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THE CRYSTAL STRUCTURES
OF THREE
ASSOCIATED METHYLZINC COMPLEXES:

1. TETRAMERIC METHYLZINC METHOXIDE,
2. DIMERIC METHYL(DIPHENYLAMINO)ZINC,
3. TETRAMERIC METHYLZINC ACETOXIMATE.

by

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Van Mildert College, University of Durham.

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PREFACE

This thesis describes research in chemical crystallography, which was carried out between October, 1964 and September, 1967 in the Chemistry Department of the University of Durham.

I wish to express my sincere thanks to Dr. H.M.M. Shearer under whose direction this research was undertaken, for his invaluable advice and guidance. Thanks are also expressed for the interest shown by Professor G.E. Coates and his former student, Dr. D. Ridley who first prepared the compounds and who, with Mr. P.T. Moseley, went to considerable trouble to grow crystals suitable for X-ray analysis. I am also indebted to Dr. M. Stone, Reader in Statistics, for most helpful discussion and, in particular, for suggesting the statistical treatment of apparent centring, outlined in Appendix II.

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

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SUMMARY

X-ray diffraction methods have been used to investigate the association, in the crystal, of three complexes of methylzinc. The structures were determined by the heavy-atom method, and refined by the method of least squares using three-dimensional data.

Tetrameric Methylzinc Methoxide crystallises in an orthorhombic cell with a=7·48, b=7·67, c=29·41 Å and space group $P2_12_12_1$. The unit cell contains 16 units of MeZnOMe. As in benzene solution, methylzinc methoxide is tetrameric in the solid state.

The zinc and oxygen atoms each occupy the corners of two, regular, interpenetrating, concentric tetrahedra of different size. Thus the zinc and oxygen atoms are four-coordinate and are situated on alternate corners of a distorted cube. The distortion is such that the Zn-O-Zn angles are greater than 90°. The Zn-O distances range from 2·039 to 2·105 Å with an average value of 2·076 Å. However, the lengths of four Zn-O bonds are significantly shorter than 2·105 Å. The mean Zn-C and O-C bond lengths are 1·95 and 1·44 Å. The molecular symmetry is nearly $\bar{4}3m$.

Dimeric Methyl(diphenylamino)zinc is orthorhombic with a=7·57, b=14·95, c=20·43 Å and space group $P2_12_12_1$. There are 8 monomers in the unit cell. Cryoscopic measurements in benzene indicate that the molecule is dimeric and the same degree of association is found in the crystal.

The molecule contains a four-membered, zinc-nitrogen ring in which the nitrogen atoms are four-coordinate but the zinc atoms are each bonded to two nitrogens and to a methyl carbon and are three-coordinate. The mean Zn-N and Zn-C distances are 2·07 and 1·95 Å respectively while the angles in the four-membered ring are very close to 90°. Other inter-bond angles and distances are as expected. Although the space group requirements impose no symmetry on this molecule, to a rough approximation each dimer has $\frac{2}{m}$ symmetry. Superficially, the molecular centre of symmetry holds to a very close extent, but a detailed statistical examination has shown that the probability of the apparent centring being true is less than 0·1%.

<u>Tetrameric Methylzinc Acetoximate</u> provides an example where methylzinc is complexed with a 2-atom donor group. The molecules crystallise in a monoclinic cell with space group $P2_1/c$, a=9·26, b=13·58, c=24·10 Å, Z = 16 units of $MeZnON:CMe_2$. Methylzinc acetoximate exists in the crystal as discrete tetramers, in agreement with the degree of association found from molecular weight measurements in benzene solution.

The four zinc atoms are at the corners of a slightly distorted tetrahedron and above each face of the tetrahedron in an acetoximate group in which the oxygen atom is attached to two zincs and the nitrogen to the third. A "cage" structure results which has four five-membered rings and two adjacent six-membered rings but no four-membered rings. An outcome of this arrangement is that the four zinc atoms are in three different environments. The mean Zn-O and Zn-N distances are 2·05 and 2·09 Å which are similar to the values observed in the other two structures.

