further simplifications are possible by making use of space group symmetry in combining symmetry related reflections. The expression for electron density in terms of the independent structure factors only is given for each space group in International Tables Volume I.

It can be seen from the expression that in order to evaluate $\rho(x,y,z)$ both the structure amplitudes and the phase angles must be known. While the former can be obtained from experimentally observed quantities the latter, as was noted previously cannot. It is the recovery of the relative phases of the diffracted beams which constitutes the major problem in any X-ray structural analysis. Of the several methods currently available the one to be discussed now was used in the work described in this thesis.

1.6. The Patterson Function

In an attempt to overcome the difficulty outlined in the previous section Patterson used the squares of the structure amplitudes as Fourier coefficients. These quantities can be directly obtained from the observed intensities. Patterson defines the function P(u,v,w) such that

$$P(u,v,w) = V\int_0^1\int_0^1\int_0^1 \rho(x,y,z)\,\rho(x+u,\ y+v,\ z+w)\,dx\,dy\,dz$$

The integral involves the product of the electron densities at the points (x,y,z) and (x + u, y + v, z + w). The physical significance of this is that if the electron densities at the two points are high, i.e. there are atoms at both sites, the Patterson function will contain a peak at P(u,v,w), if the electron density is low at one or both places the product of the electron densities will be small. The magnitude of a peak will depend upon the electron densities of the atoms which produce it, and its position will be related to a vector drawn between the atoms involved. An atom of large atomic number in a structure will give rise to relatively high Patterson peaks which will tend to stand out from the body of the function. A large peak occurs at the origin of the function due to the vectors between all atoms and themselves.

To obtain the form of the Patterson function commonly used the expression for the electron density are substituted leading to

$$P(u,v,w) \quad = \quad \frac{1}{V}\sum_{h}\sum_{k}\sum_{l=-\infty}^{\infty}|F(hkl)|^{2}\ \exp 2\pi i(hu + kv + lw)$$

and since $|F(\bar{h}\,\bar{k}\,\bar{l})| = |F(hkl)|$ this expression can be further reduced to

$$P(u,v,w) \quad = \quad \frac{1}{V}\sum\sum\sum_{-\infty}^{\infty}|F(hkl)|^{2}\ \cos 2\pi(hu + kv + lw)$$

1.7. The Heavy Atom Method

If the molecular structure under investigation contains one or more heavy atoms their positions can be obtained by careful examination of the Patterson function, since vectors involving these atoms will stand out from vectors involving the lighter atoms. Structure factors may then be calculated based on the heavy atom positions and used to evaluate an F_o synthesis or F_o-F_c synthesis which should reveal at least some of the lighter atom positions. This process can in theory be repeated incorporating increasing numbers of located atoms until all are found. In practice however it may not be possible to detect hydrogen atoms.

In a crystal with one heavy atom per unit cell, the structure factor involves a summation over all the atoms in the unit cell which may be subdivided into the contribution from the heavy atom (H) and those from the remaining atoms (N) thus:

$$F(h,k,l) = f_H \exp. 2\pi i(hx_H + ky_H + lz_H) + \sum_{n=1}^{N} f_n \exp 2\pi i(hx_n + ky_n + lz_n)$$

If f_H, the scattering factor of the heavy atom, is much greater than f_n, then the first term will tend to outweigh the second, since the summation being due to several atoms will usually be relatively small. It is unnecessary that f_H should be greater than $\sum_{n=1}^{N} f_n$. If it is very much greater there is a danger that the F_o synthesis will only show the heavy atom and fail to reveal the lighter ones. Sim (1961) gives a graph showing the proportion of correct signs to be expected in terms of a function r, where

$$r = \frac{\sum f^2_H}{\sum f^2_L}$$

f_H and f_L are the scattering factors for the heavy and light atoms, which for his purpose Sim takes proportional to the atomic numbers.

As a rough guide for the successful application of the method the sum of the squares of the atomic numbers of the heavy and light atoms should be equal, since on average the contribution of any atom to the diffracted intensity depends on the square of its scattering factor.

A major difficulty can arise if the space group is non-centrosymmetric or if the heavy atom is located on or near a symmetry element, the symmetry of a higher space group may then be simulated. Phases deduced from the heavy atom position alone give false information about the structure in such cases.

1.8. The Theory of Least Squares, and Structure Refinement

The common application of least squares theory is in finding the values for a set of unknown parameters (x,y, -----t) such that a set of given equations

$$a_1x + b_1y + \text{------} + f_1t = n_1$$

$$a_sx + b_sy + \text{-----} + f_st = n_s$$

the equations of condition, may be satisfied as nearly as possible, when the number of equations (s) is greater than the number of unknowns and the equations are not strictly compatible.

The equations are rearranged to be of the form:

$$E_i = a_ix + b_iy + \text{-----}\ f_it - n_i$$

Legendre's theory of least squares then states that of all possible sets (x,y, ----- t) the most satisfactory is that which renders the sum of the squares of the errors a minimum i.e. $\sum_{i=1}^{S} E_i^2$ a minimum.

After an initial structure has been obtained it is desirable to adjust the atomic parameters to give the best agreement between the observed structure amplitudes and the calculated structure factors. To do this the method of least squares is employed by minimising the squares of the differences between the observed and calculated quantities. The function most commonly used is

$$R = \sum_{hkl} w(|F_o| - |F_c|)^2$$

where the sum is over the crystallographically independent planes and w(hkl) is a weight for each term, reflecting the accuracy of the observation.

For R to be a minimum

$$\frac{\partial R}{\partial p_j} = 0 \quad (j = 1, -----, n)$$

where p_j is the j^{th} parameter, or

$$\sum_{hkl} w\,\Delta \frac{\partial |F_c|}{\partial p_j} = 0, \text{ where } \Delta = |F_o| - |F_c|$$

The parameters have to be varied until these n conditions are satisfied.

If the parameters evaluated are p_1 -----, p_n then

$$|F_c| = f(p_1, ----- p_n)$$

and for the observed quantity

$$|F_o| = f(p_1 + \epsilon_1, \text{-----}, p_n + \epsilon_n)$$

where the shifts ϵ_1, ϵ_2 ----- ϵ_n are required to give the true structural parameters. It is these shifts which are evaluated in the least squares treatment.

Taylors theorem gives

$$f(b) = f(a) + (b-a)f'(a) + \frac{(b-a)^2}{2!} f''(a) + \text{-----}$$

setting $b = p_1 + \epsilon_1$, -----; $a = p_1$, -----;

and taking the series to the first derivative gives

$$|F_o| = f(p_1,\text{---},p_n) + \sum_{i=1}^{n} \frac{\partial|F_c|}{\partial p_i} \epsilon_i$$

$$\text{i.e.} \quad |F_o| - |F_c| = \sum_{i=1}^{n} \frac{\partial|F_c|}{\partial p_i} \epsilon_i$$

Now

$$\sum_{hkl} w\Delta \frac{\partial|F_c|}{\partial p_j} = 0; \; j = 1, \text{----}, n$$

becomes

$$\sum_{i=1}^{n} \left\{ \sum_{hkl} w \frac{\partial|F_c|}{\partial p_i} \frac{\partial|F_c|}{\partial p_j} \right\} \epsilon_i = \sum_{hkl} w\Delta \frac{\partial|F_c|}{\partial p_j}$$

these are the so called normal equations of which there are n, j = 1, ----, n to determine the n unknowns. They may written out

$$\sum w\left(\frac{\partial|F_c|}{\partial p_1}\right)^2 \epsilon_1 + \sum w\left(\frac{\partial|F_c|}{\partial p_1}\right)\left(\frac{\partial|F_c|}{\partial p_2}\right) \epsilon_2 + \text{-----} = \sum w\Delta \frac{\partial|F_c|}{\partial p_1}$$

$$\sum w\left(\frac{\partial|F_c|}{\partial p_1}\right)\left(\frac{\partial|F_c|}{\partial p_2}\right) \epsilon_1 + \sum w\left(\frac{\partial|F_c|}{\partial p_2}\right)^2 \epsilon_2 + \text{-----} = \sum w\Delta \frac{\partial|F_c|}{\partial p_2}$$

etc. to j = n

Alternatively they may be expressed in matrix form as

$$\sum_i a_{ij}\cdot\epsilon_i = b_j$$

where

$$a_{ij} = \sum_{hkl} w \frac{\partial|F_c|}{\partial p_i} \frac{\partial|F_c|}{\partial p_j}$$

$$b_j = \sum_{hkl} w\Delta \frac{\partial|F_c|}{\partial p_j}$$

It is the normal equations which must be set up and solved in order to refine a structure.

In a structure with a large number of atomic parameters it is frequently impracticable to calculate all the terms of the normal equation matrix a_{ij}. The simplest approximation is to neglect all off-diagonal elements, $i \neq j$, but although workeable this requires many cycles of refinement for convergence. More useful is the "block diagonal" approximation which uses a chain of 9 x 9 matrices for the coordinates and anisotropic parameters of each atom with 2 x 2 matrix for the scale and overall isotropic vibration. If the vibrations are isotropic the coordinate matrices will be 4 x 4.

The block diagonal approximation was used for all structure refinement described in this thesis.

1.9. Accuracy of Parameters derived from Least-squares Refinement

The best choice of weights yielding parameters of the lowest variance is $w = 1/\sigma^2(F_o)$. In general with the full a_{ij} matrix for the normal equations, the variance of parameter i is

$$\sigma^2(p_i) = (a^{-1})_{ii}$$

where $(a^{-1})_{ii}$ is an element of the matrix inverse to a_{ij}.

If the relative weights only are known, so that $w = k/\sigma^2(F_o)$, the above formula becomes

$$\sigma^2(p_i) = (a^{-1})_{ii} \left(\sum w\Delta^2\right) \Big/ (m-n)$$

where m is the number of observations and n is the parameters i.e. (m-n) is the number of degrees of freedom.

In the block diagonal approximation variances may be estimated using the inverses of the block matrices. Such estimates tend to underestimate the true variances, because of the neglect of the inter-atomic interactions in the block diagonal approximation. (Hodgson and Rollett, 1963).

1.10. Intensity Data Corrections

(a) Absorption Correction

X-radiation is absorbed by all matter to a certain extent. For a crystal sample, the amount of this absorption occurring during the production of a particular reflection, is a function of the crystal shape and the relation of the incident and diffracted beams to this shape.

Busing and Levy (1957) suggest a method of calculating the correction ideally suited for automatic computation. The function to be evaluated is

$$A = \int \frac{1}{V} \exp[-\mu(r_p + r_d)]\,dv$$

where V is the crystal volume, μ the linear absorption coefficient and r_p and r_d the path lengths within the crystal along the primary and diffracted beams for reflection by the volume element dv.

In order to fix the boundaries of the crystal the n plane faces are defined by n inequalities

$$a_s x + b_s y + c_s z - d_s \geqslant 0, \quad s = 1, 2, ----, n$$

To satisfy these conditions the crystal must have no re-entrant angles.

Expressions for the evaluation of r_p and r_d are given by Wells (1960). The integral is evaluated by Gauss's method, the triple integral being reduced to a summation

$$\int_a^b dx \int_c^d dy \int_e^f g(x,y,z).dz \simeq \sum_1^m \sum_1^n \sum_1^l (b-a)(c-d)(f-e)R_i R_j R_k g(x_i y_i z_i)$$

where the R_i's are the relative weights of the terms in the sum and are tabulated for all values of $m \leqslant 16$.

(b) Polarisation Correction

In the usual experimental arrangements the primary X-ray beam is unpolarised, that is to say the azimuth of the electric vector assumes all directions with time. The effective amplitude of the radiation after it is reflected by the crystal at an angle 2θ consists only of the components of these azimuths after reflection. This feature has the effect of reducing the intensity of the X-ray beam by a factor p, the polarisation factor. The correction to be applied to the observed intensity is

$$p^{-1} = 2/(1 + \cos^2 2\theta)$$

(c) Lorentz Correction

In a perfect crystal neighbouring volume elements will be absolutely parallel, however real crystals may not have all adjacent volume elements perfectly parallel. The result is that in production of a Bragg 'reflection' the crystal will 'reflected' over a finite, albeit small, range of angle about the true angle as given by Bragg's equation. The problem may also be considered as the time taken by a specific reciprocal lattice point to pass through the sphere of reflection. When the planes are not absolutely parallel the reciprocal lattice 'point' will have a finite size whereas if the planes were perfectly parallel the point would be infinitely small.

The form of correction to be used can be developed from the concept of the time taken by a reciprocal lattice point to pass through the sphere of reflection. The form of the Lorentz factor to be applied depends upon the mode of data collection.

Chapter Two

The Coordination Chemistry of Beryllium

2.1. General Survey

Beryllium lies at the head of group II in the periodic table with the electronic configuration $1s^2 2s^2$. The increased nuclear charge over that of lithium makes the ionization potentials of beryllium at 9•32 and 18•21 eV much larger than that of lithium at 5•39 eV. The value of 0•31Å has been estimated for the ionic radius of Be^{2+} leading to a charge/radius ratio of 6•5, greater than for any other cation excepting H^+. The result is that bonds formed by beryllium (even those to the most electropositive elements) have appreciable covalent character, hence the reason for the poorly conducting nature of fused BeF_2. The increase in size for the other elements of the group Mg, Ca, Sr, Ba reduces the effect of nuclear charge on the valence electrons with a corresponding increase in the ionic nature of their compounds.

The unpairing of the $2s^2$ electrons permits beryllium to form two covalent bonds. Where free BeX_2 molecules occur the valence electrons of the beryllium atom occupy two equivalent sp hybrid orbitals and the system X-Be-X is linear. In this situation the beryllium is only two-coordinate and there is a strong tendency for the atom to increase its coordination number up to a maximum of four.

A brief outline of each of the three coordination states possible for beryllium is now given, with reference to the factors influencing the particular coordination number adopted.

Some of the principle considerations are

(a) Valence Angle Deformation

Being of low atomic number, beryllium is less tolerant of deformation of valence angles away from the values expected for the particular hybridisation state adopted, than atoms of higher atomic number. Valence angle deformation is gradually relieved with the formation of larger cyclic oligomers and polymers.

(b) Steric Influence of Bulky Substituents on the Donor Atom

Steric interference between bulky substituents would be expected to increase as the degree of association increases. This factor will be emphasised by the small size of the beryllium atom, bringing the substituents into closer proximity than occurs for the heavier metals.

(c) Entropy

The effect of entropy will always be to favour the less associated species since this affords the greatest number of independent molecules per unit mass.

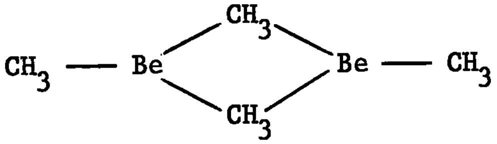
2.2. Two-fold coordination

The small size of the beryllium atom makes for shorter bond lengths and means that attached atoms find themselves in closer proximity than when bonded to larger metal atoms. When large and bulky substituents are attached to beryllium problems of steric interference may become so acute as to prevent the beryllium increasing its coordination beyond two. Such is the case with di-tertiarybutyl beryllium which is unique among the dialkyl beryllium compounds in being monomeric even in the liquid state.

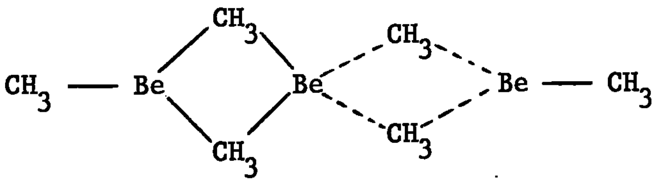
Compounds containing two coordinate beryllium are rare and most usually occur in gaseous form. In these cases entropy factors seem important. The vapour of $BeCl_2$ is known to be monomeric at 745°C, however as the temperature falls some association occurs, experiments indicating that at 564°C there is already about 20% of the dimer. The scarcity of two-coordinate beryllium compounds, indicates the readiness of that metal to increase its coordination number beyond two.

2.3. Three-fold coordination

Three-coordinate beryllium atoms are found in compounds which under more extreme physical conditions are monomeric, and are associating into dimers, trimers and higher oligomers as the first steps towards achieving maximum four-fold coordination. Beryllium chloride vapour has already been mentioned and the vapour of dimethyl beryllium is reported to consist of dimers and trimers. The structures proposed for the oligomers of dimethyl beryllium are:

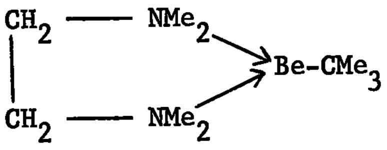


dimer


trimer

the trimer containing four- as well as three-coordinate beryllium.

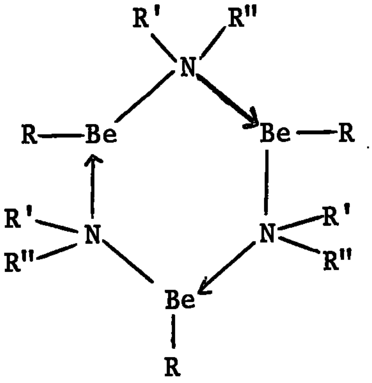
Aside from these transient species this coordination number is also found in more stable compounds, including a number of amide complexes of beryllium and alkyl beryllium (Wakefield, 1968). The compounds exhibit various degrees of association but the majority are dimeric or trimeric in solution in benzene. Two monomeric species are reported, $Me_2Be.NMe_3$ and a chelate complex which is believed to have the structure

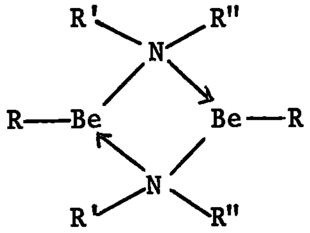


The amide complexes are prepared by the following series of reactions

$$R_2Be \xrightarrow{R'NH_2} [R_2Be \leftarrow NH_2R'] \xrightarrow{-RH} RBeNHR' \xrightarrow[-RH]{R'NH_2} Be(NHR')_2$$

In general, it appears that trimers are formed when the substituents on beryllium and especially nitrogen are small, and that dimers are formed when the substituents are large. Both types of structure involve three-coordinate beryllium, except where chelation makes four-coordination possible.





Bis(dimethylamino)beryllium when first prepared (Coates and Glockling, 1954) was shown to be trimeric by molecular weight studies in benzene and was thought to have a cyclic structure similar to that shown above. More recent n.m.r. work (Fetter and Peters, 1965) has indicated that in benzene the complex is trimeric but not cyclic. An X-ray analysis of the complex (Atwood and Stucky, 1967) has shown the following structure presented in Figure 2.1, containing both three- and four-coordinate beryllium atoms, cf. proposed structure for the trimer of dimethyl beryllium.

The non-formation of an infinite polymer with all beryllium atoms four-coordinate is thought to suggest that the differences between entropy and enthalpy factors for the three- and four-fold environments must be quite small.

The atomic arrangement in $Cl_2Be_3(OBu^t)_4$ is very similar to that shown for $[Be(NMe_2)_2]_3$. The results obtained from the X-ray analyses of these

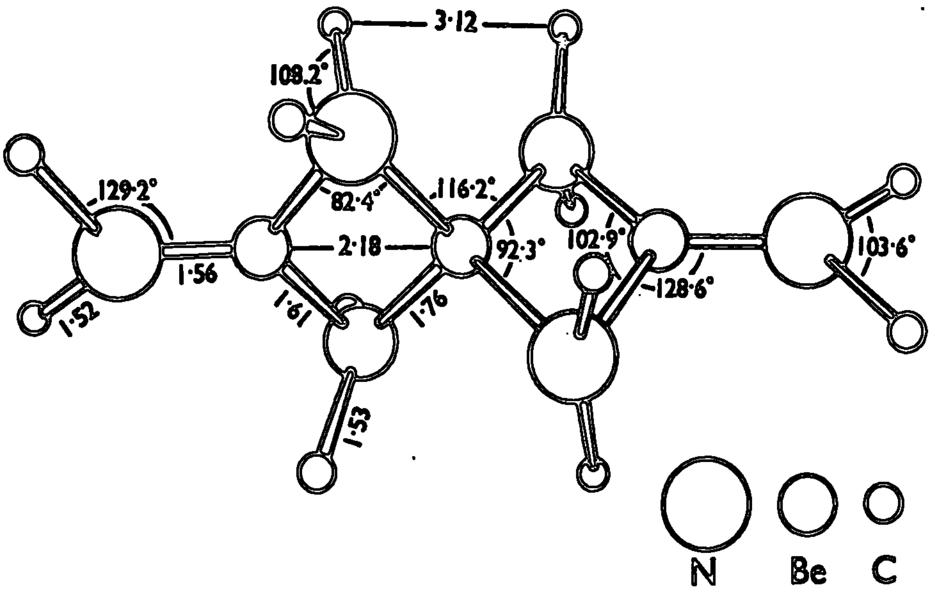


Figure 2.1.

two compounds can be used to provide evidence for dative π-bonding involving the terminal beryllium atoms, see section 4.8. It may be that such π-bonding if it does occur is influential in dictating the conformations adopted and in reducing the tendency of the three-coordinate beryllium atoms to achieve maximum four-fold coordination, via polymerisation.

2.4. Four-fold coordination

Beryllium achieves four-fold coordination in forming a large number of compounds, ranging from species containing a single beryllium atom to polymers, the latter including electron deficient compounds amply demonstrating the strong tendency towards attainment of maximum coordination.

The vapour of beryllium chloride has already been mentioned under both two- and three- coordinate compounds. In the solid the structure is that of a halogen bridged polymer (Lewis and Rundle, 1952) with the beryllium four-coordinate and the chlorine two-coordinate. The angle at chlorine, 81•8°, is less than that at beryllium 98•2°, in keeping with the considerations mentioned earlier.

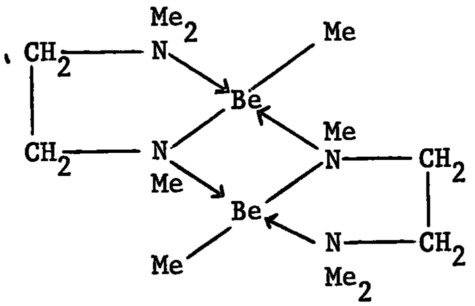
Solid dimethyl beryllium adopts a similar polymeric structure (Rundle and Snow, 1951) the bonding being 'electron deficient'. Both beryllium and carbon make use of four tetrahedral (sp^3) atomic orbitals and it seems probable that three-centre molecular orbitals, $Be(sp^3) + C(sp^3) + Be(sp^3)$, are formed from these. Each of these molecular orbitals would hold two electrons giving a 'bent' bond, and in keeping with this proposed scheme the valence angle at the carbon atom is only 66°. Since it contains electron deficient bonds the polymer would be expected to react with donor molecules, which will serve to break down the polymer and relieve the deficiency. A measure of the stability of the polymer may be gleaned from the fact that while it reacts with oxygen and nitrogen compounds to form complexes such as $(CH_3)_2Be(py)_2$, weaker donors e.g. trimethyl arsine and dimethyl sulphide, are unable to overcome the heat of polymerisation and do not react.

In general oxygen is the strongest donor to beryllium and figures prominently in a number of different four-coordinate beryllium compounds. Ethers react with polymeric species to form complexes of the type $Cl_2Be(OR_2)_2$. Lone pairs of electrons are available on the donor oxygen atoms and this can lead to various degrees of association for differing compounds. When reactions are carried out in solvents which are themselves strong donors the association may be restricted to dimers, thus t-butoxy beryllium bromide formed in ether crystallises as a dimer with two molecules of ether.

Loss of ether from these types of compounds would formally result in a species having three-coordinate beryllium atoms and oxygen atoms with available lone pair of electrons. There will obviously be a strong tendency for further association to take place giving beryllium its preferred four-coordination. Removal of the solvent molecules from $(ClBeOBu^tOEt_2)_2$ results in the trimeric $Cl_2Be_3(OBu^t)_4$ having three- and four-coordinate beryllium, and the tetrameric $(ClBeOBu^t)_4$ which presumably has a cubane-type structure similar to that found for methyl zinc methoxide (Shearer and Spencer, 1966), with all beryllium atoms four-coordinate. The alkyl beryllium alkoxides are reported to be tetrameric in benzene, e.g.

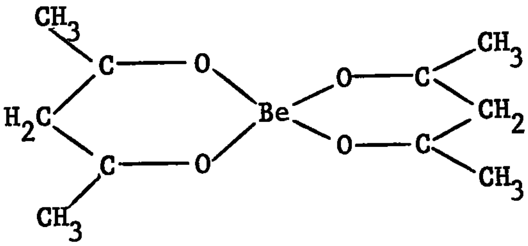
$(MeBeOMe)_4$, and are also thought to have a cubane type structure.

Beryllium also forms several chelate complexes involving both oxygen and nitrogen chelating groups. It was previously mentioned in section 2.3 that the dimeric amide complexes could achieve four-fold coordination of the beryllium atoms, via chelation. The following compound is an example of such a situation,

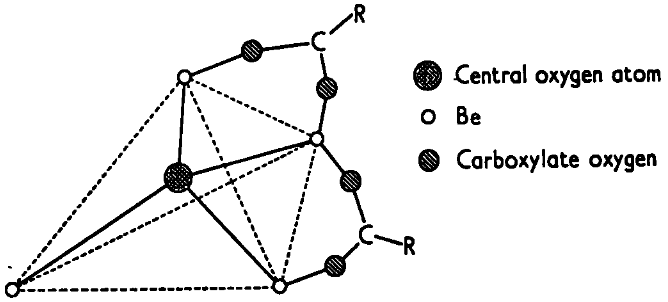


If the ethylenediamine has two or more reactive hydrogens, methane would be eliminated and polymeric products obtained.

The chelate complexes involving oxygen include beryllium acetyl acetonate (Amirthalingham et al., 1960), in which one beryllium atom is surrounded by four oxygen atoms in the following manner,



and beryllium oxyacetate (Tulinsky and Worthington, 1959), in which an oxygen atom sits at the centre of a tetrahedron of beryllium atoms, which are linked by acetate groups.



The structure of the carboxylate complexes $Be_4O(OOCR)_6$. Only two RCOO groups are shown.

Chapter Three

The Crystal Structure of the Diethyl Ether Complex of t-Butoxyberyllium Bromide

3.1. Introduction

The solution of the crystal structure of the t-butoxy-magnesium bromide dietherate complex[x] showed that the ether and t-butoxy oxygens both had trigonal geometries. It was also established that the Mg-O distances in the ring were significantly shorter than the Mg-O distances involving the ether molecules. The latter distances were in agreement with expected Mg-O bond lengths. Some form of dπ-pπ interaction between empty magnesium 3d orbitals and doubly occupied oxygen 2p orbitals, seemed to be indicated.

Replacement of magnesium by beryllium precludes the possibility of dπ-pπ interactions of the type mentioned above.

The compound was prepared by adding an ethereal solution of beryllium chloride with stirring to a similar solution of lithium t-butoxide. Lithium chloride was precipitated and to the solution beryllium bromide was added. The resulting solution was filtered and the ether removed until colourless needle-shaped crystals of the compound appeared. (Bell, 1968). The crystal used in the structural analysis was sealed in a pyrex tube in a dry atmosphere of nitrogen.

3.2. Crystal Data

Zero-level precession photographs taken with Mo-Kα radiation showed the compound to have a monoclinic cell with the following dimensions,

$a = 9{\cdot}035, \quad b = 13{\cdot}18, \quad c = 9{\cdot}805$ Å

$\beta = 96^{\circ}\ 22'$

[x] (Moseley and Shearer, 1968)

$U = 1160{\cdot}5\ \mathring{A}^3$, $Z = 2$ units of $(Bu^tOBeBrOEt_2)_2$

$D_{calc} = 1{\cdot}351$ gm.cm.$^{-3}$, M.W. of $(C_4H_9OBeBrOC_4H_{10})_2 = 472{\cdot}06$

Absorption coefficient for Mo-Kα radiation, $\mu = 37{\cdot}1$ cm^{-1}

The space group was unambiguously determined by the conditions limiting the observed reflections

h 0 l; h + l = 2n

0 k 0; k = 2n

as $P2_1/n$.

The statistical standard deviations in unit cell lengths are of the order 0·005Å for a, b and c, but systematic errors, about 0·2%, increase this to the more realistic overall uncertainty of about 0·02Å. The uncertainty in β is of the order of 7'.

3.3. Data Collection and Correction

The crystal used for data collection was an elongated needle of square cross section of side 0·2 mm. The a axis of the crystal lay along the direction of the needle axis. Three dimensional intensity data were recorded photographically using the precession technique for the nets hkn, n = 0 to 4 and hnl, n = 0 to 5. It was noted that the intensities of the reflections fell off markedly with increasing values of θ. Using the precession method reduces absorptions effects and collection of data up two axes allows good net to net correlation.

The intensities were estimated visually using a calibrated scale prepared on the Weissenberg camera and were corrected for Lorentz and polarisation factors. No attempt was made to correct for absorption but the effects of this were thought to be small.

Correlation of the structure amplitudes from the various nets was performed using a least-squares method (Monahan, Schiffer and Schiffer, 1966) and where two values of the structure factor for a reflection had been obtained the mean value was adopted. A total of 526 independent reflections was obtained.

3.4. The Patterson Function

The corrected value of the intensities were multiplied by a weighting function w, which took the form of the Lorentz and polarisation factor used for the zero-level nets. The use of this weighting function makes some allowance for the fall off of intensities at higher $\sin\theta/\lambda$ values due to the thermal motions of the atoms and decrease in the atomic scattering factors. The Patterson function was then calculated using these weighted intensities as Fourier coefficients.

For the monoclinic space group the general expression for the Patterson function reduces to

$$P(u,v,w) = \frac{4}{V}\sum_{-h}^{h}\sum_{o}^{k}\sum_{o}^{l} w(hkl)\,|F(hkl)|^2(\cos2\pi hu\,\cos2\pi lw - \sin2\pi hu\,\sin2\pi lw)\,\cos2\pi kv$$

The symmetry for this vector set being P_2/m.

The function was then calculated over one quarter of the unit cell:

'u' at intervals of 0·301Å from 0 to a/2
'v' " 0·220Å " 0 to b/2
'w' " 0·245Å " 0 to c

The principle features of the Patterson function are a Harker section at $(u,\frac{1}{2},w)$ containing vectors between atoms related by the twofold screw axis, and a Harker line at $(\frac{1}{2},v,\frac{1}{2})$ containing vectors between atoms related by the glide plane. On both the line $P(\frac{1}{2},v,\frac{1}{2})$ and the section $P(u,\frac{1}{2},w)$ one peak of a height corresponding to a double weight Br-Br vector was found. From the positions of these two peaks the values of x, y and z for the bromine atom were obtained and confirmed by the location of a single weight peak at (2x,2y,2z) corresponding to the vector between bromine atoms related by the centre of symmetry. The coordinates of the bromine atom were:

	x/a	y/b	z/c
Br	0·2333	0·1275	0·0438

No other large peaks were found in the Patterson function.

3.5. Light Atom Positions

Structure factors were calculated based on the position of the bromine atom, the high R value ($R = 0{\cdot}52$ where $R = \Sigma \left||F_o| - |F_c|\right| / \Sigma |F_o|$) reflecting an appreciable error in the scaling. The structure factors were used to calculate an F_o synthesis which revealed the positions of the eleven light atoms. The synthesis was evaluated over one quarter of the unit cell:

'x' at intervals of 0·301Å from 0 to a/2
'y' " 0·220Å " 0 to b/2
'z' " 0·245Å " 0 to c

3.6. Refinement

The atomic parameters were refined by the method of least squares using the block diagonal approximation. For two cycles of refinement isotropic temperature factors were assigned to all the atoms and R was reduced to 0·173. With anisotropic temperature factors for the bromine atom, a further two cycles saw R improve to 0·123. Finally the beryllium and the two oxygen atoms were refined anisotropically and the R value converged to 0·0946. In view of the limited amount of data obtained experimentally, it was decided to restrict the number of atoms being refined anisotropically.

In the final cycle the parameter shifts were all less than one third of the corresponding estimated standard deviation (e.s.d.). Final values for the positional and thermal parameters together with their e.s.d.'s are given in Tables 3a and 3b.

In order to confirm the positioning of the methyl carbons of the t-butyl group a set of structure factors was calculated omitting the contribution of these three atoms. A partial difference map based on these structure factors, revealed the three atoms in the same positions as obtained from the least-squares computations. However the peak heights for the three atoms were very low namely C(2) 1·1; C(3) 1·2; C(4) 1·8 e.Å^{-3}. Furthermore on plotting an estimate of the electron density in the plane of C(2), C(3) and C(4) it was found that the three sites were linked by a ring of electron density never falling below 0·5 e.Å^{-3}. The atoms of the t-butyl group are thus seen to be undergoing a form of rigid body vibration about the direction of the C(1)-O(1) bond.

The structure factors calculated in the final cycle of refinement were used to compute an F_o-F_c syntheses. The main features of this difference map were the ripples of electron density in the vicinity of several of the carbon atoms reaching a maximum of 0·6 e.Å^{-3} around C(2) of the t-butyl group. In only a few other regions did the background on the final difference map reach a height of 0·5 e.Å^{-3}, but no other systematic structural feature was observed. The inferences to be drawn from the two difference maps are that completely free rotation of the t-butyl group about the direction of the C(1)-O(1) bond, and disordering of the methyl carbon atoms of the group, are precluded by the existence of preferred sites for these atoms.

During the final cycles of refinement the structure factors were weighted using the function w, where

$$\sqrt{w} = 1/(p_1 + |F_o| + p_2|F_o|^2 + p_3|F_o|^3)^{\frac{1}{2}}$$

with values of the parameters of

$(\mathrm{Bu^tOBeBr.OEt_2})_2$ TABLE 3a

Final values of atomic coordinates and their standard deviations

Atom	x/a	y/b	z/c	σ(x/a)	σ(y/b)	σ(z/c)
Br	0·26647	0·12794	-0·04317	0·00027	0·00023	0·00034
Be	0·11333	-0·00099	-0·04275	0·00267	0·00247	0·00369
O(1)	0·05836	-0·02358	0·10367	0·00127	0·00110	0·00140
O(2)	0·18520	-0·10081	-0·11308	0·00138	0·00107	0·00160
C(1)	0·13241	-0·05510	0·22830	0·00254	0·00203	0·00268
C(2)	0·28203	-0·07011	0·23524	0·00476	0·00403	0·00499
C(3)	0·16236	0·03095	0·31112	0·00526	0·00394	0·00545
C(4)	0·04842	-0·12831	0·29573	0·00453	0·00397	0·00459
C(5)	0·33075	-0·08792	-0·30557	0·00329	0·00249	0·00341
C(6)	0·33771	-0·11221	-0·15515	0·00302	0·00256	0·00306
C(7)	0·09113	-0·19137	-0·15167	0·00279	0·00213	0·00282
C(8)	0·13562	-0·28005	-0·07264	0·00444	0·00354	0·00427

$(Bu^tOBeBr.OEt_2)_2$ TABLE 3b

Final Values of Isotropic and Anisotropic Temperature Parameters ($\mathring{A}^2$) and their Standard Deviations

($\mathring{A}^2 \times 10^4$ for Br and O, $\mathring{A}^2 \times 10^3$ for Be and C)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br	0·0609(12)	0·0702(15)	0·0930(19)	0·0071(27)	-0·0002(13)	-0·0241(16)
Be	0·024 (12)	0·062 (19)	0·083 (24)	0·022 (25)	0·010 (16)	-0·022 (13)
O(1)	0·0343(65)	0·0475(89)	0·0389(78)	0·0089(91)	-0·0078(62)	0·0017(61)
O(2)	0·0427(75)	0·0452(92)	0·0678(103)	-0·0127(97)	0·0121(81)	0·0097(62)
	U_{iso}					
C(1)	0·063 (7)					
C(2)	0·155 (17)					
C(3)	0·161 (17)					
C(4)	0·139 (14)					
C(5)	0·089 (9)					
C(6)	0·085 (9)					
C(7)	0·069 (7)					
C(8)	0·130 (14)					

$(Bu^tOBeBr.OEt_2)_2$ TABLE 3c

Least squares totals

Number of observed planes 526

$\Sigma|F_o|$ 16609•86 $\Sigma|F_c|$ 16327•04 $\Sigma|\Delta|$ 1572•00 R 0•095

Weighting analysis

$\lvert F_o \rvert$ ranges	N	$\Sigma w\Delta^2/N$	R
0-15	35	0•17	0•13
15-17	35	0•23	0•13
17-19	45	0•26	0•13
19-21	67	0•17	0•10
21-23	47	0•24	0•11
23-25	30	0•23	0•10
25-30	59	0•35	0•11
30-35	64	0•21	0•08
35-40	26	0•31	0•09
40-50	55	0•27	0•09
50-60	26	0•29	0•09
60-150	37	0•24	0•08

$(Bu^tOBeBr.OEt_2)_2$ TABLE 3d

The Observed and Calculated Structure Factors

H	K	L	|FO|	FC
2	0	0	225	-216
4	0	0	64	63
6	0	0	55	-58
8	0	0	24	70
2	1	0	67	61
3	1	0	60	57
5	1	0	55	-56
6	1	0	31	33
7	1	0	23	21
8	1	0	28	-26
9	1	0	23	-21
1	2	0	46	-60
3	2	0	171	162
5	2	0	69	-47
7	2	0	56	62
9	2	0	25	-24
1	3	0	49	50
2	3	0	18	12
3	3	0	44	-47
4	3	0	23	-22
5	3	0	20	17
6	3	0	45	48
7	3	0	24	-21
8	3	0	24	-24
0	4	0	170	-175
1	4	0	75	82
2	4	0	170	180
3	4	0	18	-17
4	4	0	103	-110
6	4	0	32	33
8	4	0	21	-20
1	5	0	57	49
3	5	0	28	-34
4	5	0	34	32
6	5	0	24	-25
7	5	0	28	-33
8	5	0	22	20
9	5	0	21	20
1	6	0	91	103
2	6	0	33	31
3	6	0	59	-76
5	6	0	67	80
6	6	0	34	-37
7	6	0	43	-42
9	6	0	19	17
4	7	0	48	53
5	7	0	23	-19
6	7	0	32	-34
7	7	0	20	13
8	7	0	24	24
0	8	0	85	75
1	8	0	31	-33
2	8	0	76	-74
3	8	0	33	35
4	8	0	55	59
6	8	0	28	-33
8	8	0	15	15
3	9	0	30	24
5	9	0	24	-22
6	9	0	22	15
1	10	0	58	-60
3	10	0	49	55
4	10	0	19	-19
5	10	0	24	-26
7	10	0	21	23
2	11	0	23	20
6	11	0	24	25
0	12	0	42	-38
1	12	0	23	20
2	12	0	29	30
4	12	0	25	-26
6	12	0	14	16
5	13	0	16	12
1	14	0	23	23
3	14	0	21	-20
-9	0	1	24	-25
-7	0	1	44	39
-5	0	1	50	-52
-3	0	1	66	72
3	0	1	38	-36
5	0	1	70	-65
7	0	1	26	-29
-6	1	1	49	-42
-5	1	1	68	67
-4	1	1	82	69
-3	1	1	111	-100
-2	1	1	33	-29
2	1	1	208	-182
3	1	1	127	135
4	1	1	48	63
5	1	1	81	-79
6	1	1	48	-54
7	1	1	51	49
9	1	1	27	-24
-8	2	1	45	48
-6	2	1	84	-67
-4	2	1	112	106
-3	2	1	59	52
-2	2	1	53	-62
-1	2	1	54	-39
2	2	1	51	50
5	2	1	24	-17
6	2	1	25	20
-8	3	1	28	-18
-6	3	1	34	32
-5	3	1	27	20

H	K	L	|FO|	FC
-4	3	1	68	-65
-3	3	1	67	-66
-2	3	1	154	167
-1	3	1	144	156
0	3	1	114	-103
1	3	1	43	-37
2	3	1	122	115
3	3	1	87	78
4	3	1	100	-98
5	3	1	82	-76
6	3	1	37	40
7	3	1	43	48
-7	4	1	33	-34
-6	4	1	33	-29
-5	4	1	31	29
-3	4	1	61	-59
-1	4	1	140	140
1	4	1	31	-32
2	4	1	70	55
7	4	1	37	-38
-7	5	1	27	27
-5	5	1	63	-68
-4	5	1	56	-49
-3	5	1	72	65
-2	5	1	110	97
-1	5	1	106	-105
0	5	1	96	-87
1	5	1	126	121
2	5	1	123	124
3	5	1	67	-71
4	5	1	55	-55
5	5	1	56	59
7	5	1	37	-35
-8	6	1	31	-36
-6	6	1	53	51
-4	6	1	85	-82
-2	6	1	45	27
-1	6	1	47	31
4	6	1	26	25
-6	7	1	27	-25
-5	7	1	31	-27
-4	7	1	52	51
-2	7	1	68	-64
-1	7	1	49	-49
0	7	1	91	94
1	7	1	64	54
2	7	1	70	-69
3	7	1	31	-30
4	7	1	44	43
5	7	1	54	49
6	7	1	53	-54
7	7	1	26	-23
8	7	1	29	-29
-7	8	1	31	31
-5	8	1	34	-29
-3	8	1	50	48
-1	8	1	45	-39
0	8	1	43	31
1	8	1	28	27
3	8	1	32	-29
-7	9	1	31	-31
-5	9	1	27	28
-3	9	1	50	-48
-2	9	1	36	-39
-1	9	1	74	70
0	9	1	56	54
1	9	1	51	-43
2	9	1	35	-40
3	9	1	56	61
4	9	1	26	20
5	9	1	35	-36
-6	10	1	36	-35
-4	10	1	32	27
0	10	1	33	23
1	10	1	28	25
-4	11	1	33	-33
-2	11	1	26	24
0	11	1	29	-27
2	11	1	49	43
3	11	1	35	35
4	11	1	35	-35
-3	12	1	28	-25
-1	13	1	28	-29
1	13	1	30	29
-8	0	2	23	16
-6	0	2	41	-35
-4	0	2	123	113
-2	0	2	175	-152
0	0	2	45	66
2	0	2	74	-76
4	0	2	78	82
6	0	2	78	-90
8	0	2	31	35
-8	1	2	33	32
-7	1	2	33	33
-6	1	2	57	-54
-4	1	2	119	109
-3	1	2	73	86
-2	1	2	102	-88
-1	1	2	129	-118
1	1	2	88	80
2	1	2	35	-22
3	1	2	50	-48
5	1	2	23	-21
-5	2	2	25	26

H	K	L	|FO|	FC
-4	2	2	43	40
-3	2	2	74	-62
-2	2	2	77	71
3	2	2	120	130
4	2	2	40	-34
5	2	2	87	-96
7	2	2	57	59
9	2	2	32	-29
-8	3	2	33	32
-7	3	2	31	-32
-6	3	2	68	-71
-5	3	2	55	61
-4	3	2	71	74
4	3	2	23	-21
5	3	2	31	-35
-6	4	2	42	44
-5	4	2	46	-43
-4	4	2	57	-55
-3	4	2	27	25
-2	4	2	121	118
2	4	2	113	121
4	4	2	92	-111
6	4	2	34	40
8	4	2	35	-37
-8	5	2	31	-32
-6	5	2	32	28
-5	5	2	40	38
-4	5	2	54	-56
-3	5	2	41	-36
-2	5	2	66	59
-1	5	2	67	77
1	5	2	64	-60
2	5	2	56	50
3	5	2	32	28
7	5	2	31	-31
-5	6	2	34	-31
-3	6	2	54	55
-1	6	2	55	-56
0	6	2	37	37
1	6	2	111	113
2	6	2	24	-26
3	6	2	87	-89
5	6	2	67	76
7	6	2	38	-40
-8	7	2	31	-31
-7	7	2	31	34
-6	7	2	38	36
-5	7	2	35	-36
-4	7	2	54	-52
-3	7	2	35	37
-2	7	2	50	49
-1	7	2	37	-37
1	7	2	47	45
3	7	2	34	-28
-7	8	2	33	-27
-4	8	2	32	28
-3	8	2	30	-27
-1	8	2	24	23
0	8	2	81	86
2	8	2	77	-79
4	8	2	35	41
6	8	2	39	-45
-6	9	2	32	-29
-5	9	2	28	-25
-4	9	2	28	24
-3	9	2	30	26
-2	9	2	26	-24
-1	9	2	30	-33
0	9	2	54	49
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-3	10	2	34	-30
-1	10	2	54	49
1	10	2	32	-28
3	10	2	45	45
5	10	2	37	-37
-4	11	2	32	30
-3	11	2	35	-30
-1	11	2	28	17
0	12	2	33	-26
2	12	2	36	36
4	12	2	32	-32
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-5	0	3	49	-51
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-1	0	3	231	-211
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3	0	3	75	-64
-4	1	3	65	52
-2	1	3	61	-74
-1	1	3	66	61
0	1	3	76	58
1	1	3	151	-135
2	1	3	43	-52
3	1	3	82	88
4	1	3	38	34
5	1	3	50	-53
6	1	3	66	-59
7	1	3	32	34
8	1	3	33	31
-8	2	3	36	37
-6	2	3	67	-72
-4	2	3	86	66
-3	2	3	26	18
-2	2	3	65	-70

H	K	L	|FO|	FC
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3	2	3	24	-24
4	2	3	46	45
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-6	3	3	35	36
-4	3	3	33	-32
-2	3	3	50	42
2	3	3	57	54
3	3	3	64	68
4	3	3	84	-86
5	3	3	41	-51
6	3	3	31	25
-5	4	3	66	90
-3	4	3	95	-109
3	4	3	33	26
5	4	3	36	-32
-3	5	3	64	61
3	5	3	57	-47
4	5	3	48	-49
5	5	3	46	43
6	5	3	33	30
7	5	3	37	-41
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-4	6	3	47	-55
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0	6	3	40	-44
2	6	3	26	35
4	6	3	29	-31
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0	7	3	52	59
1	7	3	45	53
2	7	3	53	-57
3	7	3	51	-56
4	7	3	36	35
5	7	3	37	33
6	7	3	40	-38
-5	8	3	42	-48
-3	8	3	51	50
-1	8	3	38	-42
1	8	3	53	56
3	8	3	38	-38
-1	9	3	36	44
3	9	3	35	32
-4	10	3	38	41
-2	10	3	40	-38
0	10	3	41	46
2	11	3	34	29
-6	0	4	21	22
-4	0	4	36	26
-2	0	4	36	-35
2	0	4	101	-85
4	0	4	50	49
6	0	4	68	-63
8	0	4	45	45
-7	1	4	47	52
-6	1	4	41	-44
-5	1	4	48	-49
-4	1	4	67	65
-3	1	4	75	81
-2	1	4	54	-41
-1	1	4	118	-101
0	1	4	64	73
1	1	4	59	56
2	1	4	48	-58
3	1	4	70	-64
4	1	4	48	44
6	1	4	32	-30
-4	2	4	27	-26
-1	2	4	84	79
1	2	4	66	-67
2	2	4	37	-20
3	2	4	78	74
5	2	4	56	-58
-5	3	4	52	52
-4	3	4	54	46
-3	3	4	92	-96
-2	3	4	47	-47
-1	3	4	56	59
0	3	4	52	57
1	3	4	78	-67
2	3	4	31	-35
3	3	4	46	42
4	3	4	41	40
5	3	4	38	-39
6	3	4	34	-29
2	4	4	42	35
4	4	4	58	-62
6	4	4	42	46
-6	5	4	38	41
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-4	5	4	35	-35
4	5	4	34	-33
3	6	4	51	-63
-5	7	4	33	-31
-3	7	4	31	37
-2	7	4	42	47
-1	7	4	42	-48
0	7	4	31	-32
1	7	4	31	40
2	7	4	32	30
3	7	4	37	-38
4	7	4	33	-31
-4	9	4	36	45
-3	9	4	30	33

H	K	L	|FO|	FC
-2	9	4	30	-16
-1	9	4	28	-13
0	9	4	33	42
-7	0	5	48	50
-5	0	5	70	-71
-3	0	5	70	79
-1	0	5	113	-132
1	0	5	35	31
3	0	5	66	-69
5	0	5	40	40
-1	1	5	28	31
0	1	5	43	-32
1	1	5	25	-32
2	1	5	38	-40
3	1	5	23	27
4	1	5	26	24
5	1	5	32	-30
-4	2	5	54	55
-3	2	5	31	-25
-2	2	5	86	-91
0	2	5	125	134
1	2	5	27	-24
2	2	5	84	-82
4	2	5	44	40
6	2	5	35	-35
-2	3	5	27	-21
-1	3	5	22	18
0	3	5	32	-26
1	3	5	27	-29
2	3	5	35	24
4	3	5	29	-18
5	3	5	37	-30
6	3	5	33	25
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-1	4	5	46	52
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3	4	5	51	53
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3	5	5	38	-31
4	5	5	25	-26
-6	0	6	31	24
-4	0	6	42	-41
0	0	6	24	-18
4	0	6	29	28
-5	1	6	41	-42
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-3	1	6	33	29
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-1	1	6	49	-52
0	1	6	70	67
1	1	6	28	20
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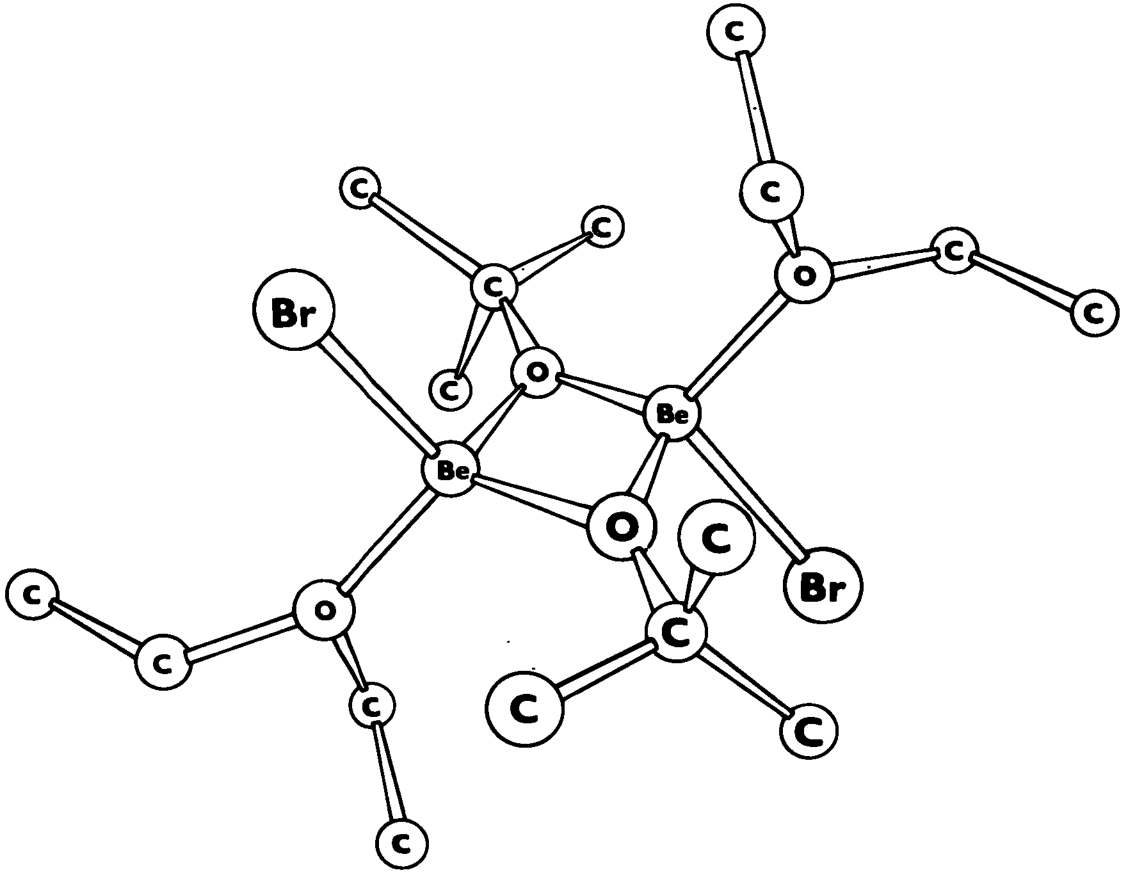
4	1	6	32	37
5	1	6	38	39
-5	3	6	36	37
-3	3	6	59	-60
-2	3	6	37	-41
-1	3	6	26	20
0	3	6	61	65
1	3	6	40	-50
2	3	6	71	-74
3	3	6	42	45
4	3	6	31	24
-2	4	6	30	-34
-5	5	6	27	-23
-4	5	6	28	-27
-3	5	6	42	-44
-2	5	6	47	47
0	5	6	36	-40
2	5	6	25	23
4	5	6	36	-39
-5	0	7	25	-27
-3	0	7	26	27
-1	0	7	57	-59
1	0	7	52	55
3	0	7	25	-17
5	0	7	33	38
7	0	7	23	-23
-6	1	7	28	24
-4	1	7	46	-42
-4	2	7	28	26
-2	2	7	42	-42
0	2	7	49	42
2	2	7	53	-52
4	2	7	39	43
-2	3	7	33	-32
-3	4	7	40	-43
-1	4	7	26	28
1	4	7	32	-37
3	4	7	37	44
-2	5	7	32	-33
-4	0	8	41	-38
-2	0	8	22	17
0	0	8	24	-14
2	0	8	27	22
-2	1	8	26	-23
1	1	8	39	39
-1	2	8	32	-30
1	2	8	26	20
-2	3	8	30	-23
3	3	8	36	30
0	5	8	29	-28
3	5	8	34	29
1	0	9	30	28



$(Bu^tOBeBr{\cdot}OEt_2)_2$

Figure 3.1

$p_1 = 10{\cdot}0$ $\quad p_2 = 0{\cdot}013$ $\quad p_3 = 7 \times 10^{-5}$

The value of p_3 was included to allow for the systematic overestimation of the intensities of the stronger reflections. The parameters p_1, p_2 and p_3 were chosen to bring the values of $w\Delta^2$ as nearly as possible uniform when the data was analysed in terms of the magnitudes of the F_o's. The final values of the least squares totals together with the analysis of the weighting scheme are presented in Table 3c. The observed and calculated structure factors are given in Table 3d.