CHAPTER ONE

PART ONE

CRYSTAL SYMMETRY

1.1 Symmetry Elements

Systematic repetition of a motif results in a periodic pattern which can extend in one, two, or three dimensions. A systematic study shows that there are only two hundred and thirty types of three dimensional patterns and since crystals are built up from a periodic array of atoms, ions or molecules, they must be arranged in one of these pattern types. Pattern theory is thus basic to the study of crystallography.

Periodic angular repetition can be described by means of symmetry elements known as rotation axes. An n-fold symmetry axis implies that rotation through $2\pi/n$ about the axis produces geometrical coincidence with the original configuration. In crystals the values of the angular repetitions are restricted by the simultaneous occurrence of repetition by not only rotation, but also translation; crystals can only have 1-fold, 2-fold, 3-fold, 4-fold and 6-fold axes. Pure axial symmetries are symbolised 1, 2, 3, 4, 6 as the case may be.

Another fundamental notion is that of a symmetry plane, by which reflection through the plane produces geometrical self-coincidence. Hence, such planes are termed mirror planes and are given the symbol m. Reflecting through a mirror is equivalent mathematically to inverting through a centre, $\bar{1}$.

1.2 Combination of Symmetry Elements

Symmetry axes may be combined systematically with other symmetry elements. If vertical mirror planes are added to the pure axial symmetries this results in the symmetries 1m, 2m, 3m, 4m, 6m. Extra vertical mirrors are however automatically introduced in accordance with the relevant axial symmetry and these symmetries are conventionally written m, 2mm, 3m, 4mm, 6mm. 3m is not written 3mm since here the interleaving mirrors coincide with those generated directly.

Combining each symmetry axis with a horizontal mirror results in the symmetries $\frac{1}{m}$, $\frac{2}{m}$, $\frac{3}{m}$, $\frac{4}{m}$, $\frac{6}{m}$. Again, $\frac{1}{m}$ implies nothing more than a single mirror and $\frac{1}{m} \equiv 1m \equiv m$.

As with vertical mirrors, the introduction of one horizontal 2-fold axis automatically implies the presence of others, and these symmetries, the dihedral symmetries, are therefore written, $12 \equiv 2$, 222, 32, 422, 622. Combining dihedral symmetries with a horizontal mirror yields the following:

$$\frac{2}{m}\,2\,2 \equiv \frac{2}{m}\,m\,m \equiv \frac{2}{m}\,\frac{2}{m}\,\frac{2}{m}, \qquad \frac{3}{m}\,2 \equiv \frac{3}{m}\,m \equiv \frac{3}{m}\,m\,2,$$

$$\frac{4}{m}\,2\,2 \equiv \frac{4}{m}\,m\,m \equiv \frac{4}{m}\,\frac{2}{m}\,\frac{2}{m}, \qquad \frac{6}{m}\,2\,2 \equiv \frac{6}{m}\,m\,m \equiv \frac{6}{m}\,\frac{2}{m}\,\frac{2}{m}.$$

The six symmetries $\frac{2}{m}$, $\frac{4}{m}$, $\frac{6}{m}$, $\frac{2}{m}\frac{2}{m}\frac{2}{m}$, $\frac{4}{m}\frac{2}{m}\frac{2}{m}$, $\frac{6}{m}\frac{2}{m}\frac{2}{m}$ may be seen to possess an inversion centre. If the remaining symmetries are inverted with respect to the centre three new symmetries are generated: $\bar{1}$, $\bar{3}$, $\bar{3}\frac{2}{m}$. $\bar{3}$ signifies a 3-fold axis combined with an inversion centre and is termed a 3-fold rotatory inversion axis.