3.7. Description and Discussion of the Structure

The molecule is a dimer by virtue of a four-membered square beryllium-oxygen ring as shown in Figure 3.1. The consequences of this are that beryllium is four coordinate and adopts a distorted tetrahedral arrangement, and the t-butyl oxygens O(1) and O(1'), (where O(1') is related to O(1) via the centre of symmetry) are three coordinate and adopt a trigonal planar arrangement. The ether oxygen O(2), attached to the beryllium is also three coordinate and the trigonal geometry is again in evidence. From Table 3e giving details of the mean planes it can be seen that the deviations of the atoms from their respective mean planes are all less than one standard deviation. The coplanarity of both sets of atoms is further indicated by the small values of χ^2.

The three Be-O distances which are the same within experimental error are Be-O(1) 1·60 ± 0·04Å, Be-O(1') 1·63 ± 0·03Å and Be-O(2) 1·65 ± 0·03Å,

$(Bu^tOBeBr.OEt_2)_2$ TABLE 3e

Mean planes

Atoms in plane	Orthogonalised Coordinates (Å) X	Y	Z	Distance from plane P	e.s.d.(P)
Be	1•0702	-0•0130	-0•4166	-0•0007	0•0328
O(1)	0•4152	-0•3108	1•0103	-0•0094	0•0144
C(1)	0•9495	-0•7263	2•2248	0•0154	0•0266

$\chi^2 = 0{\cdot}759$

Equation of the plane (passing through these three atoms and the centre of symmetry)is

$$-0{\cdot}1128X - 0{\cdot}9595Y - 0{\cdot}2582Z = 0$$

Atoms in plane	X	Y	Z	Distance from plane P	e.s.d.(P)
Be	1•0702	-0•0130	-0•4166	0•0225	0•0351
O(2)	1•7955	-1•3287	-1•1020	-0•0136	0•0153
C(6)	3•2189	-1•4789	-1•5120	0•0218	0•0304
C(7)	0•9873	-2•5223	-1•4781	0•0157	0•0275

$\chi^2 = 2{\cdot}043$

Equation of the plane is

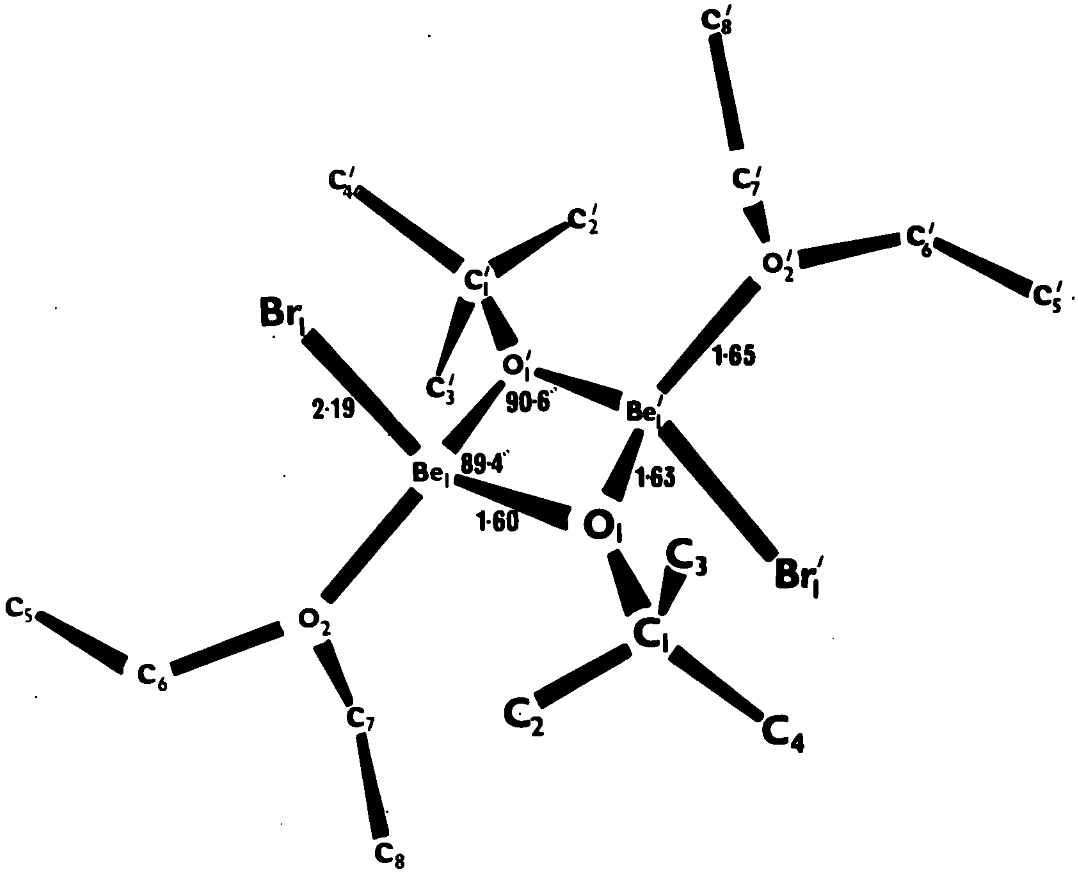
$$-0{\cdot}1932X + 0{\cdot}3900Y - 0{\cdot}9003Z - 0{\cdot}1406 = 0$$

The dihedral angle between the planes = $96^{\circ}\ 52'$

in contrast with the magnesium analogue where the metal-ether oxygen length is longer than the metal-ring oxygen lengths. Final values for all bond lengths and angles together with their e.s.d.'s are given in Tables 3f and 3g, and some lengths and angles are shown on Figure 3.2. The mean Be-O bond length of 1·63Å is in good agreement with values of 1·655 and 1·647Å found in beryllium oxide (Jeffrey et al., 1956) and of 1·666 and 1·624Å in beryllium oxyacetate (Tulinsky and Worthington, 1959). The bromine atom completes the four coordination of the beryllium. The Be-Br length of 2·19Å agrees well with the sum (2·17Å) of the tetrahedral covalent radii (Pauling, 1948).

The ring angles at beryllium and oxygen are 89·4° and 90·6° respectively so that within experimental error the ring is square. For the metal this means a distortion in the other bond angles at beryllium making them all greater than the tetrahedral value of 109·47°. These distortions are however not very large, a maximum angle of 114·9° being reached for Br-Be-O(1').

The distance C(1)-O(1) of 1·39 ± 0·03Å in the t-butoxide group is not significantly shorter than the carbon oxygen distances in the ether molecule which are C(6)-O(2) 1·49 ± 0·03Å and C(7)-O(2) 1·49 ± 0·03Å. This can be demonstrated in the following manner by using the Student distribution function 't'. This is defined as



$(Bu^{t}OBeBr{\cdot}OEt_2)_2$

Some Lengths and Angles

Figure 3.2

$(Bu^tOBeBr.OEt_2)_2$ TABLE 3f

Bond lengths and their standard deviations

	Distance	e.s.d.
Be-Br	2·19 Å	0·03 Å
Be-O(1)	1·60	0·04
Be-O(1')	1·63	0·03
Be-O(2)	1·65	0·03
O(1)-C(1)	1·39	0·03
O(2)-C(6)	1·49	0·03
O(2)-C(7)	1·49	0·03
C(1)-C(2)	1·36	0·05
C(1)-C(3)	1·40	0·06
C(1)-C(4)	1·43	0·05
C(5)-C(6)	1·50	0·04
C(7)-C(8)	1·44	0·05

$(Bu^tOBeBr.OEt_2)_2$ TABLE 3g

Bond angles with their standard deviations

	Angle	e.s.d.
Br-Be-O(1)	113•9°	1•7°
Br-Be-O(2)	109•9	1•6
Br-Be-O(1')	114•9	1•7
O(1)-Be-O(2)	113•7	2•0
O(1)-Be-O(1')	89•4	1•7
O(1')-Be-O(2)	114•0	2•0
Be(1)-O(1)-Be(1')	90•6	1•7
Be(1)-O(1)-C(1)	132•7	1•8
Be(1')-O(1)-C(1)	136•6	1•8
Be(1)-O(2)-C(6)	127•9	1•9
Be(1)-O(2)-C(7)	120•3	1•8
C(6)-O(2)-C(7)	111•6	1•8
O(1)-C(1)-C(2)	117•8	2•8
O(1)-C(1)-C(3)	108•1	2•7
O(1)-C(1)-C(4)	112•3	2•6
C(2)-C(1)-C(3)	87•8	3•3
C(2)-C(1)-C(4)	116•9	3•3
C(3)-C(1)-C(4)	110•8	3•3
O(2)-C(6)-C(5)	108•1	2•3
O(2)-C(7)-C(8)	113•4	2•5

$$t = \frac{\Delta}{(\sigma_1{}^2 + \sigma_2{}^2)^{\frac{1}{2}}}$$

where Δ is the difference between two measurements, and σ_1 and σ_2 are their e.s.d.'s. Comparing C(1)-O(1) and C(6)-O(2) lengths, $\Delta = 0{\cdot}10$, $\sigma_1 = 0{\cdot}03$, $\sigma_2 = 0{\cdot}03$Å giving the value $t = 2{\cdot}38$. Reference to tables shows that $t = 2{\cdot}58$ at the 1% probability level and accordingly the difference between the two lengths is not significicant at the 1% probability level. None of the C-O distances differs significantly from the value of 1·43 ± 0·03Å obtained for dimethyl ether (Kimura and Kubo, 1959).

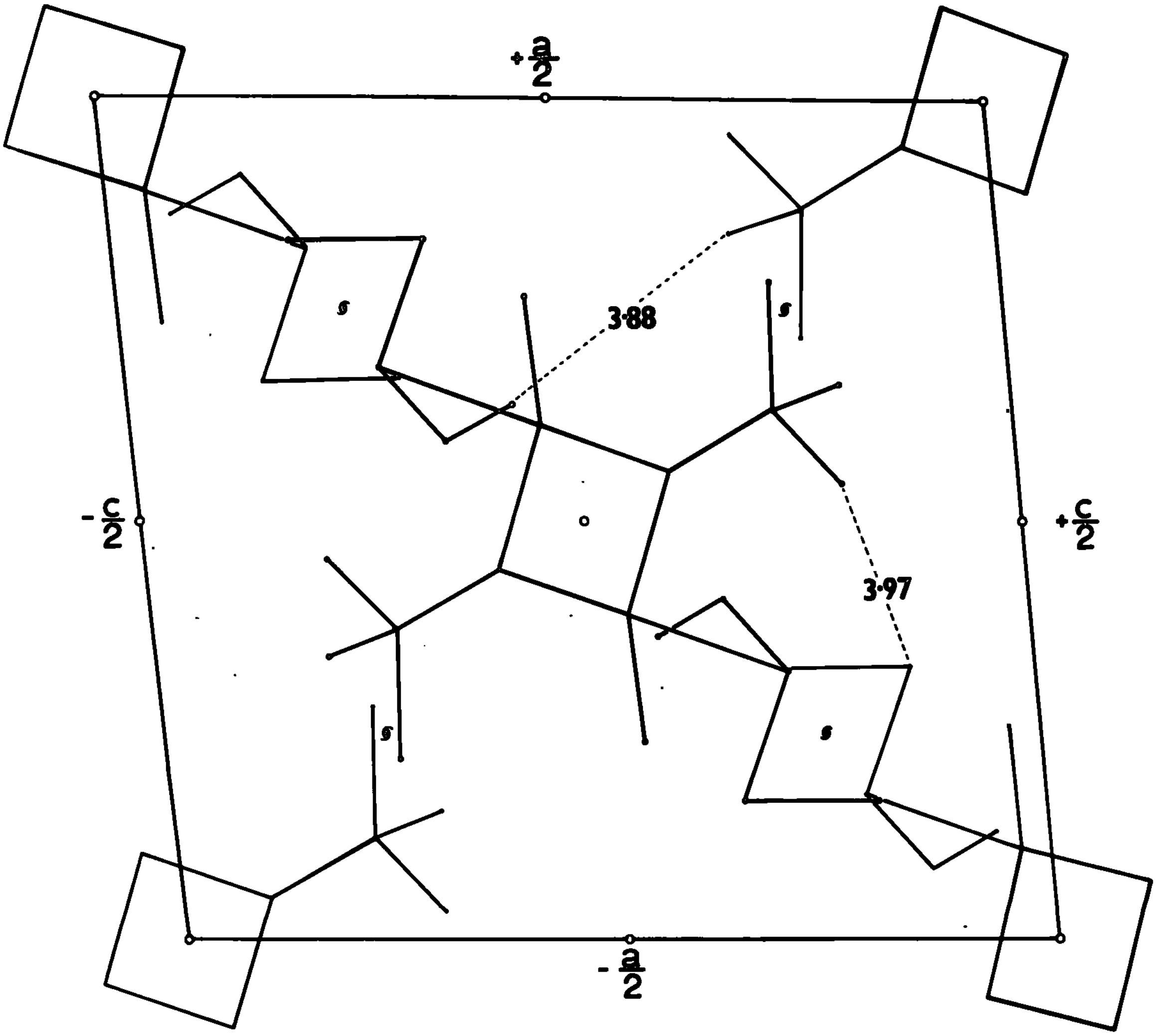
The C-C distances in the t-butyl group do not differ significantly from one another and their mean is 1·40Å. The angles subtended at C(1) show very marked departures from the expected tetrahedral values. The greatest discrepancies occur in the angles involving C(2), namely O(1)-C(1)-C(2) 117·8°, and C(2)-C(1)-C(3) 87·8°. The values of B for the methyl carbons of the t-butyl groups are very large and the difference maps calculated at the completion of refinement showed that these atoms appear to be involved in large atomic librations. The values of bond lengths and angles obtained are a consequence of these effects.

The C-C bond lengths in the ether molecule do not differ significantly from each other nor from the value 1·54Å found in diamond, their mean being 1·47Å. The angles in the ether molecule are not significantly different from each other nor from the tetrahedral value. The value of the angle O(2)-C(6)-C(5) is 108·1 ± 2·3° and that of O(2)-C(7)-C(8) is 113·4 ± 2·5°.

The mean value of B for the methyl carbons of the t-butyl group is 12Å², indicating the large vibrations these atoms undergo. For the ether carbons the mean value of B is 7Å², the atomic vibrations are smaller and the angles and lengths found are much closer to the expected values. In general the values of B show a marked gradation from the more tightly bonded ring atoms to the peripheral atoms, the values are Br 5Å², O mean 3Å², Be 4Å² and C mean 9Å².

Table 3h lists the principle non-bonding intramolecular contacts less than 4Å, (aside from those between atoms of the same ethyl and t-butyl groups). Inspection of the table prompts the thought that the molecular arrangement is such as to equalise non-bonding distances of the same type, for example the three bromine-oxygen distances are all approximately equal. In this connection it should also be mentioned that the buckled arrangement of the ether molecule around the 2_1 screw axis means that the majority of ether C-Br contacts are all much the same about 4·5Å. Figure 3.3, showing the molecular packing in projection on the (010) plane, illustrates this point.

The only intermolecular non-bonding distances less than 4Å are those between C(3) of the t-butyl group and C(8) of the ether at $(\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z)$,



$(Bu^tOBeBr{\cdot}OEt_2)_2$

(010) Projection

Figure 3.3

$(Bu^tOBeBr.OEt_2)_2$ TABLE 3h

Intramolecular non-bonding contacts less than 4Å

Equivalent positions 1 = (x,y,z), 2 = ($\bar{x},\bar{y},\bar{z}$)

Atoms A	Atoms B	Equivalent Position of B	A-B (Å)
Br	O(2)	1	3·16
Br	O(1)	1	3·19
Br	O(1)	2	3·24
Br	C(6)	1	3·43
Br	C(4)	2	3·56
Br	C(2)	1	3·77
Br	C(1)	1	3·88
Br	C(6)	2	3·88
Br	C(3)	1	3·91
Br	C(5)	1	3·92
Br	C(1)	2	3·97
O(1)	O(1)	2	2·27
O(1)	O(2)	1	2·72
O(1)	O(2)	2	2·75
O(1)	C(7)	2	3·19
O(1)	C(7)	1	3·38
O(1)	C(8)	1	3·90
O(1)	C(6)	1	3·95
O(2)	C(2)	1	3·46
O(2)	C(1)	1	3·49
O(2)	Be	2	3·51
O(2)	C(1)	2	3·61
O(2)	C(3)	2	3·62
O(2)	C(4)	2	3·99
Be	Be	2	2·30
C(1)	C(7)	2	3·86
C(2)	C(6)	1	3·95
C(3)	C(7)	2	3·37

the distance between the two being 3·97A. Both distances are indicated on the Figure.

The Be-Be distance across the ring of 2·30 is to be compared with the distance found in the metal of 2·226 (Pearson, 1957). Both this and the possible influence of packing forces on the adopted molecular arrangement are discussed in the following section.

3.8. Comparison of the Magnesium and Beryllium Structures

An important feature emerging from the structural studies is that both molecules adopt the same basic conformation with trigonal geometries for all the oxygens. A pyramidal environment for these atoms would have provided one direction in space free to accommodate a lone pair of electrons.

The crystal structures pf Grignard reagents provide examples of both trigonally ($EtMgBr(OEt_2)_2$; Guggenberger and Rundle, 1964) and tetrahedrally coordinated ($PhMgBr(OEt_2)_2$; Rundle and Stucky, 1964) ether oxygen atoms. In the latter case it was pointed out that the trigonal configuration is more characteristic of expectations for ionic than for covalent bonding.

If the bonding in the beryllium compound were purely covalent, then beryllium with a half share in four bonding pairs of electrons would be designated Be^{2-}, while the oxygens with half shares in three bond pairs and a full share of two non-bonding electrons would be written O^{+}. The electronegatives of the two elements are Be 1·5, O 3·5 and obviously a bonding system leaving oxygen positive while beryllium had excess negative charge would not be tolerated. Unequal sharing of the electrons and a consequent degree of ionic character in the Be-O bonds is therefore to be expected, and must be taken into account in a description of the molecular structure.

The existence in the magnesium compound of the shorter Mg-O distances in the ring as compared to the Mg-O ether length, prompted the thought that a bonding system involving empty magnesium 3d orbitals and the doubly occupied 2p-orbitals of the ring oxygen atoms would also require trigonal oxygens. Two factors mitigate against this as the chief cause of the trigonal geomtery for the oxygens, first, a very approximate molecular orbital calculation performed on the four ring atoms alone indicated a very small 3d-2p interaction, and more significantly the oxygen atoms of the beryllium compound adopt the same configuration and here dπ-pπ interactions are ruled out; in fact all the Be-O distances are equivalent. Any extra bonding in the magnesium compound is envisaged as a secondary consequence of the relevant atoms finding themselves with suitable geometries.

In both the structures, especially in the beryllium one, the molecular arrangement is extremely compact. Hence it seems likely that considerations of steric interference play a significant part in determining the actual conformations adopted. Further support for this theory is the lack of disordering of the coordinately bound ether molecules cf. ($Mg_4Br_6O(OEt_2)_4$; Rundle and Stucky, 1964a) and ($Na_2Be_2Et_4H_2(OEt_2)_2$; Adamson and Shearer, 1965).

The other main differences between the compounds are those arising from the replacement of magnesium by the smaller beryllium. The ring angle at beryllium $89{\cdot}4^{\circ}$, is much greater than that at magnesium $83{\cdot}3^{\circ}$. In consequence the distortions in the other bond angles away from the tetrahedral value are much less pronounced for beryllium. However the t-butoxy oxygens for this compound are placed in a more strained environment, the angle at the oxygens being $90{\cdot}6^{\circ}$, than their counterparts in the magnesium compound where the angle at the ring oxygen is $96{\cdot}7^{\circ}$. The smaller ring in the beryllium compound also means that intra-molecular non-bonding contacts are shorter. This is probably the reason for the more compact arrangement of the beryllium compound.

Finally it may be pertinent to mention the metal-metal distances across the ring. For the beryllium compound this is 2•30Å, the Be-Be distance in the metal being 2•226Å. The Mg-Mg distance of 2•85Å is only slightly greater than the sum of the tetrahedral covalent radii, 2•80Å the Mg-Mg distance in the metal being 3•197A (Pearson , 1957). The approximate molecular orbital calculation mentioned previously, suggested that there may be an interaction across the ring involving magnesium 3d orbitals, which is energetically more important than any involving the oxygen 2p orbitals. The physical significance of this is not easily envisaged, however it seems most probable that any metal-metal interactions would be less important in determining the conformations adopted than the other factors discussed.

Chapter Four

The Crystal Structure of $Cl_2Be_3(OBu^t)_4$

4.1. Introduction

When beryllium chloride is reacted with lithium t-butoxide in ether a precipitate of lithium chloride is formed. If this is filtered off and the excess ether removed, colourless crystals of the dimeric diethyl ether complex of chloro-beryllium t-butoxide are formed. On gently warming this compound ether is lost to give a colourless solid with the empirical formula ($ClBeOBu^t$). Molecular weight measurements in benzene showed the compound to be tetrameric.

To obtain crystals for an X-ray examination the above procedure was repeated, but yielded a white powder which did not redissolve in benzene. The intermediate etherate was then refluxed in benzene with pumping to preferentially remove the ether. Small colourless cube-shaped crystals were obtained. The subsequent crystal structure analysis showed that this substance was not the tetrameric species $(ClBeOBu^t)_4$, but was in fact $Cl_2Be_3(OBu^t)_4$. This compound can be thought of as being composed of two $ClBeOBu^t$ fragments both joined to one $Be(OBu^t)_2$. It differs from the tetramer by the entity $BeCl_2$.

4.2. Crystal Data

Photographs taken on the precession camera with Mo Kα radiation showed the compound to crystallise in an orthorhombic space group. Reflections later obtained on the four circle diffractometer at θ values around 20°, gave the following unit cell dimensions which are in good agreement with those obtained from the zero level precession photographs

$$a = 13{\cdot}91 \qquad b = 12{\cdot}19 \qquad c = 13{\cdot}71\ \text{Å}$$

Estimated error in all unit cell lengths = 0•02Å

$U = 2325{\cdot}8\text{Å}^3$; $Z = 4$ units of $Cl_2Be_3(OBu^t)_4$

$D_{calc} = 1{\cdot}114\ g.cm^{-3}$; M.W. $Cl_2Be_3(OBu^t)_4 = 390{\cdot}48$

Measurements made later with various solvents, employing the flotation principle, showed the density to lie between 1•1 and 1•2 $g.cm^{-3}$

Absorption coefficient for Mo Kα radiation, $\mu = 3{\cdot}04\ cm^{-1}$

The conditions limiting the observed reflections are

hkl: h + k = 2n

Okl: (k = 2n); hOl: 1 = 2n(h = 2n); hkO: (h + k = 2n)

hOO: (h = 2n); OkO: (k = 2n) OOl: (1 = 2n)

The space group is hence either Cmcm No.63 in International Tables or the non centrosymmetric alternative $Cmc2_1$ No.36.

4.3. Data Collection and Correction

The crystals used for data collection were small cubes with well formed faces. The crystallographic axes appeared to pass roughly through opposite corners of the cube. Two sets of three dimensional intensity data were obtained, both with Mo Kα radiation. The first set was recorded photographically on the precession camera in the same manner as previously described for the bromide compound. The second set was collected later on a Hilger and Watts four-circle automatic diffractometer. For the purpose of data collection the instrument employed bisecting geometry, and this is illustrated and discussed briefly in Appendix II. An octant of the sphere of reflection was recorded up to $\theta = 30^{\circ}$.

Both sets of data were corrected for Lorentz and polarisation effects but not absorption since the value of the correction for Mo Kα is so small. The photographic data was scaled in the same manner as previously described for intersecting nets. For the diffractometer data, the intensities of three standard reflections were measured after every fifty normal reflections, and scale factors evaluated from these standard reflections, were used to bring the various batches onto a common scale.

A total of 428 independent observed reflections was obtained photographically compared to a total of 1841 obtained from the diffractometer, of which 720 were classed as observed reflections. This classification was effected by comparing the net count of a reflection with the e.s.d. of that net count. This e.s.d. is defined as

$$\sigma(\text{net}) = \left(\frac{\text{total count} + t \times \text{total background}}{n} \right)^{\frac{1}{2}}$$

where t = the ratio of the time spent measuring the total count to that spent measuring the background count.

and n = the number of independent measurements made of the reflection.

All reflections with a net count less than three e.s.d.'s of that net count were classed as unobserved reflections.

4.4. The Patterson Function

The corrected value of the intensity data obtained photographically, were multiplied by the weighting factor w, which again took the form of the Lorentz and polarisation factor used for the zero-level nets. The Patterson function was then evaluated using these weighted intensities as Fourier coefficients.

For both space groups the expression for the Patterson function reduces to:

$$P(u,v,w) = \frac{8}{V} \sum_{0}^{h} \sum_{0}^{k} \sum_{0}^{l} w(hkl)|F(hkl)|^2 \cos 2\pi hu \cos 2\pi kv \cos 2\pi lw$$

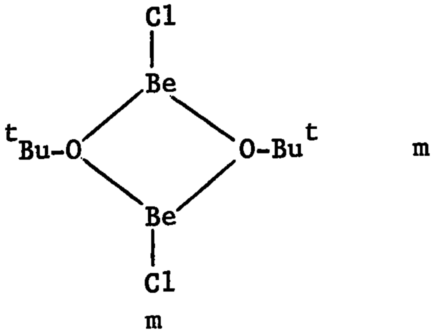
the symmetry of this vector set being Cmmm. The function was evaluated over one eighth of the unit cell:

u at intervals of 0•232Å from 0 to a/2
v " 0•244Å " 0 to b/2
w " 0•229Å " 0 to c/2

The initial work on the Patterson synthesis was done in the belief that the compound under investigation was the tetramer $(ClBeOBu^t)_4$.

The h0l net showed an approximate four-fold symmetry, and sections (uv0) and (0vw) of the Patterson function had many features in common.

These factors seemed strongly to indicate the space group Cmcm which with two intersecting mirror planes can possess a type of four-fold symmetry. A Wilson plot and the distribution and statistics of the normalised structure factors also indicated the centrosymmetric space group. A cubane type structure can be postulated having mm symmetry, one 'end' of which is shown in the following diagram:

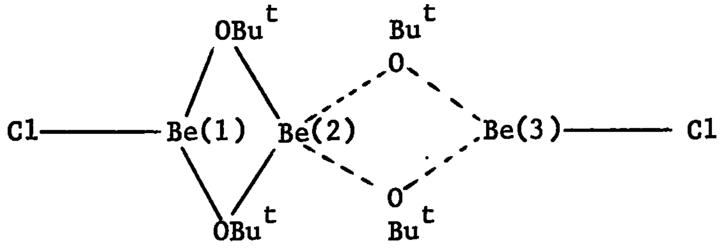


the other 'end' would appear the same except rotated through 90°.

It was not found possible to reconcile a tetrameric cubane-type structure with the Patterson function. A tetrameric chain-like structure was also incompatible with the function, and similar attempts with the alternative space group $Cmc2_1$ failed to give any significant improvement.

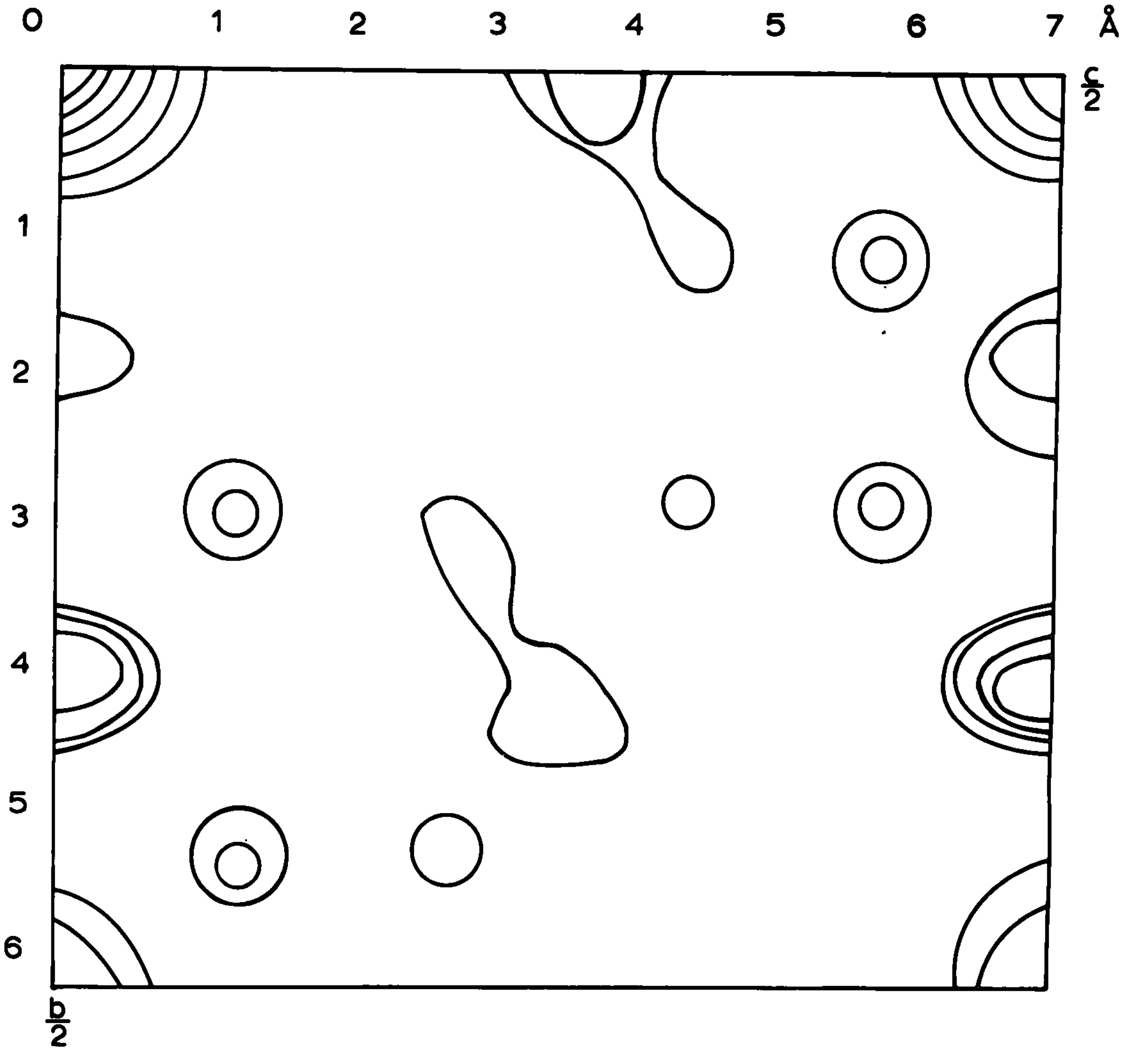
The Patterson function contains three very large peaks all about one third of the size of the origin peak at $0, \frac{1}{3}, \frac{1}{2}$; $0, \frac{1}{3}, 0$; and $0, 0, \frac{1}{2}$. It was found that these peaks could be satisfied by placing two chlorine atoms on the intersection of the mirror planes in Cmcm. These two atoms lie on the line $0, y, \frac{1}{4}$, with values of $y = 0$ and $\frac{2}{3}$ and they give rise to two symmetry related atoms at $0,0,\frac{3}{4}$; and $0,-\frac{2}{3},\frac{3}{4}$. The large peaks thus arise from vectors between these four atoms.

Three beryllium atoms were then placed initially at approximately equal intervals, between the two chlorine atoms on the line $(0,y,\frac{1}{4})$, an arrangement consistent with the peaks on the Patterson function. The beryllium atoms were bridged by means of four t-butoxy groups, two on each mirror plane.



There are two possible ways in which such an arrangement may occur, the t-butoxy groups bridging Be(1) and Be(2) may lie on the mirror plane at $x = 0$ with the groups bridging Be(2) and Be(3) on the mirror plane at $z = \frac{1}{4}$, or vice versa. The Harker section (0,v,w) illustrated in Figure 4.1 did not distinguish between these two possibilities. However by considering both alternatives and looking in the Patterson function for the positions of the Cl-O, Cl-C vectors, it was possible to distinguish the correct arrangement, this also showed the correct positions of themethyl carbon atoms with respect to the mirror planes.

(Cl$_2$Be$_3$(OBu^t)$_4$) Patterson Function



Section at u=0

Contours are at equal arbitrary intervals except for the origin peak

Figure 4.1

$Cl_2Be_3(OBu^t)_4$ TABLE 4a

Vector Table

The table gives the positions and peak heights, where applicable, of all vectors between the four chlorine atoms and the beryllium, oxygen and carbon atoms. The height of the origin peak was 900.

u/60 v/50 w/60

Atom	Position	The Chlorine Atom Positions			
		0,0,15	0,33,15	0,17,$\overline{15}$	0,0,$\overline{15}$
Be(1)	0,8½,15	0,8½,0 (74)	0,24½,0 (111)	0,8½,30 (123)	0,8½,30 (123)
Be(2)	0,17,15	0,17,0 (290)	0,16,0 (290)	0;0,30 (367)	0,17,30 (391)
Be(3)	0,25,15	0,25,0 (111)	0,8,0 (74)	0,8,30 (116)	0,25,30 (159)
O(1) <u>or</u>	0,21,10	0,21,5 (105)	0,12,5 (98)	0,4,25 (104)	0,21,25 (21)
	0,12½,10	0,12½,5 (98)	0,21,5 (105)	0,4½,25 (104)	0,12½,25 (112)
O(2) <u>or</u>	5,12½,15	5,12½,0 (92)	5,21,0 (102)	5,4½,30 (97)	5,12½,30 (-)
	5,21,15	5,21,0 (102)	5,12,0 (92)	5,4,30 (97)	5,21,30 (125)
C(1)	0,12½,4	0,12½,11 (53)	0,21,11 (60)	0,4½,19 (63)	0,12½,19 (52)
C(4)	11,21,15	11,21,0 (50)	11,12,0 (50)	11,4,30 (52)	11,21,30 (49)
C(2) <u>or</u>	0,8,1	0,8,14 (-)	0,25,14 (-)	0,9,16 (-)	0,8,16 (-)
	0,17,1	0,17,14 (89)	0,16,14 (89)	0,0,16 (115)	0,17,16 (89)

contd./

$Cl_2Be_3(OBu^t)_4$ TABLE 4a (contd.)

		The Chlorine Atom Positions			
Atom	Position	0,0,15	0,33,15	0,17,$\overline{15}$	0,0,$\overline{15}$
C(3)	5,8,1	5,8,14 (63)	5,25,14 (78)	5,9,16 (95)	5,8,16 (95)
C(5) <u>or</u>	14,17,15	14,17,0 (70)	14,16,0 (70)	14,0,30 (79)	14,17,30 (48)
	14,25,15	14,25,0 (40)	14,8,0 (30)	14,8,30 (-)	14,25,30 (79)
C(6)	14,25,10	14,25,5 (63)	14,8,5 (42)	14,8,25 (41)	14,25,25 (91)

The Harker section (0,v,w) does contain the basic structure and may be compared with the projection of the structure onto the (100) plane in Figure 4.4.

The vector table, Table 4a, shows the vectors from the two chlorine atoms and their two symmetry related atoms, to the other possible sites for the beryllium, oxygen and carbon atoms, indicating how the correct positional assignments were made.

The solution of the Patterson function reveals a molecule with mm symmetry and explains the apparent four-fold symmetry of the h0l net and the similarities between the two sections (u,v,0) and (0,v,w).

The Patterson function calculated using the diffractometer data was identical, apart from minor differences in the values of the peak heights, with that obtained using the photographic data.

4.5. Refinement of the Structure

The structure was refined using both sets of data, but since both the quantity and quality of the data collected on the diffractometer were superior to that recorded photographically the information to be presented will be largely centred on the diffractometer data.

The refinement was carried out by the method of least squares using the block diagonal approximation. Isotropic temperature factors were assigned to all atoms and the first set of structure factors calculated, based on the positions obtained from the Patterson function, yielded the value 0·303 for R. Two cycles of refinement reduced this to 0·206, then with anisotropic temperature parameters for the chlorine atoms three more cycles of refinement improved R to 0·118. For the next three cycles all the atoms were refined anisotropically and R became 0·085. Further refinement with adjustments to the parameters of the weighting scheme, reduced R to 0·074.

The corresponding R value at the end of a similar refinement of the photographic data was R = 0·080. The lower R value for the diffractometer data with the increased number of planes, indicated the better quality of the diffractometer data.

4.6. Hydrogen Atom Positions

At this stage a difference map was computed from the diffractometer data. The main features of this map were a series of peaks of sizes 0·4 to 0·5 e.$\mathring{A}^{-3}$. On close inspection it was found possible to assign these peaks to probable positions occupied by hydrogen atoms attached to the methyl carbons of the t-butyl groups. No peaks were found other than those assigned as hydrogen atoms, and it was possible to assign positions to all the hydrogen atoms. For both C(2) and C(5) one of the attached hydrogens was located on a mirror plane.

With isotropic temperature parameters chosen at 10$\mathring{A}^2$; roughly one and half times those for the methyl carbon atoms, the hydrogen atom positions were included in the structure factor calculations but were not refined. This inclusion reduced the $w\Delta^2$ values for the low order planes and resulted in an R value of 0·056.

Since the number of degrees of freedom had been reduced, the R value obtained was tested to determine whether the improvement in R was significant This was done in the manner outlined by Hamilton (Hamilton, 1965), the hypothesis was advanced that the inclusion of the hydrogen atoms did not improve the R value significantly. The ratio of the R values before and after inclusion of these atoms, gave $\overline{R}$ as 1·32. At the 0·01% probability level the value given for $\overline{R}$ = 1·260 and at the 0·005% probability level, the smallest tabulated, $\overline{R}$ = 1·274. Hence the hypothesis can be rejected at the most stringent probability level and the inclusion of the hydrogen atoms can be said to improve the R value significantly.

Refinement of the parameters was continued for a further two cycles by which time all shifts were less than one third of the corresponding e.s.d. and the refinement was deemed complete. The final value of the R factor was 0·054. The final values for the positional and thermal parameters together with their e.s.d.'s are given in Tables 4b and 4d. The symbol beside each atom represents a set of equivalent positions of the space group Cmcm, and the four sets relevant to the structure are presented in Table 4c. The values of the positional parameters obtained using the photographic data did not differ significantly from the values in the tables, which were obtained from the diffractometer data, but their e.s.d.'s were increased by a factor of about two.

During the final cycles of refinement the structure factors were weighted using the same function as employed in the first compound with values for the parameters of

$$p_1 = 20, \qquad p_2 = 0{\cdot}005, \qquad p_3 = 10^{-6}$$

The final values of the least squares totals together with the analysis of the weighting scheme, the data being analysed in terms of the magnitudes of the F_o's, are presented in Table 4e. The observed and calculated structure factors are given in Table 4f.

$Cl_2Be_3(OBu^t)_4$ TABLE 4b

Final Values of Atomic Coordinates and their Standard Deviations

Symbol	Atom	x/a	y/b	z/c	σ(x/a)	σ(y/b)	σ(z/c
c	Cl(1)	0·0	-0·00045	0·25000	0·0	0·00020	0·0
c	Cl(2)	0·0	0·67271	0·25000	0·0	0·00019	0·0
c	Be(1)	0·0	0·15266	0·25000	0·0	0·00095	0·0
c	Be(2)	0·0	0·33573	0·25000	0·0	0·00092	0·0
c	Be(3)	0·0	0·51801	0·25000	0·0	0·00094	0·0
f	O(1)	0·0	0·23867	0·16769	0·0	0·00031	0·00027
g	O(2)	0·08143	0·43295	0·25000	0·00030	0·00031	0·0
f	C(1)	0·0	0·23393	0·06080	0·0	0·00054	0·00043
f	C(2)	0·0	0·35101	0·02357	0·0	0·00072	0·00051
h	C(3)	0·09019	0·17386	0·02822	0·00051	0·00062	0·00042
g	C(4)	0·18606	0·44250	0·25000	0·00050	0·00056	0·0
g	C(5)	0·22818	0·32860	0·25000	0·00054	0·00068	0·0
h	C(6)	0·21549	0·50483	0·15886	0·00042	0·00061	0·00052
f	H(21)	0·0	0·36000	-0·05000	0·01000	0·01000	0·01000
h	H(22)	0·07500	0·38000	0·04170	0·01000	0·01000	0·01000
h	H(31)	0·07500	0·17000	-0·04170	0·01000	0·01000	0·01000
h	H(32)	0·10000	0·08000	0·05000	0·01000	0·01000	0·01000
h	H(33)	0·13300	0·22000	0·07500	0·01000	0·01000	0·01000
h	H(51)	0·19200	0·26000	0·20800	0·01000	0·01000	0·01000
g	H(52)	0·30800	0·33000	0·25000	0·01000	0·01000	0·01000
h	H(61)	0·18790	0·44730	0·10570	0·01000	0·01000	0·01000
h	H(62)	0·18500	0·58000	0·15000	0·01000	0·01000	0·01000
h	H(63)	0·29200	0·50000	0·15000	0·01000	0·01000	0·01000

$Cl_2Be_3(OBu^t)_4$ TABLE 4c

Equivalent Positions of Cmcm

$(000;\frac{1}{2}\frac{1}{2}0)$ +

Symbol	Equivalent Positions	
h	$x,y,z;\ x,\bar{y},\bar{z};\ x,y,\frac{1}{2}-z;\ x,\bar{y},\frac{1}{2}+z;$ $\bar{x},\bar{y},\bar{z};\ \bar{x},y,z;\ \bar{x},\bar{y},\frac{1}{2}+z;\ \bar{x},y,\frac{1}{2}-z;$	General positions
g	$x,y,\frac{1}{4};\ \bar{x},y,\frac{1}{4};\ x,\bar{y},\frac{3}{4};\ \bar{x},\bar{y},\frac{3}{4};$	Atoms lying on the mirror planes, at $z = \frac{1}{4}$ and $\frac{3}{4}$
f	$0,y,z;\ 0,\bar{y},\bar{z};\ 0,y,\frac{1}{2}-z;\ 0,\bar{y},\frac{1}{2}+z;$	Atoms lying on the mirror planes $x = 0$ and $\frac{1}{2}$
c	$0,y,\frac{1}{4};\ 0,\bar{y},\frac{3}{4};$	Atoms lying on the lines of intersection of mirror planes in 'g' and 'f'

$Cl_2Be_3(OBu^t)_4$ TABLE 4d

Final Values of Anisotropic Temperature Parameters ($\mathring{A}^2$)

and their Standard Deviations ($\mathring{A}^2$ x 10^4)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl(1)	0·0756(17)	0·0313(10)	0·0783(16)			
Cl(2)	0·1002(22)	0·0341(10)	0·0531(13)			
Be(1)	0·0370(65)	0·0414(59)	0·0514(66)			
Be(2)	0·0396(62)	0·0388(50)	0·0331(50)			
Be(3)	0·0592(77)	0·0423(63)	0·0366(56)			
O(1)	0·0603(26)	0·0380(20)	0·0288(19)	-0·0024(17)		
O(2)	0·0351(22)	0·0378(20)	0·0512(24)			-0·0048(19)
C(1)	0·0604(42)	0·0571(37)	0·0316(30)	-0·0067(29)		
C(2)	0·1714(100)	0·0681(50)	0·0363(44)	0·0184(37)		
C(3)	0·0988(49)	0·1283(59)	0·0510(31)	-0·0232(35)	0·0098(32)	0·0350(44)
C(4)	0·0432(38)	0·0577(38)	0·0604(42)			-0·0062(34)
C(5)	0·0386(42)	0·0693(51)	0·1380(80)			0·0090(41)
C(6)	0·0582(35)	0·1153(49)	0·1048(49)	0·0358(44)	0·0153(34)	-0·0201(42)

$Cl_2Be_3(OBu^t)_4$ TABLE 4e

Least Squares Totals

Number of observed planes 720

$\Sigma\|F_o\|$	$\Sigma\|F_c\|$	$\Sigma\|\Delta\|$	$\Sigma w\Delta^2$	R
18987.96	18815.45	1031·62	62·69	0·054

Weighting Analysis

$\|F_o\|$ranges	N	$\Sigma w\Delta^2/N$	R
0-10	74	0·10	0·144
10-14	192	0·14	0·125
14-20	165	0·04	0·058
20-30	112	0·10	0·051
30-50	88	0·04	0·037
50 upwards	89	0·08	0·032

$Cl_2Be_3(OBu^t)_4$ TABLE 4f

The Observed and Calculated Structure Factors

H	K	L	|FO|	FC
2	0	0	194	205
4	0	0	233	228
6	0	0	75	74
8	0	0	57	63
10	0	0	104	103
12	0	0	51	51
14	0	0	37	38
16	0	0	11	8
1	1	0	52	-50
3	1	0	90	87
5	1	0	66	-64
7	1	0	71	72
2	2	0	146	-148
4	2	0	20	-22
6	2	0	36	-35
8	2	0	58	-55
12	2	0	12	-12
1	3	0	24	26
3	3	0	141	138
5	3	0	86	82
7	3	0	83	82
9	3	0	23	20
13	3	0	10	9
0	4	0	91	97
4	4	0	87	85
6	4	0	66	63
8	4	0	34	33
10	4	0	32	31
14	4	0	15	15
1	5	0	68	70
3	5	0	40	38
5	5	0	29	-28
7	5	0	25	24
11	5	0	29	31
0	6	0	92	86
2	6	0	17	22
4	6	0	73	73
6	6	0	19	20
8	6	0	38	38
10	6	0	15	17
14	6	0	13	11
1	7	0	11	11
3	7	0	13	-10
5	7	0	26	-27
7	7	0	11	-13
9	7	0	16	-18
11	7	0	19	19
2	8	0	26	26
4	8	0	49	51
6	8	0	39	42
8	8	0	31	32
10	8	0	10	8
1	9	0	72	74
3	9	0	54	55
5	9	0	50	52
7	9	0	35	34
9	9	0	23	24
11	9	0	25	25
13	9	0	14	14
0	10	0	15	-16
2	10	0	10	-11
3	11	0	10	-9
5	11	0	13	-13
0	12	0	53	53
2	12	0	41	39
4	12	0	38	34
6	12	0	22	22
8	12	0	25	25
10	12	0	19	19
12	12	0	12	13
14	12	0	12	10
1	13	0	16	16
3	13	0	19	21
5	13	0	18	20
7	13	0	18	19
9	13	0	11	9
3	15	0	14	13
5	15	0	12	13
0	16	0	14	13
1	1	1	85	-87
3	1	1	7	0
5	1	1	28	-24
7	1	1	11	10
9	1	1	23	-23
11	1	1	11	-12
13	1	1	15	-16
0	2	1	31	30
2	2	1	83	-82
4	2	1	30	-32
6	2	1	58	-55
8	2	1	34	-34
3	3	1	50	49
5	3	1	57	56
7	3	1	50	48
9	3	1	24	24
0	4	1	89	97
2	4	1	94	86
6	4	1	18	17
10	4	1	21	24
12	4	1	21	22
1	5	1	84	-82
3	5	1	35	-31
5	5	1	22	-20
7	5	1	10	-12
11	5	1	24	-26
0	6	1	7	6
2	6	1	26	-25
4	6	1	27	-25
6	6	1	21	-22
8	6	1	25	-23
1	7	1	40	42
3	7	1	54	53
5	7	1	32	33
7	7	1	35	35
9	7	1	17	16
11	7	1	12	12
2	8	1	15	-16
1	9	1	11	-12
3	9	1	23	-24
5	9	1	21	-20
7	9	1	22	-23
0	10	1	15	-17
6	10	1	11	12
1	11	1	16	14
11	11	1	12	9
13	11	1	11	7
0	12	1	13	-13
8	12	1	11	8
1	13	1	15	16
0	14	1	17	-16
2	14	1	12	-12
6	14	1	11	-9
2	16	1	12	12
0	0	2	189	-197
2	0	2	17	14
4	0	2	163	-156
6	0	2	70	-73
8	0	2	21	-30
10	0	2	47	-43
12	0	2	24	-28
14	0	2	27	-22
1	1	2	59	58
3	1	2	89	-89
5	1	2	36	-35
7	1	2	77	-74
11	1	2	8	7
13	1	2	8	6
0	2	2	156	-148
2	2	2	43	-46
4	2	2	13	7
6	2	2	9	10
8	2	2	11	11
10	2	2	25	-25
12	2	2	14	-14
1	3	2	96	-94
3	3	2	58	-63
5	3	2	14	-16
7	3	2	27	-28
9	3	2	36	-35
11	3	2	12	-13
13	3	2	15	-16
0	4	2	84	-85
2	4	2	51	-46
4	4	2	40	-39
6	4	2	19	-21
8	4	2	8	-8
10	4	2	16	-14
3	5	2	16	-15
7	5	2	9	-10
9	5	2	13	12
11	5	2	11	-12
0	6	2	36	-36
2	6	2	24	-26
4	6	2	94	-92
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8	6	2	55	-56
10	6	2	14	-15
14	6	2	12	-13
1	7	2	55	-56
3	7	2	19	-20
5	7	2	12	-10
7	7	2	8	-9
11	7	2	24	-23
0	8	2	14	14
2	8	2	10	-9
4	8	2	9	-9
6	8	2	13	-13
8	8	2	17	-20
1	9	2	58	-61
3	9	2	28	-29
5	9	2	24	-25
7	9	2	10	-8
9	9	2	16	-16
11	9	2	20	-20
13	9	2	14	-12
2	10	2	16	-17
4	10	2	17	-18
6	10	2	13	-11
8	10	2	13	-12
0	12	2	36	-38
2	12	2	29	-30
4	12	2	31	-32
6	12	2	19	-20
8	12	2	23	-22
1	13	2	13	-12
3	13	2	17	-15
5	13	2	15	-16
7	13	2	11	-15
3	15	2	18	-18
5	15	2	17	-17
7	15	2	16	-15
1	1	3	82	-81
3	1	3	69	-69
5	1	3	22	-16
7	1	3	46	-46
9	1	3	13	-13
11	1	3	11	-12
0	2	3	60	-60
2	2	3	57	58
4	2	3	49	49
6	2	3	59	57
8	2	3	31	29
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11	3	3	23	24
15	3	3	11	5
0	4	3	46	-49
2	4	3	35	-54
6	4	3	15	-15
8	4	3	16	17
10	4	3	13	-14
12	4	3	13	-13
1	5	3	44	42
3	5	3	10	-7
5	5	3	21	-20
7	5	3	20	-20
9	5	3	17	-17
11	5	3	16	17
0	6	3	37	-38
4	6	3	7	8
8	6	3	11	10
1	7	3	12	-14
3	7	3	20	-20
7	7	3	13	-14
0	8	3	26	25
2	8	3	34	33
4	8	3	21	20
6	8	3	20	20
8	8	3	12	14
10	8	3	10	11
1	9	3	8	-9
7	9	3	8	10
2	10	3	20	-19
4	10	3	17	-17
6	10	3	24	-25
8	10	3	14	-13
7	11	3	10	11
0	12	3	21	20
2	12	3	10	10
1	13	3	13	-19
0	0	4	246	247
2	0	4	163	165
4	0	4	52	54
6	0	4	18	17
8	0	4	26	27
10	0	4	40	41
12	0	4	42	43
14	0	4	11	11
1	1	4	23	-22
5	1	4	20	19
7	1	4	14	12
9	1	4	15	16
11	1	4	10	-11
0	2	4	9	-7
2	2	4	76	75
6	2	4	32	30
10	2	4	8	9
12	2	4	13	20
16	2	4	11	9
1	3	4	64	65
3	3	4	77	76
5	3	4	111	110
7	3	4	44	41
9	3	4	46	46
13	3	4	12	14
0	4	4	62	-56
2	4	4	9	9
4	4	4	23	-19
6	4	4	14	14
8	4	4	7	3
1	5	4	30	29
3	5	4	14	-11
5	5	4	20	-13
7	5	4	20	-19
11	5	4	10	10
0	6	4	82	79
2	6	4	94	92
4	6	4	81	79
6	6	4	59	59
8	6	4	56	58
10	6	4	22	22
12	6	4	21	20
14	6	4	11	10
1	7	4	37	37
5	7	4	10	10
7	7	4	9	-11
11	7	4	15	16
0	8	4	42	-43
6	8	4	18	19
8	8	4	13	14
10	8	4	9	-9
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3	9	4	22	24
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11	9	4	13	12
2	10	4	16	16
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6	10	4	11	11
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1	11	4	11	10
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4	12	4	24	24
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12	12	4	14	10
5	13	4	12	11
2	14	4	11	8
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3	15	4	19	18
5	15	4	19	18
7	15	4	17	15
0	16	4	11	9
1	1	5	32	-30
3	1	5	44	45
5	1	5	35	35
7	1	5	37	38
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2	2	5	47	-44
6	2	5	17	-17
8	2	5	24	-25
1	3	5	63	-60
5	3	5	8	-6
7	3	5	15	15
11	3	5	20	-19
0	4	5	85	80
2	4	5	40	41
4	4	5	19	-16
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10	4	5	23	23
12	4	5	14	15
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7	5	5	14	13
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11	5	5	8	-10
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2	6	5	13	-14
4	6	5	10	-10
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8	6	5	19	-20
3	7	5	21	23
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1	13	5	18	19
3	13	5	12	13
5	13	5	11	11
7	13	5	11	7
0	0	6	74	-75
2	0	6	66	-63
4	0	6	30	-30
6	0	6	37	-35
8	0	6	18	-18
10	0	6	22	-22
12	0	6	28	-29
1	1	6	20	19
3	1	6	15	-14
5	1	6	37	-37
7	1	6	18	-18
9	1	6	19	-19
11	1	6	14	16
0	2	6	48	-44
2	2	6	81	-80
6	2	6	20	-19
10	2	6	16	-16
12	2	6	22	-22
1	3	6	55	-56
3	3	6	39	-35
5	3	6	46	-48
7	3	6	9	-8
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8	8	6	10	-8
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4	10	6	14	-16
6	10	6	16	-16
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1	13	7	18	-17
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12	0	8	18	17
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3	1	8	13	12
7	1	8	15	15
11	1	8	10	-10
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4	2	8	18	19
6	2	8	26	26
8	2	8	8	6
10	2	8	19	20
12	2	8	15	14
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3	3	8	48	49
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7	3	8	30	31
9	3	8	28	29
13	3	8	12	11
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2	4	8	11	-12
4	4	8	19	-18
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3	5	8	10	-11
5	5	8	16	-18
7	5	8	15	-13
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2	6	8	57	58
4	6	8	62	64
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14	6	8	11	11
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5	7	8	9	11
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11	7	8	11	13
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12	8	8	13	-8
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8	2	9	10	-10
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11	3	9	9	-10
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12	4	9	12	10
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2	6	9	8	-10
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7	7	9	17	15
2	8	9	16	-16
5	9	9	10	-11
2	10	9	9	10
6	10	9	12	9
8	10	9	11	8
1	11	9	10	9
0	12	9	16	-15
1	13	9	11	11
0	0	10	111	-108
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4	0	10	53	-53
6	0	10	32	-33
8	0	10	24	-24
10	0	10	36	-36
12	0	10	21	-21
14	0	10	13	-15
1	1	10	12	12
3	1	10	12	-14
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4	8	10	14	-14
6	8	10	10	-11
8	8	10	10	-11
1	9	10	28	-27
3	9	10	20	-20
5	9	10	16	-17
7	9	10	13	-12
11	9	10	13	-11
0	12	10	20	-21
2	12	10	17	-17
4	12	10	16	-16
8	12	10	12	-11
5	13	10	13	-8
5	1	11	15	15
7	1	11	8	8
2	2	11	20	20
4	2	11	27	28
6	2	11	29	29
8	2	11	18	18
3	3	11	23	-24
5	3	11	23	-23
7	3	11	20	-21
9	3	11	13	-11
0	4	11	25	-25
2	4	11	20	-21
4	4	11	17	-18
6	4	11	16	-17
1	5	11	38	40
3	5	11	21	21
5	5	11	9	11
4	6	11	11	11
6	6	11	10	10
1	7	11	26	-27
3	7	11	23	-22
5	7	11	13	-13
7	7	11	13	-13
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0	0	12	54	59
2	0	12	32	35
4	0	12	43	43
6	0	12	29	30
8	0	12	18	18
10	0	12	23	21
12	0	12	15	15
1	1	12	12	-12
3	1	12	8	10
7	1	12	12	14
0	2	12	8	7
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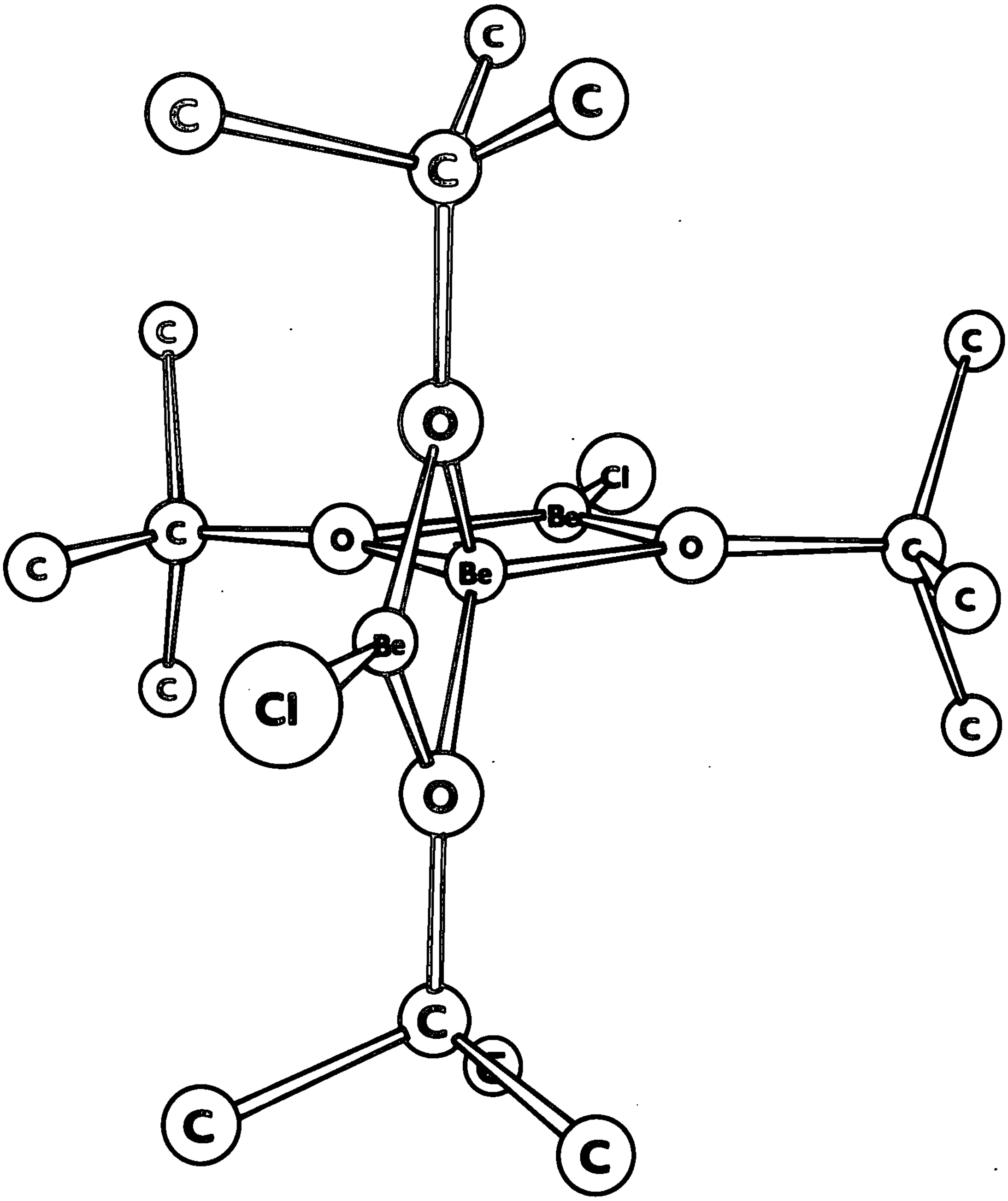
0	6	12	9	9
2	6	12	10	10
4	6	12	22	23
6	6	12	16	16
8	6	12	14	14
3	9	12	14	15
5	9	12	15	12
11	9	12	17	11
0	12	12	14	16
2	12	12	16	14
4	12	12	13	14
1	1	13	12	-12
0	4	13	16	19
2	4	13	9	10
3	9	13	12	-8
5	9	13	11	-7
0	12	13	12	-9
0	0	14	43	-45
2	0	14	28	-29
4	0	14	16	-17
8	0	14	12	-10
1	3	14	10	-8
3	3	14	14	-16
5	3	14	18	-18
6	4	14	10	-4
0	6	14	17	-15
2	6	14	16	-17
4	6	14	15	-14
6	6	14	12	-10
1	9	14	14	-11
4	2	15	11	11
6	2	15	11	10
3	3	15	11	-6
0	4	15	11	-12
0	0	16	13	13
2	0	16	14	13
4	0	16	11	14
6	0	16	15	13
2	6	16	11	8
6	6	16	12	11
1	9	16	12	11
2	6	17	11	-2
1	7	17	11	-3
0	6	18	12	-15
2	6	18	14	-15
1	1	19	11	-8
1	3	19	13	10