Some of the symmetries we have already derived can also be described in terms of rotatory axes of inversion. Thus a mirror plane m is equivalent to a $\bar{2}$ axis. The combination of a horizontal mirror with a 3-fold axis, $\frac{3}{m}$, is equivalent to a $\bar{6}$ axis and the symmetries $\frac{3}{m}$ and $\frac{3}{m}$ m 2 are commonly termed $\bar{6}$ and $\bar{6}$ m 2. In the case of a 4-fold rotatory inversion axis however, the set of points generated by a $\bar{4}$ axis <u>cannot</u> alternatively be described by adding an inversion centre, or a perpendicular plane, to the set of points generated by a pure axis and $\bar{4}$ must be added to our list of independent symmetries. Combining $\bar{4}$ with either a vertical mirror or a horizontal 2-fold axis gives the symmetry $\bar{4}$ m 2.

Two rotations about intersecting axes inevitably create a third rotation equivalent to the combination. As a result, it may be shown, using Euler's half-angle construction and the trigonometric formulae of a spherical triangle, that crystallographic symmetry axes may be combined with each other to give only six independent triaxial combinations. Of these, the four combinations of an n-fold axis with perpendicular 2-fold axes 222, 223, 224, 226 have already been encountered. Two further possibilities remain, the cubic symmetries given by the triaxial combinations 233 and 234.

Combining a 3-fold axis with a 2-fold axis (these two axes having directions related as the diagonal and edge of a cube respectively) results in the crystallographic symmetry denoted 23. This symmetry implies three additional 3-fold axes and two additional 2-fold axes, with directions related as before. This symmetry is shown by an array of four identical atoms at the vertices of a regular tetrahedron and, from this point of view, this symmetry is known as the tetrahedral group.

Combining a 3-fold axis, direction [111], with a 4-fold axis, direction [100], implies, as before, three additional 3-fold axes and two additional 4-fold axes. Six 2-fold axes, direction [011], are also generated. This set corresponds with the crystallographic symmetry 432. Symmetry 432 is realised by eight identical atoms at the eight corners of a cube and, from this point of view, it is known as the octahedral group.

If 23 and 432 are combined with an operation which inverts all points with respect to the origin two new groups are generated: $\frac{2}{m}\bar{3}$ and $\frac{4}{m}\bar{3}\frac{2}{m}$. Replacing 4 by $\bar{4}$ in 432 yields $\bar{4}3m$ (2 is automatically replaced by m).

This brings the total number of possible independent crystallographic symmetries up to thirty-two.

The symmetry elements we have encountered generate geometrical operations which may be described by operators in the mathematical sense. Successive application of a rotation operator, or the product of a rotation operator with a reflection or an inversion operator, produces a configuration identical with the original. A complete set of such operators may be shown to satisfy the criteria of a finite group, and the n independent operators comprising the group generate n equivalent atoms from any arbitrary atom in space. The thirty-two symmetries which have been enumerated are thus termed the crystallographic point groups since they are indicative of configurations centred around a fixed point. A complete list is shown in Table 1.1.

TABLE 1.1

The thirty-two crystallographic point groups

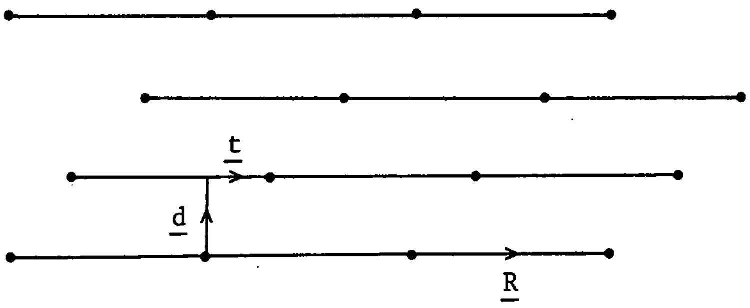
1	2	3	4	6	axis
$\frac{1}{m}$	$\frac{2}{m}$	$\frac{3}{m}$	$\frac{4}{m}$	$\frac{6}{m}$	axis + horizontal mirror
	222	32	422	622	axis + 2-fold horizontal axis
	2mm	3m	4mm	6mm	axis + vertical mirror
	$\frac{2}{m}\frac{2}{m}\frac{2}{m}$	$\frac{3}{m}$ m 2	$\frac{4}{m}\frac{2}{m}\frac{2}{m}$	$\frac{6}{m}\frac{2}{m}\frac{2}{m}$	axis + vertical mirror + horizontal mirror
$\bar{1}$	$\bar{3}$	$\bar{3}\frac{2}{m}$			1, 3, 3m or 32 + inversion centre
			$\bar{4}$		4-fold rotatory inversion axis
			$\bar{4}$m2		4-fold rotatory inversion axis + vertical mirror
	23	432			tetrahedral, octahedral
	$\frac{2}{m}\bar{3}$	$\frac{4}{m}\bar{3}\frac{2}{m}$			tetrahedral, octahedral + inversion centre
		$\bar{4}$3m			replace 4 by $\bar{4}$ in octahedral group