$Cl_2Be_3(OBu^t)_4$

Figure 4.2

4.7. Description and Discussion of the Structure

The molecule lies at the intersection of two mutually perpendicular mirror planes with the two chlorine and three beryllium atoms situated on the line of intersection. The two beryllium atoms attached to the terminal chlorine atoms are three-coordinate and each is linked to the third beryllium at the centre of the molecule, by two bridging t-butoxy groups lying on the two mirror planes. The view looking down the chlorine-beryllium direction, which is the direction of the 'y' axis, is shown in Figure 4.2.

The difference in coordination states between the two types of beryllium atom manifests itself in the geometries of the beryllium-oxygen rings. The molecular geometry very closely resembles that recently found for $[Be(NMe_2)_2]_3$ (Atwood and Stucky, 1967), see Figure 2.1.

It was previously noted that the values of the positional parameters obtained from the two sets of data, were not significantly different. The bond lengths and angles obtained from the data sets do not differ significantly either. However the values obtained using diffractometer data have the lower e.s.d.'s and show the greater consistency, i.e. similar bond lengths are in much better agreement, in fact none of them differ from each other by more than twice the individual e.s.d.'s. These are the values quoted in this section and presented in Tables 4g and 4h as bond lengths and angles respectively.

$Cl_2Be_3(OBu^t)_4$ TABLE 4g

Bond Lengths and their Standard Deviations

	Distance	e.s.d.
Cl(1)-Be(1)	1•867Å	0•012Å
Cl(2)-Be(2)	1•886	0•012
O(1)-Be(1)	1•541	0•009
O(2)-Be(3)	1•536	0•009
O(1)-Be(2)	1•635	0•009
O(2)-Be(2)	1•639	0•009
O(1)-C(1)	1•467	0•007
O(2)-C(4)	1•460	0•008
C(1)-C(2)	1•516	0•011
C(1)-C(3)	1•520	0•008
C(4)-C(5)	1•507	0•011
C(4)-C(6)	1•519	0•008

$Cl_2Be_3(OBu^t)_4$ TABLE 4h

Bond Angles and their Standard Deviations

	Angle	e.s.d.
Cl(1)-Be(1)-O(1)	132·9°	0·4°
Cl(2)-Be(3)-O(2)	132·5	0·4
O(1)-Be(2)-O(2)	121·6	0·4
Be(1)-O(1)-Be(2)	89·3	0·4
Be(1)-O(1)-C(1)	134·9	0·4
Be(2)-O(1)-C(1)	135·9	0·4
Be(2)-O(2)-Be(3)	88·8	0·4
Be(2)-O(2)-C(4)	138·3	0·4
Be(3)-O(2)-C(4)	133·0	0·4
O(1)-C(1)-C(2)	107·4	0·4
O(1)-C(1)-C(3)	108·2	0·4
C(2)-C(1)-C(3)	110·8	0·5
C(3)-C(1)-C(3')	111·2	0·5
O(2)-C(4)-C(5)	108·3	0·4
O(2)-C(4)-C(6)	108·0	0·5
C(5)-C(4)-C(6)	110·9	0·5
C(6)-C(4)-C(6')	110·7	0·5

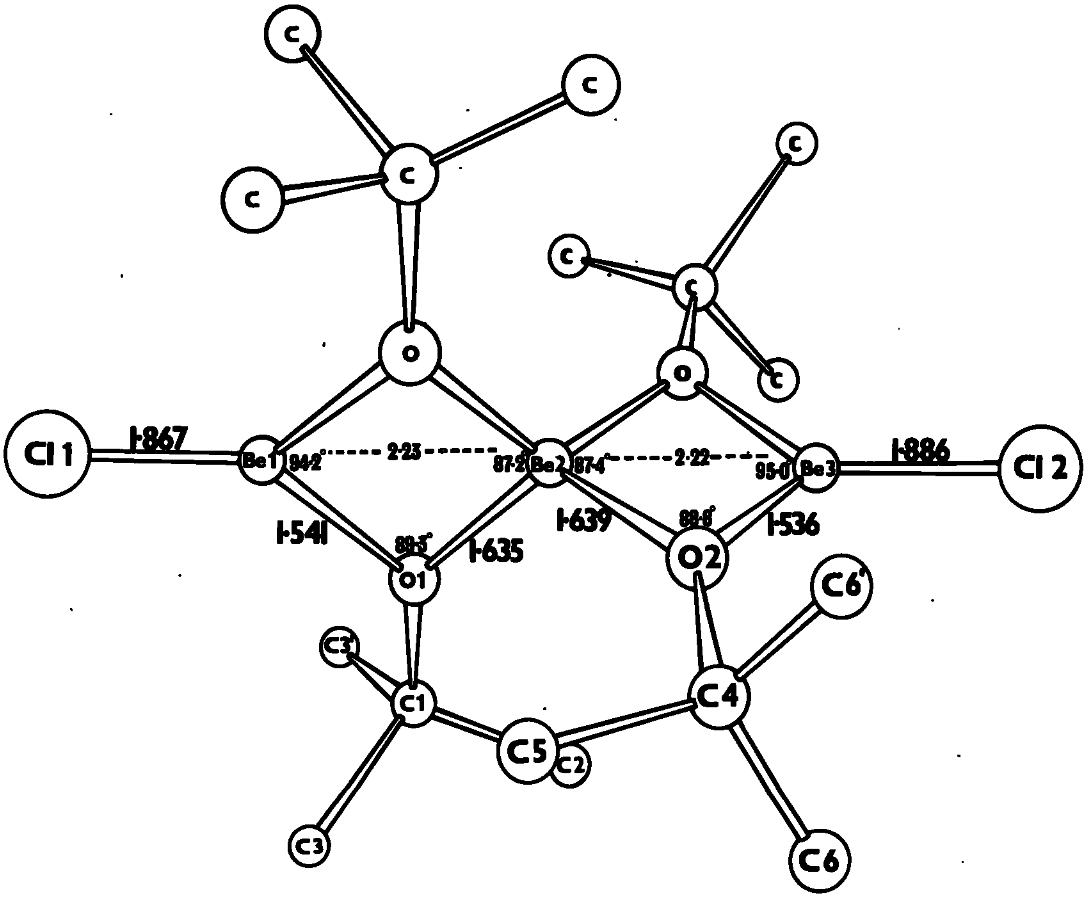
C(3') refers to the atom at ($\bar{x}$,y,z)

C(6') refers to the atom at (x,y,$\frac{1}{2}$-z)

The Be(1)-Cl(1) and Be(3)-Cl(2) distances are 1•867 and 1•866Å respectively and their mean of 1•867Å contrasts with the distance 2•05Å found in solid beryllium chloride (Rundle and Lewis, 1952), which is the same as the sum of the tetrahedral covalent radii. The chlorine and beryllium atoms in solid beryllium chloride are two and four coordinate respectively, but the angle at chlorine is 81•8°. In $Cl_2Be_3(OBu^t)_4$, Be(1) and Be(3) are three coordinate and will try to reduce their coordinate unsaturation by using empty 2p orbitals to form dative π-bonds if possible, resulting in a shortening of the bonds. The evidence for this type of bonding is discussed in the next section.

In the t-butoxy-beryllium bromide complex, the beryllium atoms have the same environment and the central beryllium-oxygen ring is approximately square. The two such rings of the trimer are not square owing to the differences in coordination and bonding of the constituent beryllium atoms.

The three-coordinate beryllium atoms form the significantly shorter bonds to the oxygen atoms, these distances being Be(1)-O(1), 1•541Å and Be(3)-O(2), 1•536Å, as compared to those involving Be(2) of 1•635 and 1•639Å. Consequently the angles at Be(2) are smaller than those at Be(1) and Be(3), while those at O(1) and O(2) are the same within experimental error and intermediate between the angles at beryllium. The dimensions of the rings are given along with other values of the lengths and angles on Figure 4.3, which shows a view of the molecule perpendicular to the direction of the y axis.



$Cl_2Be_3(OBu^t)_4$

Some Lengths and Angles

Figure 4.3

The greatest distortions in the values of the ring angles are found at the atoms Be(1), Be(3), O(1) and O(2). These atoms could be formally regarded as sp^2 hybridised, the undistorted angle between the three valence lobes being 120°. The angles at Be(2) do not represent distortions quite as large, since being four-coordinate this atom would be expected to have a tetrahedral environment with valence angles for the undistorted geometry of 109•47°.

The C(1)-O(1) and C(4)-O(2) bond lengths of 1•467 and 1•460Å respectively, may be compared with the values quoted in section 3.7 and also with the C-O distance in the t-butoxy group of the t-butoxy magnesium complex, equal to 1•449 ± 0•025Å. The Be-O-C angles are of course much greater than 120°, but whereas those at O(1) are approximately the same, at O(2) the angles Be(2)-O(2)-C(4), 138•3° and Be(3)-O(2)-C(4), 133•0°, differ significantly from one another. These values imply a movement of the carbon atoms of the t-butoxy groups bridging Be(2) and Be(3), away from the centre of the molecule.

The carbon-carbon distances do not differ significantly from each other, nor from the mean C-C distance of 1•53Å found in the t-butoxy group of the magnesium complex, their mean is 1•516Å. The angles between similar atoms in the two groups are in good agreement, but the O-C-C angles are slightly less than the tetrahedral value and the C-C-C angles are slightly greater.

The non-bonding distances less than 4Å are given in Table 4i, apart from those between atoms of the same t-butoxy group. Once again corresponding distances between different parts of the molecule are in close agreement. The slight movement of the t-butoxy group mentioned previously has two results; a lengthening in non-bonding C-Be(2) distances as compared to similar distances involving the other t-butoxy group, e.g. Be(2)-C(5) 3·18Å and Be(2)-C(2) 3·11Å, and a shortening in Cl-C non-bonding distances in a similar comparison, e.g. Cl(2)-C(6) 3·84Å and Cl(1)-C(3) 3·92Å.

There are only four intermolecular distances shorter than 4Å, they are

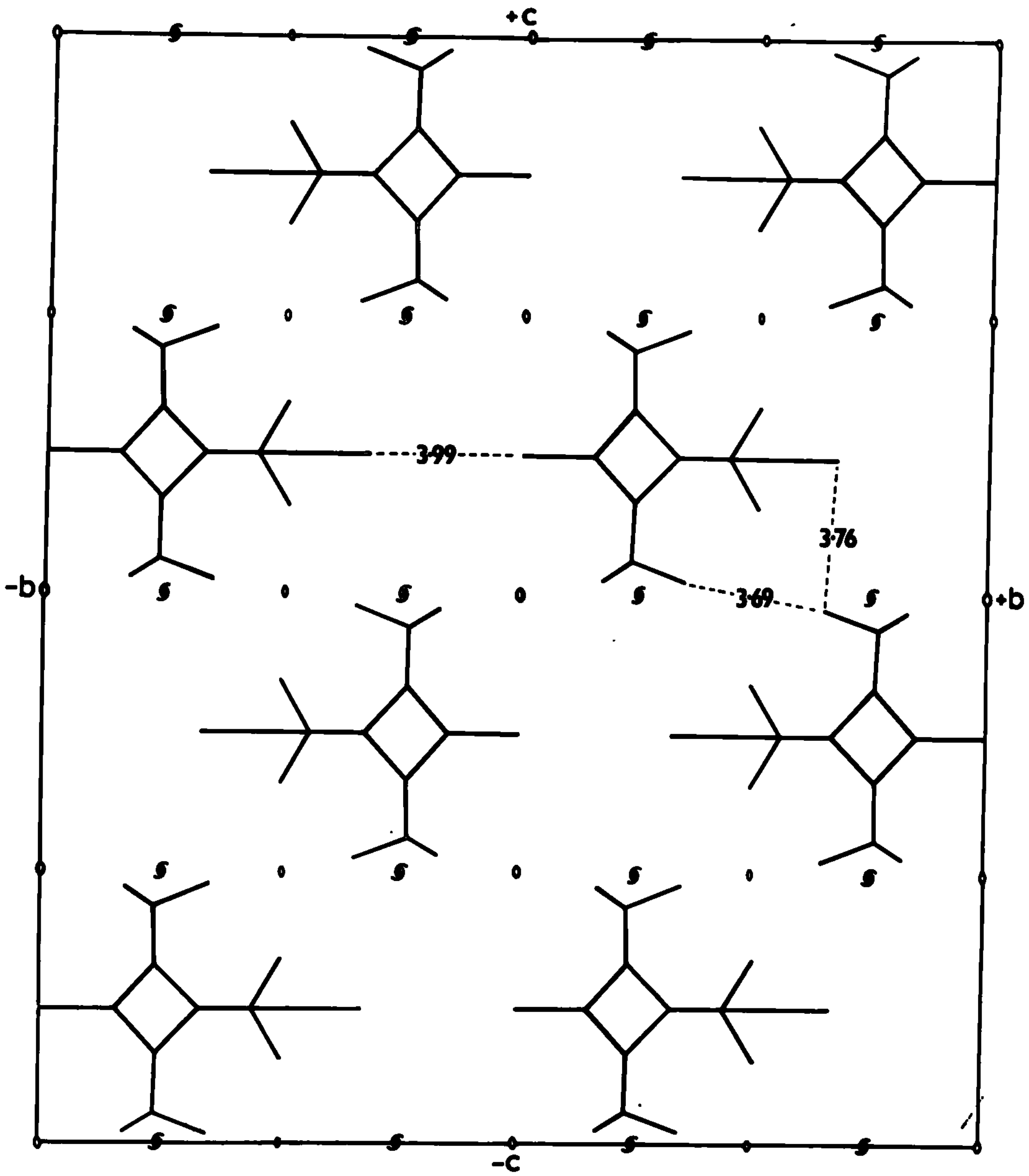
Cl(1)-Cl(2)	at $(0, 1+y, z)$	3·99Å
Cl(2)-C(2)	at $(0, 1-y, z)$	3·76
C(2)-C(2)	at $(0, 1-y, \bar{z})$	3·69
C(3)-C(6)	at $(\frac{1}{2}-x, \frac{1}{2}+y, z)$	3·84

The first three are shown in Figure 4.4 which shows the molecular packing in projection on the (100) plane, the (001) projection would be very similar to this. The fourth distance occurs between a molecule on the mirror plane at $x = 0$ and one on the mirror plane at $x = \frac{1}{2}$ and does not appear on the figure. A movement of the t-butoxy group to which C(2) belongs, (similar to that shown by the other t-butoxy group), would increase the C(2)-C(2) intermolecular distance, however this would be offset by reductions in the distances between both the chlorine atoms and the atoms C(1), C(2) and C(3).

$Cl_2Be_3(OBu^t)_4$ TABLE 4i

Non-Bonding Intra-Molecular Distances less than 4Å

A	B	A - B Å
Cl(1)	O(1)	3·13
Cl(1)	C(1)	3·86
Cl(1)	C(3)	3·92
Cl(2)	O(2)	3·13
Cl(2)	C(4)	3·82
Cl(2)	C(6)	3·84
Be(1)	O(2)	3·60
Be(1)	C(1)	2·78
Be(1)	C(2)	3·93
Be(1)	C(3)	3·30
Be(1)	C(5)	3·83
Be(1)	Be(2)	2·23
Be(2)	Be(3)	2·22
Be(2)	C(1)	2·88
Be(2)	C(2)	3·11
Be(2)	C(3)	3·84
Be(2)	C(4)	2·90
Be(2)	C(5)	3·18
Be(2)	C(6)	3·85
Be(3)	O(1)	3·59
Be(3)	C(2)	3·71
Be(3)	C(4)	2·75
Be(3)	C(5)	3·92
Be(3)	C(6)	3·25
O(1)	O(2)	2·86
O(1)	C(4)	3·76
O(1)	C(5)	3·54
O(1)	O(1) $(0,y,\frac{1}{2}-z)$	2·26
O(2)	O(2) $(\bar{x},y,\frac{1}{4})$	2·27
O(2)	C(1)	3·73
O(2)	C(2)	3·45
C(2)	C(6)	3·99



$Cl_2Be_3(OBu^t)_4$

(100) Projection

Figure 4.4

From the foregoing discussion and the tables and diagrams it will be appreciated that the molecule is composed of two very geometrically similar halves joined perpendicularly at Be(2). The space group requires the molecule to have the symmetry mm but the possibility existed that the molecule might possess the higher point group symmetry $\bar{4}2m$. In order to test this hypothesis, the position of the centre of the molecule on the line $(0,y,\frac{1}{4})$ was calculated using the y-coordinates of the atoms weighted by a factor inversely proportional to the square of their e.s.d.'s. The coordinates of the atoms were then evaluated taking this 'molecular centre' as origin. Statistical tests showed that while the chlorine, beryllium and oxygen atoms are related by $\bar{4}2m$ symmetry, the carbon atoms are not. In view of the distortions involving these latter atoms this is hardly surprising. The coordinates of the atoms referred to the molecular centre, based only on the positions of the chlorine, beryllium and oxygen atoms, are given in Table 4j. It can be seen that the positions of these atoms are related by the requirements of symmetry $\bar{4}2m$, but that for the carbon atoms, differences up to 0·09Å are observed between relative coordinates.

This symmetry, or in the case of carbon atoms near symmetry is closely paralleled in the values of the isotropic and anisotropic temperature factors, corresponding atoms having roughly equal values of B, (and also approximately equal values of corresponding U_{ij}'s, see Table 4d.). The

$Cl_2Be_3(OBu^t)_4$ TABLE 4j

Test for $\bar{4}2m$ symmetry

The coordinates in Ångstroms of the atoms referred to the weighted centre based on the positions of the chlorine, beryllium and oxygen atoms.

Atom	X	σ(X/a)	Y	σ(Y/b)	Z	σ(Z/c)
Cl(1)	0·0		-4·102	0·002	0·0	
Be(1)	0·0		-2·235	0·011	0·0	
O(1)	0·0		-1·187	0·004	-1·129	0·004
C(1)	0·0		-1·244	0·007	-2·594	0·006
C(2)	0·0		0·183	0·009	-3·105	0·007
C(3)	1·255	0·007	-1·977	0·008	-3·041	0·006
Be(2)	0·0		-0·003	0·011	0·0	
Cl(2)	0·0		4·105	0·002	0·0	
Be(3)	0·0		2·219	0·012	0·0	
O(2)	1·133	0·004	1·182	0·004	0·0	
C(4)	2·588	0·007	1·298	0·007	0·0	
C(5)	3·174	0·008	-0·090	0·008	0·0	
C(6)	2·997	0·006	2·058	0·007	-1·250	0·007

The matrix relating the atomic coordinates of the first set to those of the second set is

$$\begin{vmatrix} 0 & 0 & \bar{1} \\ 0 & \bar{1} & 0 \\ \bar{1} & 0 & 0 \end{vmatrix}$$

mean values of B show a steady gradation from the ring atoms to the peripheral atoms, the mean values being Cl 3·9, Be 3·6, O 2·9, t-butyl C 4·0, methyl C 6·5 Å^2.

Although the hydrogen atom positions were not refined the values of the C-H bond lengths were in good agreement, their mean being 1·10Å. Of the bond angles involving these atoms only two were in poor agreement with the tetrahedral value. The sum of the Van der Waal's radii of a chlorine atom and a methyl group is 3·80Å, and since the shortest non-bonding distance between a chlorine and a methyl carbon atom is 3·76Å, the possibility of any strong interaction between the chlorine and the hydrogen atoms would seemed to be ruled out.

4.8. π-Bonding in Three-Coordinate Beryllium Compounds

The evidence in favour of dative beryllium-nitrogen π-bonding has been the subject of two recent papers, and the results obtained in this present structure analysis seem to substantiate that evidence. In this context the important facts are the geometries at the beryllium atoms and the Be-Cl and Be-O bond distances.

In assessing the importance of any bond shortening it is important to remember that the change from sp^3 to sp^2 hybridisation will lead to a reduction in bond length. For carbon, values of bond distances quoted indicate bond shortenings of the order of 0·04Å for a change from $C(sp^3)$-$C(sp^2)$ to $C(sp^2)$-$C(sp^2)$.

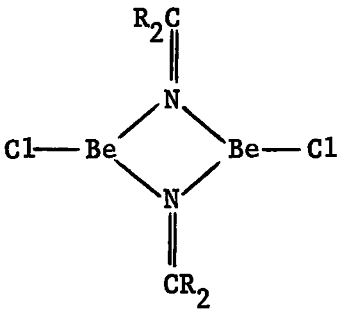
The mean Be-Cl distance of 1·88Å has been compared to the sum of the tetrahedral covalent radii, 2·05Å; a similar comparison for the Be-Br distance in the previous compound gave good agreement. Two types of Be-O distances exist involving the three- and four-coordinate beryllium atoms, their mean values are $Be(sp^2)$-O, 1·54Å and $Be(sp^3)$-O, 1·64Å, this latter value being in good agreement with the Be-O distances found in the bromide complex. The bond shortenings then appear to be in the sequence $Cl\text{-}Be(sp^2) > O\text{-}Be(sp^2) > O\text{-}Be(sp^3)$.

This same sequence is found, although involving different atoms, in $(Be(NMe_2)_2)_3$. The Be (terminal)-N (terminal) distance of 1·56Å may be compared with distances of 1·61Å for Be (terminal)-N(bridging) and 1·76Å for Be(central)-N(bridging) this last distance being equal to the sum of the tetrahedral covalent radii. The trends are in the expected direction if π-bonding effects are considered.

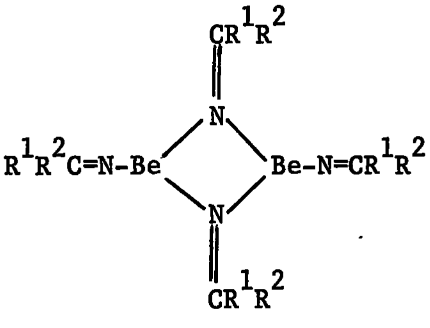
In both compounds the terminal berylliums and their three attached atoms are coplanar. This geometry permits filled p orbitals on the terminal nitrogen and chlorine atoms and on the bridging oxygen atoms to form dative π-bonds with the empty p-orbitals of the three-coordinate beryllium atoms.

Further support for this thoery comes from the n.m.r. studies on $[Be(NMe_2)_2]_3$ (Fetter and Peters, 1965). Extension of the work to measurements of the ^{13}C-H spin-spin coupling constants yielded a value indicative of a degree of π-bonding between the terminal nitrogen and beryllium atoms. (Niedzieski et al., 1964).

Additional evidence is provided by studies of the infrared spectra of a series of bis(ketimino)-derivatives of beryllium. (Summerford, Wade and Wyatt, 1969).



(I)



(II)

Compounds of type (I) have $\nu(C{=}N)$ at ca. 1610 cm^{-1}, whereas the coloured derivatives of type (II) absorb in the region of 1630 cm^{-1} and also in the region of 1735 cm^{-1}. This last band was taken as evidence of a linear $C{=}N{=}Be$ skeleton for the terminal ketimino groups.

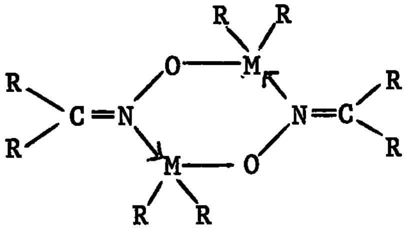
Structural investigations of derivatives of type (II) could prove most useful in providing further evidence for dative π-bonding in three coordinate beryllium compounds.

Chapter Five

The Crystal Structure of Dimeric Dimethylindium Pyridine-2-carbaldehyde Oximate

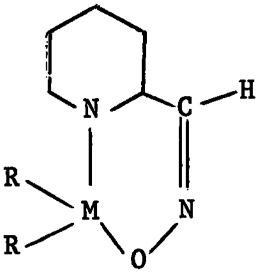
5.1. Introduction

Following upon the well known fact that oximes, RR'C:NOH, cleave alkyl groups from reactive organometallic compounds, the acetoxime derivatives $(Me_2C{:}NOMMe_2)_n$ of boron, aluminium, gallium and thallium have recently been prepared, by the cleavage of methane from the methyl derivative of the appropriate element using acetoxime (Jennings and Wade, 1967). These compounds have structures based on a six membered ring as shown in (I):



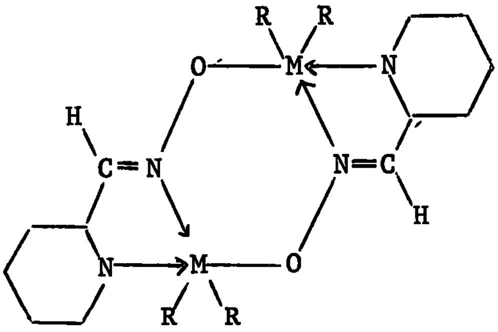
(I)

The products of the reaction between pyridine-2-aldoxime and the group III metal alkyls were investigated to determine the possibility of obtaining monomeric derivatives of type (II) rather than derivatives of type (I)



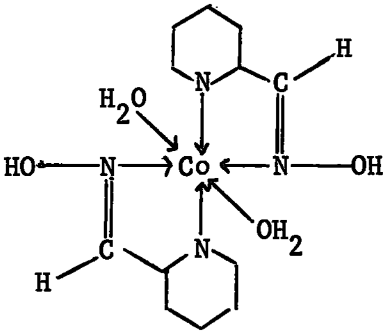
(II)

Of the derivatives prepared only that of boron was found to exist in solution, and probably in the solid, as a monomer. The aluminium, indium and thallium derivatives were found to be dimers in solution and in the solid. Certain aspects of the n.m.r. and i.r. data, namely the downfield movement of the M-CH_3 attached protons and the weakness of M-CH_3 symmetric stretching vibrations, were taken as indicative of an increase in coordination number of the metal atom to five, and structure (III) was proposed for these derivatives



(III)

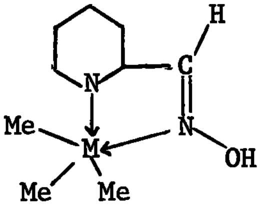
This structure incorporates two types of heterocyclic ring as well as pyridine rings. One is the MONMON ring which is thought to exist in all associated metal derivatives of oximes, and the other is a five membered ring which is thought to be very common among transition metal derivatives of pyridine-2-aldoxime, for example in the following cobalt complex. (Blackmore and Magee, 1967)



The dimer (III) can be regarded as being formed either by,

(a) elimination of alkane, formation of the $(MON)_2$ ring and finally coordination of the pyridine nitrogen or by,

(b) formation of the monomer



elimination of methane, and finally coupling of two monomers to give the $(MON)_2$ ring.

The indium derivative of type (III) was the most suitable for an X-ray analysis and crystals for that purpose were prepared in the following manner. Trimethyl indium was condensed into a cold trap at -196°C containing pyridine-2-aldoxime in solution in toluene, and the trap was allowed to warm up. Methane was evolved and the solution was slightly yellow in colour. Toluene was removed until the solid was deposited, this was then filtered off and recrystallised from benzene as very thin, transparent plate-like crystals with a faint yellow colouration, m.p. 164°C. Though hydrolysed by water the crystals did not decompose in relatively dry air and it was not found necessary to work with them sealed in glass tubes (Pattison and Wade, 1967).

5.2. Crystal Data

Preliminary photographs taken on the Weissenberg and precession cameras showed the compound to crystallise in the orthorhombic system. The conditions limiting the observed reflections are,

hk0: $h + k = 2n$; h0l: $l = 2n$; 0kl: $k = 2n$;

h00: $(h = 2n)$; 0k0: $(k = 2n)$; 00l: $(l = 2n)$;

from which the space group was unambiguously assigned as Pbcn, No.60 in International Tables for X-ray Crystallography.

The unit cell dimensions and their standard deviations were obtained from a least squares treatment of the θ values of several high order reflections, measured on the four-circle diffractometer

	Length (Å)	e.s.d.
a	33·15	0·01
b	9·541	0·004
c	14·30	0·01

$U = 4523\text{Å}^3$; $Z = 8$ units of $[(C_5H_4NCH{:}NOInMe_2)_2\cdot\frac{1}{2}C_6H_6]$

$D_{calc} = 1{\cdot}618\ g.cm^{-3}$; $D_{obs} = 1{\cdot}61\ g.cm^{-3}$;

M.W $[(C_5H_4NCH{:}NOInMe_2)_2 \cdot \frac{1}{2}C_6H_6]$ = 571·02

Absorption coefficient for Mo Kα radiation = 20·5 cm^{-1}.

5.3. Data Collection

The crystal used for data collection was a very thin plate with well developed {100} faces, of dimension 0·35 by 0·22 by 0·01 mm. The data was collected on the Hilger and Watts four circle instrument in the manner previously outlined in section 4.3, using Mo Kα radiation. The length of the $\underline{a}$ axis necessitated a small scanning range for each reflection. An octant of the sphere of reflection up to $\theta = 20^o$ was collected for both the set of reflections (hkl) and the equivalent set $(hk\bar{l})$.

The data was corrected for Lorentz and polarisation factors but not for absorption. It was then scaled as described previously and equivalent reflections averaged.

A total of 2120 independent planes was obtained, of which 1377, having a net count greater than two e.s.d.'s of that net count, were classed as observed reflections.

5.4. The Patterson Function

The corrected values of the intensity data, weighted by the factor w which took the same form as mentioned earlier, were employed in evaluating the Patterson function.

The expression for the function reduces to

$$P(u,v,w) = \frac{8}{V}\sum_{0}^{h}\sum_{0}^{k}\sum_{0}^{l} w(hkl)|F(hkl)|^{2}\cos 2\pi hu\ \cos 2\pi kv\ \cos 2\pi lw$$

the symmetry of this vector set being Pmmm. The function was calculated over one eighth of the unit cell:

u at intervals of 0·276Å from 0 to a/2
v " 0·239Å " 0 to b/2
w " 0·358Å " 0 to c/2

The principle vectors in the function arise from the two independent indium atoms in the dimer and their symmetry related atoms. The expected size of an In-In single-weight peak was 300 and that of a double-weight peak 600.

The basic solution of the Harker sections and lines was straight forward and is summarised below.

Harker Section/Line	Peak Size	x/120	y/40	z/40
u, v, $\frac{1}{2}$	710	24	7	
	572	11	5	
$\frac{1}{2}$, v, w	609		7	8$\frac{1}{2}$
	611		5	3
u, 0, w	671	11		3
	647	24		8$\frac{1}{2}$
u, $\frac{1}{2}$, 0	1370 *	24		
	1229	11		
0, v, $\frac{1}{2}$	1408		6$\frac{1}{2}$	
$\frac{1}{2}$, $\frac{1}{2}$, w	1453			8$\frac{1}{2}$
	1294			3

* The Harker lines are common to four asymmetric units and hence the peaks have quadruple weight.

The (x,y,z) coordinates obtained for the two independent indium atoms are $\left(\frac{24}{120}, \frac{7}{40}, \frac{8\frac{1}{2}}{40}\right)$ and $\left(\frac{11}{120}, \frac{5}{40}, \frac{3}{40}\right)$. These positions were confirmed by the location of two peaks at (2x,2y,2z) with heights of 284 and 261 respectively, corresponding to vectors between the above two atoms and an atom related to each of them by a centre of symmetry.

It was then necessary to fix the positions of the indium atoms with reference to each other. The above coordinates were initially assigned as In(1) and In(2) respectively, and the vectors between In(1) and In(2), in all the latter's equivalent positions, were evaluated and found to be present in the function. The magnitudes of the peaks were all in the range 600 to 680, and a total of eight In(1)-In(2) vectors were found. No other large peaks were present in the function and the coordinates of the atoms obtained were

	x/a	y/b	z/c
In(1)	0·200	0·175	0·2125
In(2)	0·0917	0·125	0·075

5.5. Light Atom Positions

The coordinates of the indium atoms were improved through two cycles of least squares refinement, after which the value for R was 0·26. The structure factors based on the positions of the two heavy atoms were then used to compute a Fourier map. From this it was possible to assign positions to all the remaining atoms except the hydrogens. The position of the pyridine nitrogen atoms were chosen on the basis of peak heights, the sites chosen having values of 6·1 and 5·1 e.Å^{-3}, while the electron density at the other ring sites was on average 4 e.Å^{-3}. The initial arrangement gave the indium atoms a coordination number of five. There were also four peaks of height 2 e.Å^{-3} arranged about the two-fold axis of which no account was taken at this stage.

5.6. Refinement

The first set of structure factors based on the atomic positions obtained from the Fourier synthesis, yielded a value of 0·17 for R. Two cycles of refinement, all atoms being refined isotropically, reduced R to 0·13. The atoms were then refined with anisotropic temperature parameters and account was taken of the anomalous scattering of the indium atoms, although the maximum value for the imaginary dispersion correction $\Delta f''$, was only 1·7 electrons. After several cycles of refinement R reduced to 0·094.

A difference map calculated at this point revealed the four peaks mentioned previously, again of approximate size 2 e.Å^{-3}. These peaks formed part of a benzene ring situated on the two-fold rotation axis parallel to the <u>b</u> axis, with two atoms lying on the rotation axis. These additional four carbon atoms were then assigned isotropic temperature parameters and were included in the overall refinement, R improving to 0·060.

At this stage an attempt was made to test the validity of the initial assignments of the atoms in the pyridine rings, by refining the atoms at the sites occupied by N(3) and N(4) as carbons and those at C(5) and C(13) as nitrogens. A rerun of the previous few cycles saw R increase to the slightly higher value of 0·061. An inspection of the temperature parameters revealed that while the 'new' carbon atoms had values appreciably lower than the other carbon atoms of the rings the 'new' nitrogen atoms had values appreciably higher than the atoms N(1) and N(2), in contrast to the values obtained with the initial assignment where no appreciable differences were noted. These facts appear to support the initial assignment.

After adjustments to the parameters of the weighting scheme the final cycle of refinement with all shifts less than one third of the corresponding e.s.d.'s, yielded the value 0·059 for R. A difference map calculated after this cycle showed no peaks larger than 0·8 e.Å^{-3}. The principle features were several peaks of size 0·5 e.Å^{-3} in positions which could possibly be attributable to the hydrogen atoms of the benzene and pyridine rings, though not all possible hydrogen atoms were found. Positions for the hydrogen atoms of these rings were then calculated and included in the structure factor calculations. They failed to produce any marked effect and R remained at 0·059.

No peaks were located on the map which could have been due to hydrogen atoms to the sites N(3) and N(4), providing further confirmation of the assignment of nitrogen atoms to these sites.

The final values of the atomic coordinates and anisotropic temperature parameters both with their standard deviations are given in Tables 5a and 5b respectively. The details of the four carbon atoms of the benzene of crystallisation are given in Table 5c.

During the final cycle of refinement the weighting scheme employed for both the previous refinements was used, with the following values for the parameters,

$$p_1 = 350, \qquad p_2 = 10^{-3}, \qquad p_3 = 3 \times 10^{-5}$$

A large value for p_1 was necessary in order to down weight the planes with small values of $|F_o|$. The averaged $w\Delta^2$ for the planes in the lower ranges of $|F_o|$ are still greater than for the other ranges. The least squares totals and the weighting analysis, in terms of the magnitudes of the $|F_o|$, are given in Table 5d. An almost identical pattern was observed in the weighting analysis of an iridium complex, the data for which had been collected in a similar manner and for which the reflections were classed as observed at the two e.s.d. level (Schneider, 1969). That the same situation did not occur for $Cl_2Be_3(OBu^t)_4$, for which the observed reflections were accepted only at the three e.s.d. level, suggests that with a higher acceptance level the discrepancies in the weighting analysis could have been alleviated for the present compound.

$(C_5H_4NCH:NOInMe_2)_2$ TABLE 5a

Final Values of the Atomic Coordinates and their Standard Deviations

Atom	x/a	y/b	z/c	σ(x/a)	σ(y/b)	σ(z/c)
In(1)	0·19925	0·17446	0·21639	0·00005	0·00017	0·00011
In(2)	0·09112	0·12740	0·07348	0·00005	0·00017	0·00013
O(1)	0·12657	0·32148	0·10143	0·00041	0·00150	0·00096
O(2)	0·18606	0·07565	0·07754	0·00044	0·00173	0·00109
N(1)	0·15107	0·33536	0·17627	0·00047	0·00156	0·00106
N(2)	0·15032	0·00852	0·06376	0·00047	0·00178	0·00106
N(3)	0·19896	0·37567	0·32850	0·00050	0·00166	0·00121
N(4)	0·07859	-0·12107	0·02279	0·00054	0·00193	0·00141
C(1)	0·25774	0·23771	0·16633	0·00081	0·00297	0·00171
C(2)	0·17063	0·02221	0·30697	0·00084	0·00259	0·00156
C(3)	0·14808	0·45670	0·22195	0·00064	0·00209	0·00159
C(4)	0·17321	0·47565	0·30351	0·00067	0·00198	0·00150
C(5)	0·16844	0·59977	0·35394	0·00061	0·00188	0·00152
C(6)	0·19402	0·62222	0·43068	0·00067	0·00248	0·00151
C(7)	0·22231	0·51540	0·45684	0·00083	0·00251	0·00153
C(8)	0·22447	0·39561	0·40217	0·00072	0·00254	0·00142
C(9)	0·07018	0·19761	-0·05927	0·00074	0·00253	0·00163
C(10)	0·06291	0·09038	0·20972	0·00084	0·00344	0·00195
C(11)	0·15180	-0·12604	0·04388	0·00067	0·00228	0·00135
C(12)	0·11332	-0·19474	0·02102	0·00065	0·00224	0·00138
C(13)	0·11450	-0·33972	0·00016	0·00085	0·00234	0·00180
C(14)	0·07826	-0·39999	-0·02745	0·00088	0·00292	0·00208
C(15)	0·04242	-0·32011	-0·02783	0·00088	0·00294	0·00189
C(16)	0·04332	-0·18031	-0·00452	0·00081	0·00258	0·00206

$(C_5H_4NCH{:}NOInMe_2)_2$ TABLE 5b

Final Values of Anisotropic Temperature Parameters (Å^2) and their Standard Deviations

($\text{Å}^2 \times 10^4$ for In, $\text{Å}^2 \times 10^3$ for O, N, C)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
In(1)	0·0668(11)	0·0586(10)	0·0517(9)	0·0011(9)	-0·0004(10)	0·0042(10)
In(2)	0·0629(11)	0·0562(9)	0·0741(11)	-0·0005(9)	-0·0029(10)	0·0030(10)
O(1)	0·063(9)	0·063(10)	0·064(10)	0·006(8)	-0·012(8)	-0·002(8)
O(2)	0·066(10)	0·098(13)	0·073(10)	-0·017(11)	-0·009(9)	-0·000(9)
N(1)	0·067(11)	0·025(10)	0·047(10)	-0·001(8)	-0·008(9)	-0·022(9)
N(2)	0·065(12)	0·058(11)	0·032(10)	-0·018(10)	-0·007(8)	0·013(9)
N(3)	0·072(12)	0·039(10)	0·075(12)	0·010(9)	0·025(10)	0·033(11)
N(4)	0·078(13)	0·059(12)	0·092(15)	-0·019(12)	0·015(12)	-0·001(11)
C(1)	0·092(20)	0·093(20)	0·068(16)	-0·006(15)	-0·011(15)	-0·035(17)
C(2)	0·137(23)	0·066(18)	0·050(16)	0·027(14)	0·019(15)	-0·018(17)
C(3)	0·074(16)	0·040(14)	0·065(16)	0·006(13)	0·018(14)	-0·006(11)
C(4)	0·091(17)	0·028(13)	0·060(16)	-0·017(12)	0·003(13)	-0·029(12)
C(5)	0·066(14)	0·021(12)	0·075(16)	0·019(12)	0·011(12)	-0·020(11)
C(6)	0·080(17)	0·076(16)	0·056(14)	0·029(14)	0·015(14)	-0·026(15)
C(7)	0·161(24)	0·060(16)	0·046(15)	0·023(13)	-0·027(16)	-0·085(18)
C(8)	0·099(18)	0·079(17)	0·045(15)	0·001(13)	-0·049(13)	-0·021(16)
C(9)	0·093(18)	0·073(16)	0·066(17)	0·016(15)	-0·042(15)	-0·023(15)
C(10)	0·104(22)	0·141(27)	0·085(21)	-0·003(22)	0·040(18)	0·004(21)
C(11)	0·087(17)	0·053(14)	0·039(13)	-0·022(12)	-0·001(12)	0·012(13)
C(12)	0·078(16)	0·058(14)	0·038(13)	-0·006(12)	0·023(12)	-0·010(13)
C(13)	0·140(23)	0·043(15)	0·083(19)	0·002(15)	0·030(18)	0·027(16)
C(14)	0·127(24)	0·084(21)	0·110(24)	-0·009(19)	0·037(20)	-0·031(19)
C(15)	0·128(23)	0·088(20)	0·082(20)	0·012(18)	-0·004(18)	-0·019(19)
C(16)	0·109(21)	0·065(16)	0·117(23)	0·001(18)	-0·046(19)	-0·052(17)

$(C_5H_4NCH:NOInMe_2)_2$ TABLE 5c

Benzene of Crystallisation: Final Values of Positional and Thermal Parameters

Atom	x/a	y/b	z/c	σ(x/a)	σ(y/b)	σ(z/c)	$B_{iso}(\overset{o}{A}^2)$	$\sigma(B_{iso})$
C(17)	0•0	0•41326	0•25000	0•0	0•00407	0•0	7•4	1•0
C(18)	0•03438	0•49201	0•21982	0•0084	0•00329	0•00213	8•5	0•8
C(19)	0•03243	0•63787	0•21956	0•00081	0•00295	0•00199	8•0	0•7
C(20)	0•0	0•70762	0•25000	0•0	0•00469	0•0	8•9	1•1

$(C_5H_4NCH{:}NOInMe_2)_2$ TABLE 5d

Least Squares Totals

Number of observed planes 1377

$\Sigma\|F_o\|$	$\Sigma\|F_o\|$	$\Sigma\|\Delta\|$	$\Sigma w\Delta^2$	R
120490·0	119479·8	7151·3	145·1	0·059

Weighting Analysis

$\|F_o\|$ ranges	N	$\Sigma w\Delta^2/N$	R
0-40	232	0·19	0·19
40-50	192	0·16	0·12
50-60	157	0·09	0·09
60-70	133	0·07	0·07
70-80	97	0·08	0·06
80-100	176	0·05	0·05
100-120	125	0·07	0·05
120-160	119	0·06	0·03
160 upwards	146	0·09	0·03