1.3 The Crystal Lattice

The macroscopic symmetry of a crystal must essentially conform to one of the thirty-two point groups enumerated, and thus, crystals are considered as being divided into thirty-two crystal classes. A crystal's microscopic symmetry is closely connected with its macroscopic symmetry, but it is not necessarily identical with it owing to the possibility of screw axes and glide-planes replacing symmetry axes and mirror planes. The crystal structure is characterised by its translational symmetry expressed by means of a reference lattice.

If an arbitrary origin is chosen, then it will be possible to find many further points in space which have an environment identical to that of the origin. 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 $\underline{a}$, $\underline{b}$, $\underline{c}$, is termed the "unit cell". This is said to be primitive if it contains no interior lattice points, being otherwise non-primitive.

Any three integers x,y,z then define another lattice vector $x\underline{a} + y\underline{b} + z\underline{c}$, terminating in the lattice point denoted (x,y,z). A rational plane through the origin (termed a lattice plane) has the equation $hx + ky + lz = 0$, where h, k, l are three integers known as Miller indices (hkl). Integer solutions of the above equation define lattice points lying in the plane. The equation $hx + ky + lz = 1$, defines a rational plane parallel to $hx + ky + lz = 0$, and characterised by the same arrangement of lattice points. It is generated from $hx + ky + lz = 0$ by a translation $\underline{d} + \underline{t}$ made up of a normal component $\underline{d}$ and a tangential component $\underline{t}$ and both planes are characterised by the same repeat vector $\underline{R}$. This is shown in two dimensions in the diagram below.



A set of parallel planes

$$hx + ky + lz = 0, \pm 1, \pm 2, \cdots\cdots$$

may be generated, which between them, contain all the lattice points. For a plane to have a high density of lattice points however, the axial intercepts (the reciprocals of which correspond to the Miller indices) must be relatively small. It is such planes which tend to form the faces of crystals and this was 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.

1.4 The Bravais Space Lattices

To say that a unit cell is defined by $\underline{a}$, $\underline{b}$, $\underline{c}$ means that we know the axial lengths a, b, c and the angles α, β, γ between them. In crystallography six natural axial systems are used, based on the translations of a primitive unit cell. These are as follows:

Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ$
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma$
Hexagonal	$a_1 = a_2 = a_3 \neq c$	$\beta_1 = \beta_2 = \beta_3 = 90^\circ$, $\gamma = 120^\circ$.

Unfortunately however, the translations of a primitive unit cell do not always coincide with the symmetry axes, and in these cases non-primitive cells are chosen because they exhibit symmetry features not otherwise apparent.

Bravais showed that in all, fourteen unit cell types were possible. In each of the axial systems is found a primitive lattice type, P. The monoclinic system shows two lattice types, P and face-centred, C; the cubic system three, P, body-centred, I, and all-face-centred, F; and the orthorhombic system four, P, C, F and I. The tetragonal system has only P and I Bravais unit cells. In addition there exists a non-primitive cell with lattice points at $\frac{2}{3}, \frac{1}{3}, \frac{1}{3}$ and $\frac{1}{3}, \frac{2}{3}, \frac{2}{3}$ which does not fall within any of the preceding types. This lattice may be referred to a primitive rhombohedral cell, R.

1.5 The Bravais Space Groups

We can now construct space lattices appropriate to the thirty-two crystallographic point groups. Clearly since any chosen motif structure is automatically generated at all lattice points by rigid body translations, the translational symmetry of a space lattice must be compatible with the rotational symmetry of the motif structure. A cubic lattice is implied by 23 and by all higher cubic point group symmetries and similarly the trigonal point group symmetries $\frac{3}{m}$ m 2, $\frac{3}{m}$,$\bar{3}$ $\frac{2}{m}$, 3m, 32, $\bar{3}$, 3 imply a hexagonal lattice.

Since the group 23 can be associated with all three types of cubic lattice, it yields three distinct space groups designated P23, I23, F23 respectively. Carrying out a similar procedure for all the point groups, we arrive at a total of seventy-three Bravais space groups, the relevant lattice-type symbols P, I, F, C or R prefixing the point group symbol. The space-group is said to be isogonal with its point group symmetry component.

The remainder of the two hundred and thirty space groups may be derived by taking into account the possibilities of rotation axes in the point group being represented by screw axes in the space group, and similarly of reflection planes being replaced by glide-planes.

A screw axis is a composite operator characterised by an angular component $2\pi/n$ and a translational component along the axis of rotation.

The operation of a 3_1 screw axis in the c-direction combines anticlockwise rotation through 120^o with a translation along c of $\frac{c}{3}$. Two more operations result in a position self-coincident with the original configuration but in the adjacent cell.

The combination of a reflection and a general translation results in a glide. Glide planes are termed axial glides, diagonal glide or diamond glide according to whether the direction of the translation component is characterised by $\frac{a}{2}$, $\frac{a}{2} + \frac{b}{2}$ or $\frac{a}{4} + \frac{b}{4}$ respectively. The glide-plane bears a relation to the reflection plane which is similar to the relation which the screw axis among space groups bears to the pure rotation axis among point group symmetry elements.

1.6 Operations of the first and second kinds

The symmetry elements we have encountered are conveniently classified in two general categories. In pure angular repetition, the rotational operation repeats a congruent object from another object and is termed an operation of the first sort. Pure rotation axes and screw axes are also known as proper rotation axes. On the other hand, the operation of reflection or inversion introduces a reversal of sense, and an enantiomorphic object is repeated. These operations are called operations of the second sort.

Of the two hundred and thirty space groups, twenty-two are related as enantiomorphic pairs. These pairs can only occur in the classes lacking operations of the second sort, that is, in the axial classes. The possibility of enantiomorphic pairs also requires that at least one axis is non-neutral in sense. This can only be true for axes of order greater than 2 and such space groups cannot therefore belong to the triclinic, monoclinic or orthorhombic systems. An example of an enantiomorphic pair is $P3_1$ and $P3_2$ the only difference between these two space groups being the sense of the screw axis.

CHAPTER ONE

PART TWO

STRUCTURE DETERMINATION BY X-RAY METHODS

1.7 X-Ray Diffraction by a Crystal Lattice

The theory of crystal symmetry, of which a brief outline has been given, was essentially complete before the end of the last century. In 1912, at the suggestion of Laue, the diffraction of X-rays by a crystal lattice was demonstrated by Friederich and Knipping. Their experiments established the wave-like nature of X-rays and showed crystals to be periodic arrangements of matter with separations on a molecular scale.

The lattice, already defined, is important as it decides completely the conditions for diffraction. The relationship between a crystal lattice and the scattered radiation was first placed on a physical basis by W.L. Bragg in 1913, and is expressed in the law which bears his name:

$$n\lambda = 2d\sin\theta$$

Bragg showed that the resultant beam diffracted by a crystal lattice behaves as if it were reflected from the lattice planes with Miller indices (hkl) and where d is the interplanar spacing. To describe the whole 3-dimensional diffraction pattern three sets of equidistant planes are set up perpendicular to $\underline{a}$, $\underline{b}$ and $\underline{c}$, each plane corresponding to a particular value of h, k, and l. The intersections of these planes delineate a lattice of points which is called the reciprocal lattice. The reciprocal lattice is thus defined by the vectors $\underline{a}^*$, $\underline{b}^*$ and $\underline{c}^*$ where

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

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

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

1.8 The Structure Factor

Crystals can be represented by placing within each cell of the lattice a certain arrangement of atoms and a crystal with N atoms in the unit cell can be regarded as based upon N identical interpenetrating lattices. The rays scattered by different atoms will be out of phase. To find the amplitude and phase of the resultant ray, it is necessary to recombine the waves from each atom.