$(C_5H_4NCH{:}NOInMe_2)_2$ TABLE 5e

The Observed and Calculated Structure Factors

H	K	L	|FO|	FC	H	K	L	|FO|	FC	H	K	L	|FO|	FC	H	K	L	|FO|	FC	H	K	L	|FO|	FC	H	K	L	|FO|	FC
0	2	0	130	-128	4	4	1	119	122	24	5	1	51	48	14	1	2	93	-87	8	2	3	67	-58	4	4	4	52	-40
0	4	0	444	-432	4	5	1	49	55	25	1	1	82	-83	14	2	2	95	-84	8	3	3	56	47	4	6	4	61	47
0	6	0	237	241	4	6	1	78	-85	25	2	1	90	-84	14	4	2	50	48	8	4	3	120	120	4	7	4	94	-86
0	8	0	45	41	4	7	1	77	84	25	5	1	38	53	14	5	2	109	100	8	6	3	38	-40	5	0	4	212	182
1	1	0	179	174	4	9	1	58	-53	26	1	1	69	-62	14	6	2	29	-27	8	7	3	43	-48	5	1	4	107	109
1	3	0	236	-233	5	1	1	178	-184	26	2	1	38	12	14	7	2	55	-57	8	8	3	36	-34	5	2	4	59	61
1	5	0	80	-71	5	2	1	200	-188	26	3	1	47	-39	14	8	2	35	37	9	1	3	90	-82	5	3	4	206	-199
1	7	0	77	78	5	3	1	71	72	26	5	1	37	52	15	0	2	113	-124	9	2	3	134	-130	5	4	4	92	95
2	0	0	179	-205	5	4	1	53	43	27	1	1	85	87	15	1	2	166	-166	9	3	3	85	-83	5	7	4	48	43
2	2	0	32	34	5	5	1	52	58	28	1	1	45	41	15	3	2	227	223	9	4	3	118	108	6	0	4	98	98
2	4	0	66	-62	5	6	1	48	48	28	2	1	104	90	15	4	2	91	96	9	5	3	31	41	6	1	4	120	119
2	6	0	99	-99	5	7	1	146	-136	28	4	1	45	-46	15	5	2	48	-50	10	2	3	98	-100	6	2	4	45	-34
2	8	0	77	78	5	9	1	42	45	29	2	1	60	68	15	7	2	43	-45	10	3	3	47	-37	6	3	4	212	-213
3	1	0	149	-145	6	1	1	33	37	29	3	1	38	16	15	8	2	50	-50	10	4	3	145	-144	6	5	4	65	57
3	3	0	145	154	6	2	1	53	53	30	1	1	64	67	16	0	2	173	-181	10	6	3	177	161	7	0	4	270	281
3	5	0	113	-110	6	3	1	33	33	30	2	1	61	-57	16	1	2	62	-63	10	8	3	35	36	7	1	4	60	-63
4	0	0	219	-261	6	4	1	60	60	30	3	1	37	43	16	3	2	87	83	11	1	3	62	-69	7	2	4	154	-152
4	2	0	75	-59	6	5	1	33	-40	31	2	1	43	43	16	4	2	103	107	11	2	3	147	148	7	3	4	82	83
4	4	0	176	169	6	6	1	63	-65	0	0	2	30	19	16	6	2	31	-34	11	3	3	152	-143	7	4	4	205	-206
4	8	0	68	-72	6	7	1	38	-36	0	2	2	40	56	17	0	2	45	-41	11	4	3	98	-97	7	5	4	62	-64
5	1	0	208	-216	6	8	1	33	10	0	4	2	155	-144	17	1	2	71	-70	11	5	3	57	45	7	6	4	91	90
5	3	0	25	-28	7	1	1	263	275	0	6	2	107	-108	17	3	2	27	-39	11	7	3	94	89	8	0	4	153	-156
5	5	0	284	276	7	2	1	176	173	0	8	2	128	123	17	5	2	114	108	12	1	3	36	32	8	1	4	66	66
5	7	0	76	-81	7	3	1	58	49	1	0	2	298	-301	17	7	2	60	-67	12	2	3	321	-317	8	2	4	109	101
5	9	0	125	-139	7	4	1	25	21	1	1	2	191	206	18	0	2	62	66	12	3	3	82	-77	8	3	4	43	-48
6	0	0	77	-74	7	5	1	155	-153	1	2	2	155	154	18	1	2	89	89	12	4	3	130	125	8	5	4	176	-173
6	2	0	121	105	7	6	1	136	-136	1	3	2	51	-49	18	2	2	94	-99	12	6	3	68	69	8	6	4	88	-80
6	4	0	217	209	8	1	1	201	200	1	4	2	100	95	18	3	2	111	-116	12	7	3	37	44	8	7	4	50	52
6	6	0	57	66	8	2	1	280	273	1	5	2	74	-77	18	4	2	31	29	13	1	3	155	-154	8	8	4	46	37
6	8	0	106	-113	8	3	1	109	104	1	6	2	86	-87	18	6	2	79	87	13	2	3	101	-111	9	0	4	93	89
7	1	0	266	-265	8	4	1	143	-136	1	7	2	40	50	19	0	2	231	249	13	4	3	42	23	9	2	4	113	107
7	3	0	432	423	8	5	1	136	-135	1	9	2	44	50	19	1	2	25	-23	13	5	3	119	107	9	4	4	121	-121
7	5	0	56	-52	8	6	1	28	24	2	0	2	347	356	19	3	2	25	29	14	1	3	134	-135	9	5	4	47	48
7	7	0	51	-52	8	7	1	38	-32	2	1	2	318	-325	19	4	2	104	-99	14	2	3	108	104	9	6	4	84	-84
8	0	0	401	-428	8	8	1	41	42	2	2	2	250	-242	20	0	2	111	-124	14	3	3	39	39	9	8	4	111	115
8	2	0	23	25	9	1	1	90	-97	2	3	2	184	173	20	1	2	82	84	14	4	3	34	-32	10	0	4	91	93
8	4	0	163	156	9	2	1	323	328	2	4	2	129	-121	20	2	2	92	94	14	5	3	61	55	10	1	4	57	55
8	6	0	76	-79	9	3	1	33	-28	2	5	2	130	132	20	3	2	80	-80	14	7	3	61	-67	10	2	4	119	-119
8	8	0	40	32	9	4	1	58	-61	2	6	2	135	128	20	4	2	28	18	15	1	3	258	258	10	3	4	77	-79
9	3	0	133	-129	9	5	1	95	90	2	7	2	72	-84	20	5	2	43	-49	15	2	3	33	-36	10	5	4	79	-80
9	7	0	38	39	9	6	1	103	-102	2	8	2	56	-44	20	6	2	55	-63	15	3	3	70	76	10	6	4	79	72
10	0	0	382	431	10	1	1	164	159	2	9	2	44	-48	20	7	2	43	41	15	5	3	152	-147	10	7	4	32	33
10	2	0	172	-171	10	2	1	302	-307	3	0	2	305	-319	21	1	2	56	53	16	1	3	72	71	10	8	4	58	-57
10	4	0	360	-302	10	3	1	66	69	3	1	2	59	52	21	4	2	49	-51	16	2	3	199	197	11	0	4	150	146
10	6	0	105	100	10	4	1	212	211	3	2	2	116	-99	21	5	2	47	-53	16	4	3	89	-78	11	1	4	29	-24
11	1	0	306	304	10	5	1	66	-65	3	3	2	199	-204	22	0	2	188	182	16	6	3	62	-61	11	3	4	30	26
11	3	0	274	-264	10	8	1	66	-74	3	4	2	219	216	22	2	2	49	-50	16	7	3	42	47	11	5	4	36	47
11	5	0	51	-47	11	1	1	146	-146	3	5	2	125	124	22	3	2	44	41	17	2	3	90	85	11	6	4	83	83
11	7	0	93	101	11	2	1	66	-68	3	8	2	101	-106	22	4	2	85	-88	17	3	3	114	107	12	0	4	175	-174
12	0	0	42	28	11	3	1	67	-65	3	9	2	61	-53	22	6	2	44	51	17	4	3	43	-45	12	2	4	91	87
12	2	0	165	170	11	5	1	84	83	4	0	2	366	-368	23	0	2	37	-41	17	7	3	109	-101	12	4	4	45	48
12	4	0	99	-94	11	6	1	30	37	4	1	2	55	58	23	1	2	74	74	18	1	3	50	-52	12	5	4	108	105
12	6	0	120	-126	12	1	1	125	-125	4	2	2	132	118	23	2	2	33	-30	18	3	3	42	40	12	6	4	58	-71
12	8	0	131	140	12	2	1	41	39	4	4	2	148	142	23	3	2	131	-121	18	4	3	97	92	13	0	4	336	-335
13	3	0	80	81	12	3	1	117	-123	4	5	2	103	94	23	4	2	44	46	18	5	3	36	14	13	1	4	54	-54
13	5	0	135	-134	12	4	1	119	-127	4	6	2	46	-45	24	1	2	34	-39	18	6	3	68	-74	13	3	4	108	109
14	0	0	31	31	12	5	1	75	72	4	7	2	45	-45	24	5	2	54	51	18	7	3	40	-47	13	4	4	152	155
15	3	0	59	-61	12	6	1	77	84	5	1	2	210	-208	25	0	2	65	-64	19	1	3	53	58	13	5	4	70	-66
15	5	0	164	165	12	7	1	57	55	5	3	2	345	340	25	1	2	43	-40	19	2	3	65	-62	13	6	4	61	-50
15	7	0	42	-39	13	1	1	155	155	5	4	2	44	30	25	3	2	85	84	19	3	3	28	31	14	0	4	51	47
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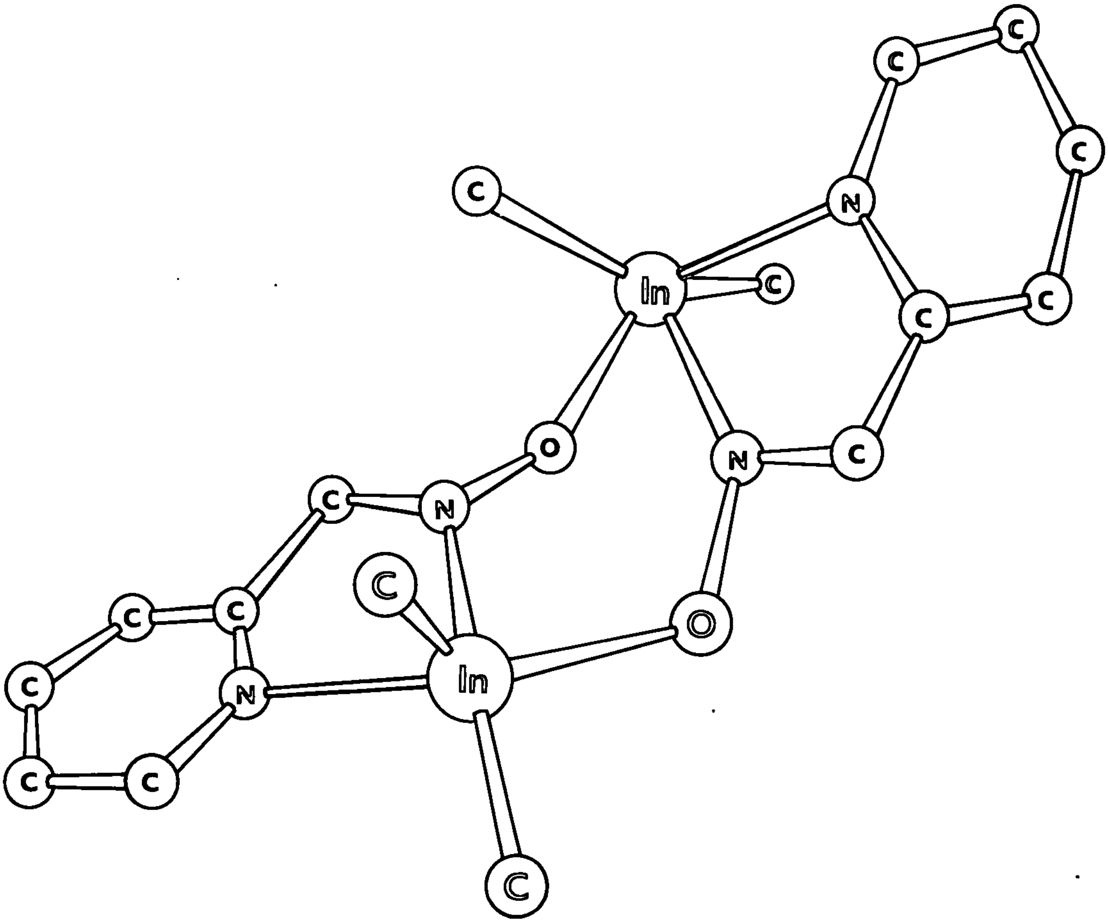
5	4	8	27	-18
5	5	8	55	-56
5	7	8	59	59
6	0	8	62	64
6	1	8	71	71
6	2	8	37	-38
6	3	8	151	-148
6	4	8	86	-90
6	5	8	80	85
7	0	8	108	108
7	1	8	31	29
7	2	8	69	-66
7	3	8	74	-83
7	5	8	42	-30
7	6	8	35	38
8	0	8	101	102
8	1	8	117	-118
8	3	8	133	131
9	0	8	231	-236
9	2	8	91	99
9	3	8	63	67
9	4	8	103	105
9	6	8	76	-68
10	0	8	91	-93
10	1	8	52	-54
10	3	8	45	33
10	4	8	104	106
11	0	8	179	174
11	1	8	88	-88
11	2	8	86	-88
11	3	8	85	84
11	5	8	55	48
11	6	8	89	94
12	0	8	108	-108
12	1	8	76	77
12	3	8	77	-79
12	4	8	45	42
13	0	8	45	-48
13	1	8	46	-42
13	2	8	46	52
13	4	8	41	-46
13	6	8	51	-52
14	1	8	31	-32
14	3	8	57	51
14	5	8	72	-71
15	1	8	44	45
15	3	8	32	-31
15	5	8	70	-64
16	0	8	88	92
16	1	8	57	52
16	3	8	119	-105
16	4	8	62	-60
16	5	8	61	57
17	0	8	84	78
17	1	8	61	57
17	2	8	56	-40
17	3	8	46	-36
18	0	8	99	93
18	1	8	34	-32
18	3	8	85	85
18	4	8	69	-64
19	0	8	168	-164
19	2	8	46	50
19	4	8	61	61
20	0	8	69	-69
20	1	8	36	-36
20	3	8	41	34
20	4	8	54	53
21	0	8	50	51
21	1	8	56	-49
21	2	8	38	-43
22	0	8	49	-51
22	3	8	61	-65
23	3	8	44	43
0	2	9	166	184
0	4	9	28	-34
0	6	9	58	-68
1	1	9	112	114
1	2	9	84	-87
1	3	9	74	70
1	4	9	107	109
1	5	9	51	-58
2	2	9	37	37
2	3	9	49	46
2	4	9	33	30
2	6	9	49	-36
3	1	9	102	-99
3	2	9	137	146
3	3	9	42	-38
3	4	9	71	-76
4	1	9	188	191
4	2	9	63	-64
4	5	9	99	-103
4	6	9	38	45
5	1	9	36	-35
5	2	9	32	30
5	3	9	40	-49
5	5	9	47	47
6	1	9	129	-127
6	2	9	110	-104
6	5	9	65	78
6	6	9	72	66
7	1	9	68	-69
7	2	9	124	-127
7	3	9	45	-52
7	4	9	87	79
7	5	9	48	43
8	1	9	32	26
8	2	9	73	-69
8	3	9	60	-63
9	1	9	51	52
9	2	9	32	33
9	4	9	91	-84
9	5	9	34	-38
9	6	9	74	76
10	1	9	29	-25
10	2	9	133	128
10	4	9	38	-41
11	1	9	83	82
11	2	9	75	-77
11	3	9	58	62
11	4	9	81	81
11	5	9	49	-49
11	6	9	35	-38
12	1	9	46	-40
12	2	9	59	60
12	3	9	34	36
12	4	9	34	36
12	6	9	52	-57
13	2	9	89	90
13	3	9	43	33
13	4	9	46	-46
14	1	9	147	149
14	5	9	85	-91
15	2	9	34	27
15	3	9	45	-47
16	1	9	83	-89
16	2	9	55	-51
16	5	9	46	48
17	1	9	70	-66
17	2	9	53	-49
17	3	9	39	-40
17	4	9	47	47
18	2	9	81	-78
19	2	9	29	24
19	4	9	72	-82
20	2	9	60	56
21	1	9	41	38
21	2	9	79	-75
22	1	9	44	-40
22	2	9	40	36
23	2	9	44	40
0	0	10	81	77
0	6	10	44	51
1	0	10	60	-61
1	2	10	56	64
1	6	10	61	-53
2	0	10	62	-57
2	1	10	51	50
2	4	10	36	17
2	5	10	89	-85
3	0	10	165	168
3	2	10	32	-38
3	3	10	30	35
3	4	10	115	-116
3	5	10	31	-22
3	6	10	44	46
4	1	10	77	79
4	3	10	148	-146
5	0	10	31	29
5	1	10	53	58
5	3	10	75	-82
6	1	10	66	-60
6	3	10	88	91
6	5	10	53	-94
7	0	10	148	-158
7	1	10	47	-47
7	2	10	36	29
7	3	10	43	44
7	4	10	92	83
7	6	10	36	-35
8	0	10	51	-54
8	1	10	29	-24
8	3	10	40	39
8	5	10	92	91
9	0	10	41	31
9	2	10	60	-74
9	4	10	37	31
10	0	10	64	64
11	0	10	124	-130
11	2	10	61	68
11	3	10	36	-27
12	0	10	76	-80
12	2	10	42	47
12	5	10	69	-71
13	0	10	143	143
13	1	10	36	-29
13	2	10	35	-36
13	3	10	50	48
13	4	10	87	-84
13	5	10	34	-13
14	1	10	87	84
14	2	10	31	-17
14	3	10	115	-110
15	0	10	74	71
15	1	10	46	30
15	3	10	39	-46
15	4	10	50	-45
16	0	10	43	40
16	3	10	62	59
17	0	10	85	-88
17	2	10	40	35
17	4	10	41	41
20	1	10	43	-48
20	2	10	40	-26
21	0	10	89	-89
0	2	11	48	50
0	4	11	66	61
1	3	11	54	50
1	4	11	77	-81
2	2	11	74	78
2	4	11	51	-63
3	1	11	45	46
3	2	11	48	-50
4	1	11	95	-93
4	2	11	83	-89
4	5	11	39	44
5	1	11	130	-137
5	3	11	41	-31
5	5	11	87	85
6	1	11	96	100
6	2	11	109	-100
6	4	11	33	33
7	2	11	55	62
7	4	11	59	-51
8	1	11	38	-42
8	2	11	43	42
8	4	11	61	-67
8	5	11	40	29
9	4	11	45	49
11	1	11	45	42
11	2	11	49	49
11	3	11	48	50
11	4	11	44	-52
12	1	11	42	39
12	2	11	98	101
13	1	11	52	60
13	2	11	43	-56
13	4	11	44	38
14	1	11	77	-80
14	2	11	37	-38
15	1	11	86	-88
15	2	11	33	-28
15	3	11	33	-11
16	1	11	51	34
16	2	11	70	-68
0	0	12	34	-25
0	2	12	36	25
0	4	12	52	-37
1	0	12	91	98
2	0	12	81	82
2	1	12	56	60
2	3	12	61	-60
3	3	12	80	-84
4	0	12	59	-59
4	4	12	45	33
5	1	12	68	-72
5	3	12	109	116
6	0	12	75	-79
6	4	12	42	42
7	4	12	37	37
8	0	12	62	66
8	2	12	43	-46
8	3	12	49	48
9	0	12	96	-87
10	2	12	56	52
11	0	12	37	37
11	2	12	43	-36
12	0	12	88	92
12	2	12	35	-38
13	1	12	36	33
15	0	12	37	37
15	1	12	57	-57
0	2	13	116	117
1	2	13	63	-64
2	1	13	67	-64
2	2	13	52	-51
2	3	13	56	-46
3	1	13	52	-50
5	1	13	49	48
7	1	13	60	-62
8	1	13	36	49
8	2	13	44	-71
10	1	13	50	36



$(Me_2InON{:}CH{\cdot}py)_2$

Figure 5.1

5.7. Description and Discussion of the Structure

The molecule is composed of five heterocyclic rings as illustrated in Figure 5.1, the indium atoms being five-coordinate. The five rings are the two pyridine and two C•N•In•N•C rings and the central InONInON ring. If the molecule is divided into two equal halves by means of a line drawn through O(1) and O(2), the two halves are to a crude approximation planar and inclined to one another at an angle of approximately 55°.

The planarities of the various parts of the molecule are examined by means of Table 5f which lists the equations of the planes, the atoms and their out-of-plane-deviations and e.s.d.'s, and the χ^2 values. These may be compared with the listed χ_p^2 values in order to ascertain the coplanarity of the groups of atoms. With the aid of this table the following facts may be deduced, the two pyridine rings with n = 3, are planar within experimental error; the atoms In(2), O(1), O(2) and N(2) are coplanar but the corresponding set In(1), O(1), O(2) and N(1) are not; while the ring In(1), N(1), N(3), C(3), C(4) is non-planar the planarity of the ring In(2), N(2), N(4), C(11), C(12) can be accepted at the 1% probability level; the atoms In(1), N(1), C(1), C(2) are non-planar as are In(2), N(2), C(9), C(10). If the indium atoms adopted undistorted trigonal bipyramidal geometries these last two groups would each be coplanar.

$(C_5H_4NCH:NOInMe_2)_2$ TABLE 5f

Some Mean Planes

$$0·683X + 0·425Y - 0·594Z - 3·249 = 0$$

Atom	N(3)	C(4)	C(5)	C(6)	C(7)	C(8)	
P	-0·014	0·021	-0·011	0·006	-0·009	0·018	Å
σ(P)	0·017	0·021	0·020	0·022	0·025	0·023	

$$\chi^2 = 2·88$$

$$0·169X + 0·247Y - 0·954Z + 0·136 = 0$$

Atom	N(4)	C(12)	C(13)	C(14)	C(15)	C(16)
P	-0·019	0·026	-0·024	0·007	-0·001	0·016
σ(P)	0·020	0·020	0·026	0·030	0·027	0·029

$$\chi^2 = 3·90$$

$$0·672X + 0·591Y - 0·447Z + 4·041 = 0$$

Atom	In(1)	O(1)	O(2)	N(1)
P	-0·001	-0·057	0·036	0·089
σ(P)	0·002	0·014	0·015	0·015

$$\chi^2 = 56·5$$

$$0·044X + 0·186Y - 0·982Z + 0·671 = 0$$

Atom	In(2)	O(1)	O(2)	N(2)
P	0·000	0·004	-0·009	0·013
σ(P)	0·002	0·014	0·016	0·015

$$\chi^2 = 1·11$$

contd./

TABLE 5f contd.

$$0{\cdot}676X + 0{\cdot}463Y - 0{\cdot}573Z - 3{\cdot}462 = 0$$

Atom	In(1)	N(1)	N(3)	C(3)	C(4)
P	0·000	-0·040	-0·037	0·054	0·033
σ(P)	0·002	0·015	0·017	0·022	0·021

$$\chi^2 = 20{\cdot}50$$

$$0{\cdot}099X + 0{\cdot}264Y - 0{\cdot}959Z + 0{\cdot}388 = 0$$

Atom	In(2)	N(2)	N(4)	C(11)	C(12)
P	0·000	0·028	0·028	-0·033	-0·019
σ(P)	0·002	0·015	0·020	0·020	0·020

$$\chi^2 = 9{\cdot}19$$

$$-0{\cdot}200X - 0{\cdot}532Y - 0{\cdot}823Z + 4{\cdot}754 = 0$$

Atom	In(1)	N(1)	C(1)	C(2)
P	0·001	-0·024	-0·119	-0·102
σ(P)	0·002	0·015	0·026	0·023

$$\chi^2 = 43{\cdot}53$$

$$-0{\cdot}475X - 0{\cdot}849Y - 0{\cdot}232Z + 2{\cdot}708 = 0$$

Atom	In(2)	N(2)	C(9)	C(10)
P	-0·003	0·060	0·199	0·290
σ(P)	0·002	0·017	0·024	0·032

$$\chi^2 = 167{\cdot}9$$

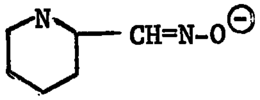
P represents the out-of-plane deviation for the atoms.

X, Y, Z refer to the coordinates in Å units

contd./

TABLE 5f contd.

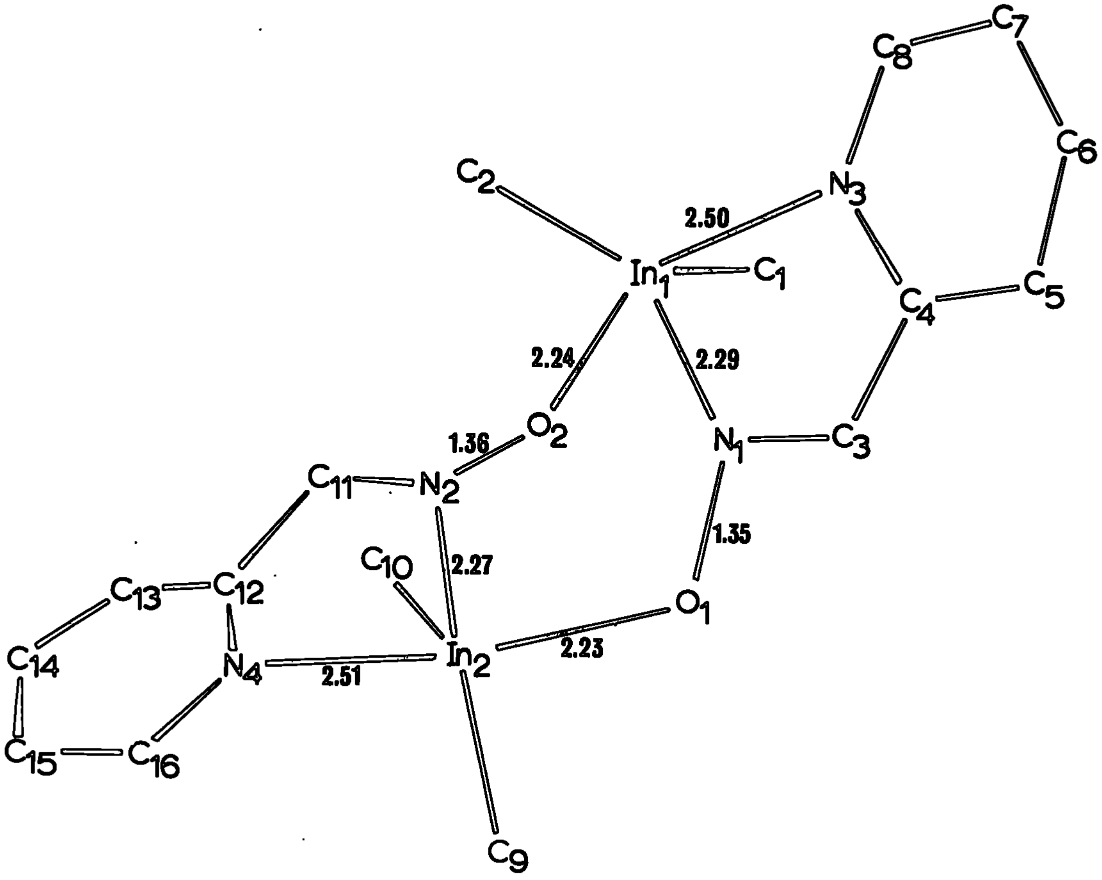
	χ^2_p		
Degrees of Freedom(n)	P = 5%	P = 1%	P = 0·1%
1	3·84	6·64	10·83
2	5·99	9·21	13·82
3	7·82	11·34	16·27

The indium atoms owe their five-coordination to the fact that the ion 

acts as a tridentate ligand. Five-coordination is further discussed in section 5.8, suffice it to say here that the arrangement adopted at the metal is that of a distorted trigonal bipyramid, as noted from Table 5f.

The distances from the indium atoms to their five attached atoms are given in Table 5g along with other bond lengths, and some distances are indicated in Figure 5.2. The In-C distances are all in agreement, the greatest discrepancy being between In(2)-C(9) 2·129Å and In(2)-C(10) 2·190Å and for these t_o = 1·7. The mean In-C distance of 2·16Å may be compared with the mean value found in $(CH_3)_3In$, see section 5.8, of 2·15Å and with the value obtained from electron diffraction work on $(CH_3)_3In$ (Laubengayer and Pauling, 1941) of 2·16 ± 0·04Å.

The two In-O distances are in good agreement, In(1)-O(2), 2·241Å, and In(2)-O(1) 2·229Å. Their mean of 2·235Å is similar to the longer distance found in $InPO_4.2H_2O$ (Monney-Slater, 1961) of 2·25Å, and the value quoted for an In-O distance of 2·23Å by Sutton (1958). The distance is longer than the sum of tetrahedral covalent radii 2·10Å, which is to be expected the indium atoms being penta-coordinate. The indium atoms form two kinds of bond to the nitrogen atoms. The shorter bonds, involving the oximate nitrogen atoms, are In(1)-N(1) 2·288Å and In(2)-N(2) 2·271Å, which are in



$(Me_2InON{:}CH{\cdot}py)_2$

SOME BOND LENGTHS

Figure 5.2

$(C_5H_4NCH{:}NOInMe_2)_2$ TABLE 5g

Bond Lengths and their Standard Deviations (Å)

	Distance	e.s.d.
In(1)-O(2)	2•241	0•016
In(1)-N(1)	2•288	0•015
In(1)-N(3)	2•501	0•017
In(1)-C(1)	2•153	0•027
In(1)-C(2)	2•165	0•025
In(2)-O(1)	2•229	0•014
In(2)-N(2)	2•271	0•016
In(2)-N(4)	2•514	0•019
In(2)-C(9)	2•129	0•024
In(2)-C(10)	2•190	0•028
O(1)-N(1)	1•350	0•021
O(2)-N(2)	1•361	0•022
N(1)-C(3)	1•333	0•026
N(2)-C(11)	1•316	0•028
C(3)-C(4)	1•445	0•031
C(11)-C(12)	1•471	0•031
N(3)-C(4)	1•329	0•026
C(4)-C(5)	1•396	0•027
C(5)-C(6)	1•403	0•030
C(6)-C(7)	1•435	0•034
C(7)-C(8)	1•387	0•033
C(8)-N(3)	1•364	0•028
N(4)-C(12)	1•349	0•028
C(12)-C(13)	1•416	0•031
C(13)-C(14)	1•389	0•040
C(14)-C(15)	1•412	0•041
C(15)-C(16)	1•375	0•038
C(16)-N(4)	1•356	0•032

good agreement, their mean being 2·28Å. A value of 2·27Å can be estimated for the In-N distance based on the In-O distance, and a value of 2·31Å may be estimated from the In-P distance recently found in bistriphenylphosphinetrichloroindium(III) (Palenik and Veidis, 1969). The above In-N distance is in good agreement with these two estimates, but is significantly shorter than the distances found involving the pyridine nitrogen atoms of In(1)-N(3) 2·501Å and In(2)-N(4) 2·514Å. These two distances are themselves in good agreement and the bond lengthening is most probably the result of geometric and steric factors operating on the pyridine rings.