Suppose the unit cell contains N atoms, situated at points with coordinates x_n, y_n, z_n where x_n, y_n, z_n are expressed as fractional coordinates of the unit cell edges. The position of the nth atom P, may be represented by the end of 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) whose 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).

Thus if ϕ_n is the phase of the wave scattered by the atom at P.

$$\frac{\phi_n}{2\pi} = \underline{R}.\underline{r}_n$$

$$= (h\underline{a}^* + k\underline{b}^* + l\underline{c}^*).(x_n\underline{a} + y_n\underline{b} + z_n\underline{c})$$

$$= hx_n + ky_n + lz_n$$

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

Thus the expression for the wave scattered by the nth lattice is $f_n \exp 2\pi i(hx_n + ky_n + lz_n)$, where f_n is the scattering factor of the nth atom. The complete wave scattered by the crystal is given by a vector:

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

F(hkl) 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 in the same direction by a single electron situated at the origin.

The distribution of the electrons about each atom in the structure is known from atomic scattering theory, and from these distributions, the atomic scattering factor f_n for each atom can be found. It is the ratio of the scattering power of the atom compared with that of a single electron in the same direction. In atoms, the electrons occupy a finite volume and phase differences will arise between rays scattered in different parts of this volume. Interference between these waves causes the scattering factor to decrease with increasing θ. The curve of scattering-factor against $\sin\theta/\lambda$ is called the scattering-factor or f curve.

The quantity F(hkl) is complex and may be expressed in terms of its real and imaginary components:

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

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

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

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

When the space group has higher symmetry than P1 the summation over all atoms n is usually split into a summation over symmetry related atoms followed by a summation over the asymmetric unit. For space groups with a centre of symmetry at the origin B(hkl) = 0. For each space group International Tables, Volume I gives simplified forms of the trigonometric summations over symmetry related atoms. These expressions however have to be modified to allow for atomic scattering.

If, instead of considering a set of point atoms with variable scattering factors, each volume of the unit cell is treated separately, an alternative form of the structure factor equation is obtained. If $\rho(x,y,z)$ is the electron density at a point (x,y,z), the contribution from the volume element Vdxdydz is a wave of amplitude ρVdxdydz and phase ϕ. And since $\rho(x,y,z)$ is continuous over the unit cell,

$$F(hkl) = \int_0^1\int_0^1\int_0^1 V\rho(x,y,z)\exp 2\pi i(hx+ky+lz)dxdydz$$

1.9 The Temperature Factor

Atoms in a crystal have a finite amplitude of oscillation at all temperatures and the frequency of this oscillation (~10^{13} per second) is much smaller than the frequency of X-rays (~10^{18} per second). Since corresponding atoms in neighbouring unit cells will not necessarily be in phase at any one instant, the atomic scattering factors are reduced by an amount which increases with the diffraction angle θ, and the function to be used in practice is given by the expression

$$f = f_0\exp(-B\sin^2\theta/\lambda^2).$$

B is the temperature factor. If the thermal motion is isotropic

$$B = 8\pi^2\overline{u^2},$$

where $\overline{u^2}$ is the mean square amplitude of vibration in any direction.