The bond lengths found in the oximate linkages are in good agreement with each other, O(1)-N(1) 1·35Å, O(2)-N(2) 1·36Å, and N(1)-C(3) 1·33Å, N(2)-C(11) 1·32Å, and can be compared with the values obtained for syn- and anti-p-chlorobenzene (Jerslev, 1957), C-N 1·29 and 1·27Å, N-O 1·36 and 1·36Å respectively in the two compounds. The bond lengths C(3)-C(4) 1·45Å and C(11)-C(12) 1·47Å are in good agreement with one another and with the value of 1·45Å in the above compounds.

The bond lengths found in the two pyridine rings are in agreement and may be compared with the values quoted for the free molecule, (and shown below) (Interatomic Distances, 1958). The mean C-N and C-C distances obtained are compatible with the assignments made for the nitrogen atoms.

$(C_5H_4NCH:NOInMe_2)_2$ TABLE 5h

Bond Angles and their Standard Deviations

	Angle	e.s.d.
O(2)-In(1)-N(1)	85•6°	0•6°
O(2)-In(1)-N(3)	152•9	0•6
O(2)-In(1)-C(1)	89•9	0•8
O(2)-In(1)-C(2)	99•3	0•8
N(1)-In(1)-N(3)	69•1	0•5
N(1)-In(1)-C(1)	110•9	0•8
N(1)-In(1)-C(2)	107•1	0•8
N(3)-In(1)-C(1)	90•1	0•8
N(3)-In(1)-C(2)	97•5	0•8
C(1)-In(1)-C(2)	141•4	1•0
O(1)-In(2)-N(2)	88•3	0•5
O(1)-In(2)-N(4)	157•3	0•6
O(1)-In(2)-C(9)	94•0	0•7
O(1)-In(2)-C(10)	101•5	0•9
N(2)-In(2)-N(4)	69•8	0•6
N(2)-In(2)-C(9)	112•6	0•8
N(2)-In(2)-C(10)	110•1	0•9
N(4)-In(2)-C(9)	89•2	0•8
N(4)-In(2)-C(10)	91•9	0•9
C(9)-In(2)-C(10)	134•8	1•0
In(2)-O(1)-N(1)	122•7	1•1
In(1)-O(2)-N(2)	119•7	1•1
In(1)-N(1)-O(1)	123•6	1•1
In(1)-N(1)-C(3)	120•8	1•3
O(1)-N(1)-C(3)	115•4	1•5
In(2)-N(2)-O(2)	120•6	1•1
In(2)-N(2)-C(11)	122•2	1•3
O(2)-N(2)-C(11)	117•2	1•6
In(1)-N(3)-C(4)	112•4	1•3
In(1)-N(3)-C(8)	126•8	1•4
In(2)-N(4)-C(12)	110•8	1•4
In(2)-N(4)-C(16)	128•2	1•6

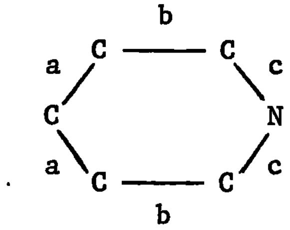
contd./

TABLE 5h contd.

N(1)-C(3)-C(4)	117·5	1·8
N(3)-C(4)-C(3)	119·8	1·9
C(3)-C(4)-C(5)	117·3	1·9
N(2)-C(11)-C(12)	116·8	1·8
N(4)-C(12)-C(11)	120·2	1·9
C(11)-C(12)-C(13)	117·3	1·9

Pyridine ring angles:

C(4)-N(3)-C(8)	120·4	1·8
N(3)-C(4)-C(5)	122·9	1·9
C(4)-C(5)-C(6)	117·7	1·9
C(5)-C(6)-C(7)	119·4	2·0
C(6)-C(7)-C(8)	118·2	2·2
C(7)-C(8)-N(3)	121·2	2·1
C(12)-N(4) -C(16)	120·9	2·0
N(4) -C(12)-C(13)	122·5	2·0
C(12)-C(13)-C(14)	116·1	2·3
C(13)-C(14)-C(15)	120·4	2·6
C(14)-C(15)-C(16)	120·3	2·6
C(15)-C(16)-N(4)	119·5	2·4



c	1·340 Å
b	1·390
a	1·400
cc	116·7°
bc	124·0
ab	118·6
aa	118·1

The bond angles and their e.s.d.'s are given in Table 5h and illustrate the distortions in the geometries at the two metal atoms. Those angles showing the greatest distortions from the trigonal bipyramidal arrangement are O-In-N(pyridine) of 152·9 and 157·3°, N-In-N (pyridine) of 69·1 and 69·8° and C-In-C of 141·4 and 134·8°. The angles for the undistorted geometry would be 180°, 90° and 120° respectively. The distortions in the angles involving N(3) and N(4) can be attributed to the fact that these atoms belong to the pyridine groups. That these groups are endeavouring to achieve the best possible compromise between the In-N bonding, steric effects and geometric considerations is evidenced by the angles at C(3) and C(11), which for undistorted sp^2 hybridised bonds would be 120° but which are found to be 117·5 and 116·8° respectively. The angular distortions involving the methyl carbon atoms are due principally to steric factors. These four atoms project above and below the planes of the molecule and feature in several short non-bonding contacts (see Table 5j), the increase in the angles is seen as an attempt to reduce the strains imposed by the crowded arrangement around the metal atoms.

The angles at O(1) and O(2) are 122•7 and 119•7° respectively in contrast to the tetrahedral value of 109•47°, and the increases are most probably due to a relieving of non-bonding contacts across the central ring. In general the angles presented in Table 5h indicate that the geometries of the two halves of the molecule closely resemble each other. However whereas similar bond lengths in the halves are in good agreement, significant differences are observed between several corresponding angles, so that the halves are not related by an element of symmetry.

The geometry of the benzene of crystallisation is summarised in Table 5i. Only the length C(19)-C(20) 1•34Å, is appreciably shorter than the expected value of 1•395Å. For this distance $t_o = 1{\cdot}5$; hence the difference is not significant. All the angles are in agreement with the expected value of 120°.

The principle non-bonding intramolecular distances across the central InONInON ring are In(1)-In(2) 4•15Å, O(1)-O(2) 3•08Å and N(1)-N(2) 3•51Å all of which conform to expectations based on the Van der Waal's radii. Table 5j lists the intramolecular non-bonding distances apart from those involving atoms of the same group or bonded to the same atom. The existence of several contacts involving the methyl carbons was noted earlier. The distances are such as to suggest that the methyl carbon atoms

$(C_5H_4NCH{:}NOInMe_2)_2$ TABLE 5i

Benzene of Crystallisation: Bond Lengths (Å) and Angles (°)

	Distance	e.s.d.
C(17)-C(18)	1·43	0·04
C(18)-C(19)	1·39	0·04
C(19)-C(20)	1·34	0·04

	Angle	e.s.d.
C(18')-C(17)-C(18)	121·6	2·2
C(17)-C(18)-C(19)	119·2	2·5
C(18)-C(19)-C(20)	122·3	2·6
C(19)-C(20)-C(19')	115·6	2·2

C(18') and C(19') are related to C(18) and C(19) respectively by the 2-fold rotation axis.

$(C_5H_4NCH:NOInMe_2)_2$ TABLE 5j

Selected Intramolecular Non-Bonding Distances less than 4Å

	Distance	e.s.d.	
In(1)-C(8)	3·49	0·02	Å
In(2)-C(16)	3·52	0·03	
O(1)-O(2)	3·08	0·02	
N(1)-N(2)	3·51	0·02	
C(1)-C(8)	3·86	0·03	
C(2)-N(2)	3·54	0·02	
C(2)-C(10)	3·89	0·04	
C(9)-C(16)	3·80	0·03	
C(10)-N(1)	3·77	0·03	

arrange themselves so as to equalise their non-bonding contacts.

The majority of the intermolecular non-bonding distances less than 4Å, Table 5k, are those involving the 'exposed' atoms, i.e. the two oxygen and two methyl carbon atoms C(9) and C(10), and the atoms of the benzene of crystallisation. Of the O-C (benzene) distances the shortest is O(1)-C(18) 3·85Å which is considerably longer than the distance obtained from the Van der Waal radii, 3·4Å, effectively precluding the possibility of any weak hydrogen bonding.

The packing arrangement is such that two molecules of benzene lie in a sandwich arrangement with a separation of just over 7Å, the two molecules being related by a centre of symmetry. The pyridine ring comprising of N(4), C(12)-C(16) projects towards the middle of this 'sandwich' and is approximately equidistant between the two benzene molecules, thus accounting for the number of contacts between these atoms. The (001) projection, Figure 5.3, illustrates this arrangement showing the pairs of benzene molecules lying on the two-fold rotation axis at $z = \pm \frac{1}{4}$ c. The length of the dimer is approximately the same as the b axis, while the width permits four molecules to lie along the a axis. The inclination of the two halves of the molecule mentioned at the beginning of the section allows the pyridine rings of neighbouring molecules to fit into each other. The numbering of the benzene molecule is indicated on Figure 5.3.

For purposes of clarity not all eight asymmetric units are shown on the projection. The relationships between the molecule which are shown are as follows:

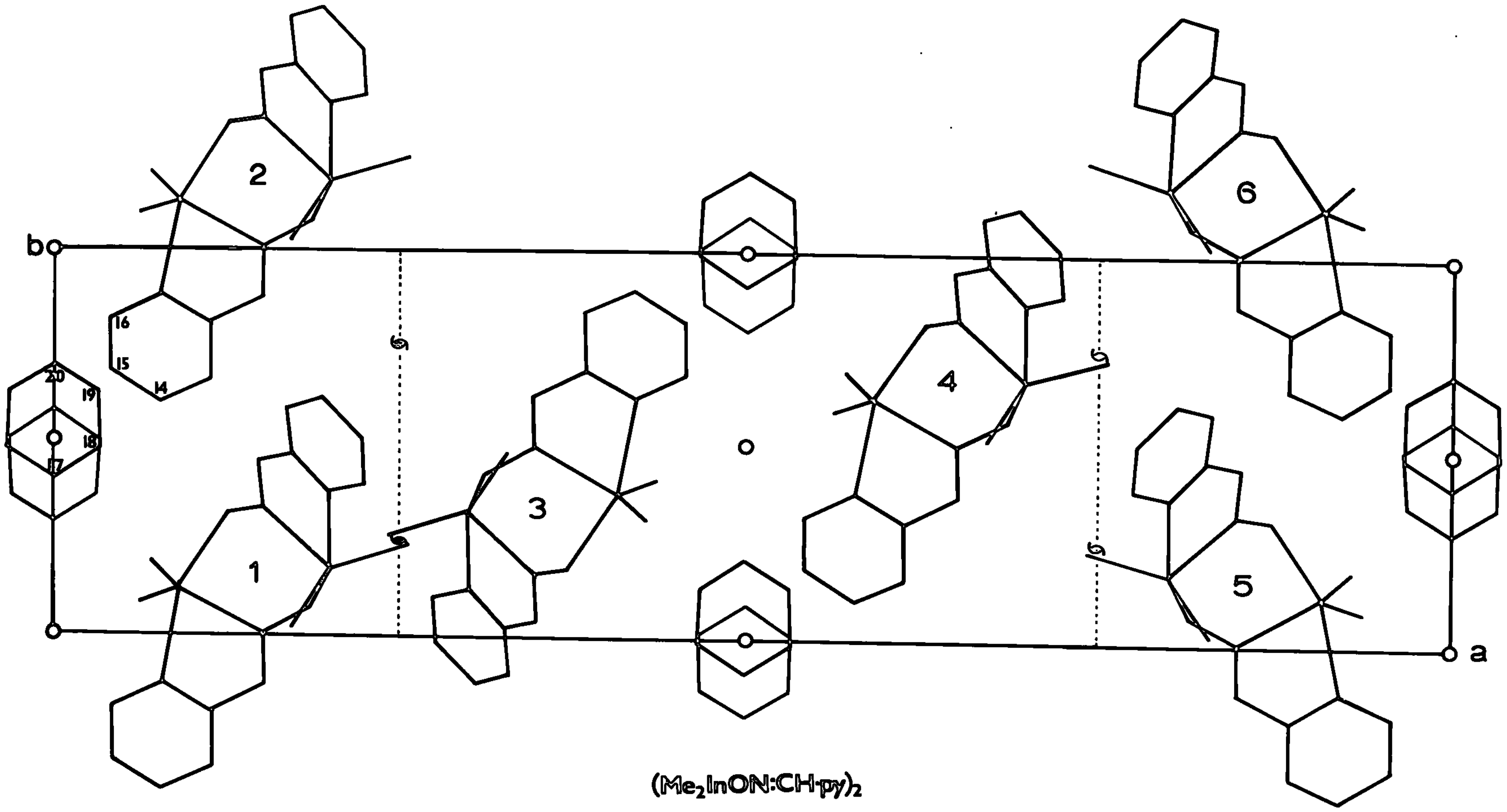
2 is related to 1 by a unit cell translation along *b*

3 " 1 by the 2_1 screw axis

4 " 3 by a centre of symmetry

5 " 4 by the *b* glide plane (dotted line)

6 " 5 by a unit cell translation along *b*



$(Me_2InON{:}CH{\cdot}py)_2$

(001) Projection

Figure 5.3

$(C_5H_4NCH{:}NOInMe_2)_2$ TABLE 5k

Selected Intermolecular Non-Bonding Distances less than 4Å

position 1 = x,y,z

position 2 = x,1+y,z

position 3 = $\bar{x},y,\frac{1}{2}-z$

position 4 = $x,\bar{y},\frac{1}{2}+z$

A	B	position of B	(A-B)Å	e.s.d.
C(17)	C(10)	3	3·76	0·04
C(17)	C(15)	4	3·59	0·03
C(18)	O(1)	1	3·85	0·03
C(18)	C(14)	2	3·96	0·04
C(18)	C(14)	4	3·99	0·04
C(18)	C(15)	3	3·98	0·04
C(18)	C(15)	4	3·97	0·04
C(19)	N(4)	2	3·94	0·03
C(19)	C(9)	4	3·75	0·04
C(19)	C(14)	2	3·86	0·04
C(19)	C(15)	2	3·58	0·04
C(19)	C(16)	2	3·66	0·04
C(20)	C(9)	4	3·70	0·03

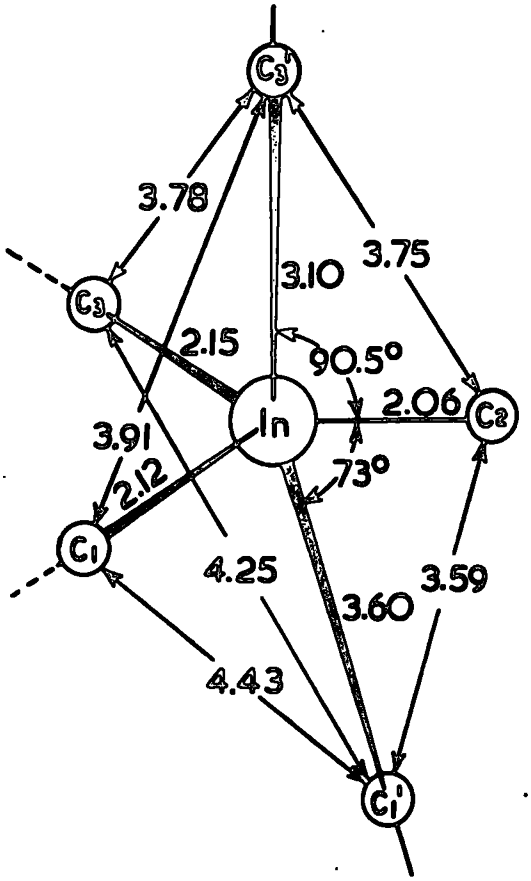
5.8. Five-Coordinate Indium

Penta-coordination has been the subject of a recent review (Muetterties and Schunn, 1966). There are two possible geometrical arrangements, the trigonal bipyramid and the tetragonal pyramid and both have been found in indium compounds. . The several approaches to the problem of deciding between these two arrangements, such as the Gillespie-Nyholm non-bonding repulsion considerations, lead to the conclusion that the trigonal bypyramid is more favourable. However the difference in energy between the two states should be small so that symmetry or steric effects could determine the arrangement obtained.

The crystal structure of trimethylindium (Amma and Rundle, 1958) revealed a metal atom surrounded by five methyl groups. The arrangement is shown in the following figure.

Although two of the In-C distances are rather long they are still sufficiently shorter than the sum of the Van der Waal's radii of indium and methyl (4·2Å), to be indicative of an interaction over and above Van der Waal's type forces. The geometrical arrangement adopted is the one which would be expected, that of the trigonal bipyramid albeit somewhat distorted, with the three methyl carbons peculiar to the central indium in equatorial positions and the two methyl carbons of neighbouring trimethyl indium groups in apical positions.

A somewhat similar arrangement has recently been found for triphenyl



Trimethylindium. The arrangement of carbon atoms about indium

indium (Malone and McDonald, 1969). The geometrical arrangement is again that of a distorted trigonal bipyramid, with the three phenyl groups of each indium atom in the equatorial positions and the apical positions occupied by the ortho-carbon atoms of phenyl groups lying above and below any particular unit.

The penta-coordination of the indium atoms in these two structures is achieved by means of certain packing arrangements.

The stereo-chemistry of indium(III) has generally been discussed in terms of either four- or six-coordinate species. Recently there has been considerable evidence that some at least of the addition compounds InX_3L_2 (X = Cl, Br, I; L = monodentate donor) involve five-coordination around the metal (Adams et al., 1968). The structural determination of tetraethylammonium pentachloroindate(III) (Brown, Einstein and Tuck, 1969) produced the first example of a main group element with an undistorted tetragonal pyramidal arrangement, in the species $InCl_5^{2-}$. That the ion prefers the above geometry is believed to rest on two facts, the energy difference between the two possible arrangements is small, and the symmetrical four-fold inversion symmetry found for the cation $[(C_2H_5)_4N]^+$, may well provide sufficient interionic energy to cause the anion to prefer the tetragonal pyramidal arrangement, and so utilise a symmetry element of the space group in which the molecule crystallises, namely P4/n.

In bistriphenylphosphinetrichloroindium(III) on the other hand, the molecule adopts the trigonal bipyramidal arrangement (Palenik and Veidis, 1969). The three chlorine atoms lie in the equatorial positions leaving the bulky triphenylphosphines to occupy the apices. This arrangement is most probably preferred since steric repulsion effects will be smaller than for a tetragonal pyramid. Steric considerations are probably also the rational for the distorted trigonal bipyramidal arrangements adopted in the dimeric oximate, coupled with the fact that the pyridine-2-carbaldehyde oxime ion acts as a tridentate ligand thus imposing geometric constraints.

APPENDICES

APPENDIX ONE

The A and B parts of the structure factor for space group $P2_1/n$

A and B are defined as follows

$$A = \sum \cos 2\pi(hx + ky + lz); \quad B = \sum \sin 2\pi(hx + ky + lz)$$

where the summation is made over all the equivalent positions in the space group. The equivalent positions for $P2_1/n$ are $(x,y,z; \bar{x},\bar{y},\bar{z}; \frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z; \frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z)$ when the origin of coordinates is taken at the centre of symmetry. Therefore B becomes zero, since sinf(xyz) will cancel with sinf$(\bar{x},\bar{y},\bar{z})$. The expression for A becomes

$$\begin{aligned} A = {} & \cos 2\pi(hx + ky + lz) + \cos 2\pi(-hx-ky-lz) \\ & + \cos 2\pi(-hx+ky-lz + \frac{h+k+l}{2}) + \cos 2\pi(hx-ky+lz+ \frac{h+k+l}{2}) \end{aligned}$$

and since cos (angle) = cos (-angle) this reduces to

$$A = 2\left\{ \cos 2\pi(hx+ky+lz) + \cos 2\pi(hx-ky+lz+ \frac{h+k+l}{2})\right\}$$

Adding the two terms together gives

$$A = 4 \cos 2\pi\left\{ hx+lz+ \frac{h+k+l}{4}\right\} \cos 2\pi \left\{ ky- \frac{h+k+l}{4}\right\}$$

For computional purpose this was divided into two groups

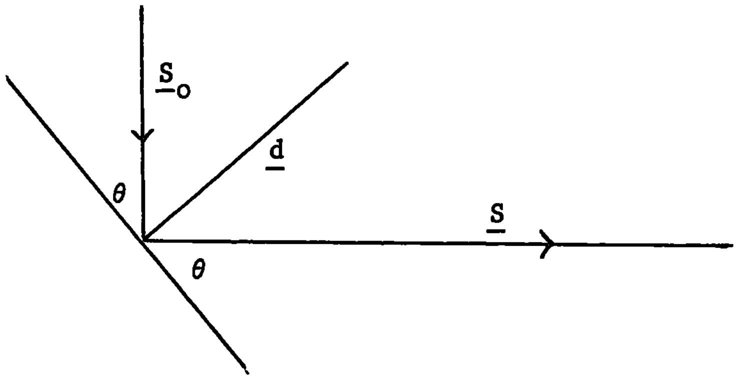
(1) $h+k+l$ even, $A = 4\cos 2\pi(hx+lz)\cos 2\pi ky$

(2) $h+k+l$ odd, $A = -4\sin 2\pi(hx+lz)\sin 2\pi ky$

APPENDIX TWO

Diffractometer Geometry

The basic geometry for the reflection of an X-ray beam from a set of crystallographic planes is summarised in the following diagram



The conditions for 'reflection' are

(i) the incident ($\underline{S}_o$) and reflected beams ($\underline{S}$) and the normal to the planes ($\underline{d}$*) must be coplanar. ($\underline{d}$* will bisect the angle between $\underline{S}_o$ and $\underline{S}$)

(ii) $\underline{S}_o$ must make an angle θ with the planes to satisfy the Bragg equation.

The arrangement of the four-circle diffractometer is shown in the figure. For the purposes of data collection the instrument normally uses bisecting geometry which places the vertical χ-circle so as to bisect the angle between the incident and reflected X-ray beams. From the foregoing discussions this means that the χ-circle must contain the normal to the reflecting planes $\underline{d}^*$, and the condition necessitates that $w = \theta$. With $\underline{d}^*$ constrained to lie in two mutually perpendicular planes there will be specific values of the angles χ and ϕ, if the reflection (hkl) is to be observed.

At high θ angles when the χ-circle would tend to obstruct the passage of the reflected beam to the detector, the instrument switches to perpendicular geometry. In this position the vector $\underline{d}$ is perpendicular to the χ-circle, and the condition $w = 90^{\circ} - \theta$ holds.

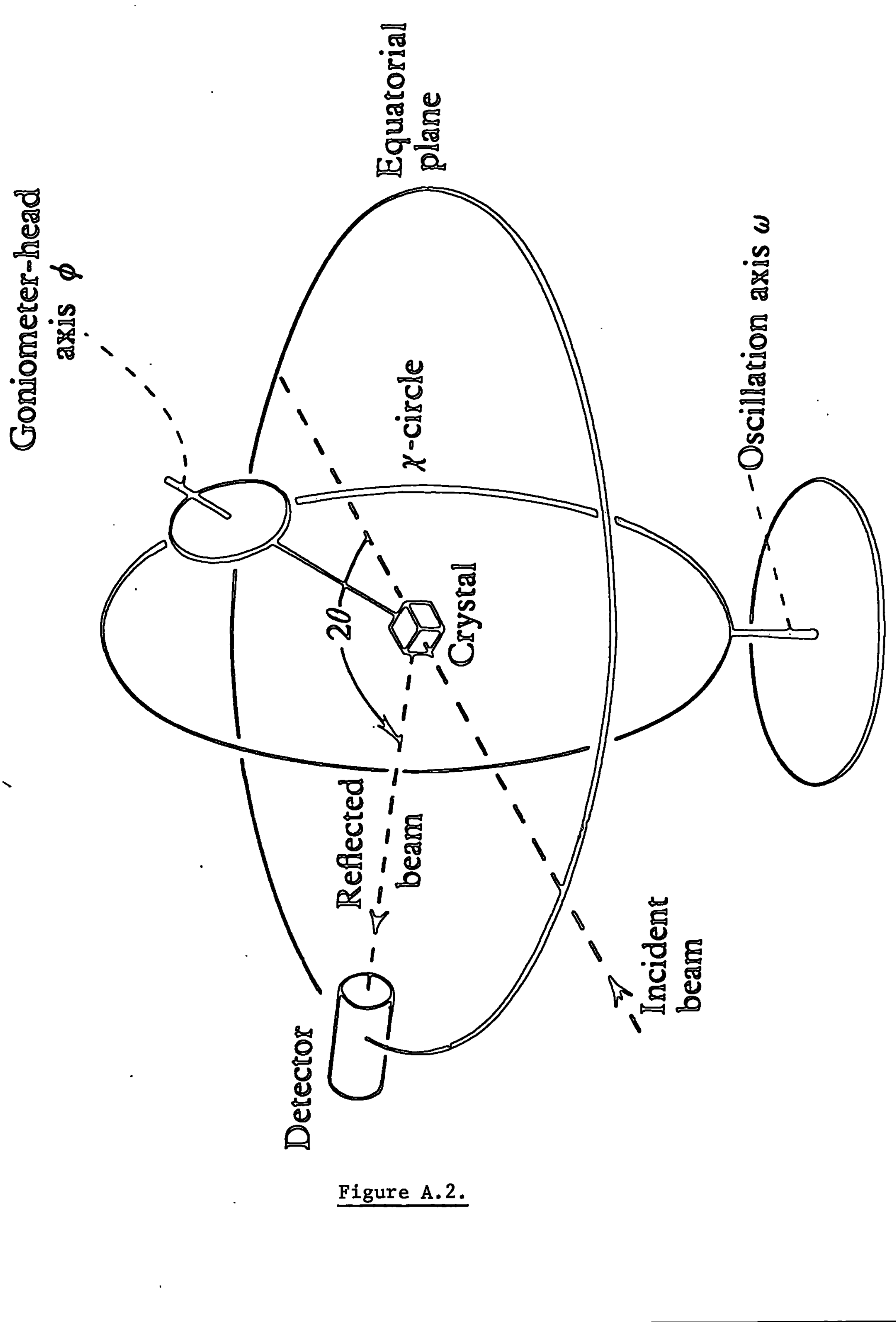

Goniometer-head axis ϕ
Equatorial plane
χ-circle
Oscillation axis ω
2θ
Crystal
Reflected beam
Incident beam
Detector

Figure A.2.

APPENDIX THREE

Computer Programmes

The extensive calculations necessary were carried out on the N.U.M.A.C. I.B.M.360 and on the I.B.M.1130 here in Durham, and I would like to thank the staff of the Computer Unit for their help and advice.

The major programmes were written by F.R. Ahmed and I am grateful for permission to use these programmes for my structural solutions.

I have personally written several smaller programmes some in collaboration with Mr. M.L. Schneider. These include a programme to correct precession data for Lorentz and polarisation effects, one to scale intersecting nets together average and 'sharpen' the intensities for Patterson functions, and a programme to print structure factor tables on the 1130 computer.

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