The thermal motion is in general not isotropic and must be described in terms of an ellipsoidal distribution. The vibrations are described by a symmetrical tensor $\underline{U}$ which has six independent components, such that the mean square amplitude of vibration in the direction of a unit vector $\underline{l} = (l_1, l_2, l_3)$ is

$$\overline{u^2} = \sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij} l_i l_j$$

U and l are here defined with respect to the reciprocal axes $\underline{a}^*$, $\underline{b}^*$ and $\underline{c}^*$. In this anisotropic case the transform of the smearing function is

$$q(s) = \exp[-2\pi^2(\Sigma\Sigma U_{ij} s_i s_j)]$$

where $\underline{s} = (s_1, s_2, s_3)$ is the reciprocal lattice vector. At a reciprocal lattice point $\underline{s} = (h\underline{a}^*, k\underline{b}^*, l\underline{c}^*)$:

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

The units of U_{ij} are $\mathring{A}^2$.

1.10 Fourier Series

Since a crystal is periodic in three dimensions, it can be represented by a three-dimensional Fourier series. Three integral indices h', k' and l' are allotted to each Fourier coefficient C and the expression for the electron density is:

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

If this expression is substituted into the structure factor equation we obtain:

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

The integral has zero value unless h = -h', k = -k', l = -l', when

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

and therefore $C(h'k'l') = \frac{1}{V}.F(hkl)$ and we see that, the Fourier coefficients C are directly related to the structure factors. The three-dimensional Fourier synthesis can thus be written:

$$\rho(xyz) = \frac{1}{V}\sum\sum\sum_{h,\,k,\,l\,=\,-\infty}^{+\infty} F(hkl)\exp\{-2\pi i(hx + ky + lz)\}.$$

This expression contains complex quantities which may be resolved into their real and imaginary parts:

$$\rho(xyz) = \frac{1}{V}\sum\sum\sum_{h,\,k,\,l\,=\,-\infty}^{+\infty} A(hkl)\cos 2\pi(hx + ky + lz) + B(hkl)\sin 2\pi(hx + ky + lz)$$

A and B are the two components of F (§ 1.8).

Since $A(\bar{h}\,\bar{k}\,\bar{l}) = A(hkl)$ and $B(\bar{h}\,\bar{k}\,\bar{l}) = -B(hkl)$ we can rewrite this expression (bearing in mind that the term 000 is its own conjugate):

$$\rho(xyz) = \frac{1}{V}\left(F(000) + 2 \sum_{h=0}^{\infty}\sum_{k,l=-\infty}^{\infty}\sum^{\infty} A(hkl)\cos 2\pi(hx + ky + lz) + B(hkl)\sin 2\pi(hx + ky + lz)\right)$$

or $$\rho(xyz) = \frac{1}{V}\left(F(000) + 2 \sum_{h=0}^{\infty}\sum_{k,l=-\infty}^{\infty}\sum^{\infty} |F(hkl)|\cos\{2\pi(hx + ky + lz) - \alpha(hkl)\}\right)$$

where $\alpha(hkl)$ is a phase angle.

Although this expression holds generally for all crystals, the expression may be simplified by making use of the space-group symmetry. For example, if a 2-fold axis along b is present $|F(hkl)| = |F(\bar{h}\,\bar{k}\,\bar{l})|$, and the terms $F(hkl)$, $F(\bar{h}\,k\,\bar{l})$, $F(h\,\bar{k}\,l)$ and $F(\bar{h}\,\bar{k}\,\bar{l})$ may be combined with due regard to their combination of signs. In International Tables, Volume I, the expression for the electron density in terms of the independent structure factors only, is given for each space-group. However, the electron density distribution of a crystal cannot be computed directly from the observed structure factors as their phases are not experimentally observable quantities.

1.11 The Patterson Function

One of the routes to the solution of the phase problem is the use of the summation first suggested by Patterson. Patterson defined a function P(u,v,w) such that:

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

If the values for the electron densities are substituted into this equation, the usual form of the Patteron function may be derived.

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

This function contains the squares of the structure amplitudes and so the series can be evaluated without ambiguity.

If there are atoms at (x,y,z) and (x+u, y+v, z+w) in the crystals then the Patterson function will have a maximum at (u,v,w). In other words, peaks occur at the point (u,v,w) when the vector $\underline{r} = u\underline{a} + v\underline{b} + w\underline{c}$, represents a vector joining atoms. A large peak occurs at the origin, caused by the products of all the atoms with themselves. The height of a peak depends on the electron-density heights of the atoms causing it.

1.12 The 'Heavy-Atom' Method

An atom of high atomic number will give rise to large, easily identifiable peaks in the Patterson function from which its coordinates may be deduced. An electron density map is then computed using $|Fo|$ as Fourier coefficients and the phase angles obtained from structure factors calculation based on the heavy atom contributions. From this electron density map, improved positions for the heavy atoms will be found and the positions of some or all of the lighter atoms may also be found. This process is continued until the positions of all of the atoms are known.

This result can be shown by writing the structure factor for a crystal with a single heavy atom as:

$$F(hkl) = f_H \exp 2\pi i(hx_H+ky_H+lz_H) + \sum_n f_n \exp 2\pi i(hx_n+ky_n+lz_n),$$

where f_H is the scattering factor for the heavy atom, whose parameters are x_H, y_H and z_H. If f_H is much greater than f_n, then the first term will tend to be much greater than the second.

As a rough guide, the method works best if the sum of the squares of the atomic numbers of the heavy atoms and of the light atoms are approximately equal. This follows, since on the average, the contribution of any one atom to the diffracted intensity depends upon the square of its scattering factor.

$$\overline{I(hkl)} = \sum_j f_j^{\,2}.$$

The signs of those structure factors to which the heavy atom makes only a small contribution are uncertain and it has been suggested (Woolfson, 1956) that each term should be weighted according to the contribution of the heavy atom to that structure factor.

The chief difficulty encountered with the heavy atom method is that of pseudosymmetry. When 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 be simulated and the phases deduced give false information about the structure.

1.13 Structure Refinement

The refinement of structures described in this thesis has been carried out almost exclusively using the method of least squares. An outline of this method will now be given.

Let $p_1, p_2, \ldots, p_n$ be the n parameters occurring in the Fc whose values are to be determined. $|Fc|$ can be written as a function of these parameters:

$$|Fc| = f(p_1, p_2, \ldots, p_n)$$

and incorporating $\epsilon_1, \epsilon_2, \ldots, \epsilon_n$, the shifts required to give the true structural parameters, a similar expression may be written for the observed structure amplitudes:

$$|Fo| = f(p_1 + \epsilon_1,\ p_2 + \epsilon_2, \ldots, p_n + \epsilon_n)$$

For a trial set of p_j close to the correct values, we may expand Fo as a function of the parameters by a Taylor series of the first order:

$$|Fo| = f(p_1, p_2, \ldots, p_n) + \sum_{i=1}^{n} \frac{\partial f(p_1, p_2, \ldots, p_n)}{\partial p_i} \epsilon_i$$

$$|Fo| = |Fc| + \sum_{i=1}^{n} \frac{\partial |Fc|}{\partial p_i} \epsilon_i$$

An equation of this type may be derived for each reflexion. Each Fo is subject to random errors and suitable values of ϵ_i have to be found to give the most acceptable fit between Fo and Fc. The theory of errors predicts that the most acceptable set of ϵ_i is that which minimises the sum of the weighted squares of the discrepancies, $\Sigma w\Delta^2$, where $\Delta = |Fo| - |Fc|$. The weight w allows for the reliability of the observation. If the standard deviation for each $|Fo|$ is $\sigma(hkl)$, the value of w which gives the lowest standard deviations in the derived parameters may be shown to be $w(hkl) = \dfrac{1}{\sigma^2(hkl)}$.

The criterion that $\Sigma w\Delta^2$ should be a minimum leads to a set of simultaneous equations, the normal equations:

$$\sum_{hkl} w\left(\frac{\partial |Fc|}{\partial p_i}\right)^2 \epsilon_i + \sum_{hkl} w \frac{\partial |Fc|}{\partial p_i} \left\{ \sum_{j \neq i}^{n} \frac{\partial |Fc|}{\partial p_j} \epsilon_j \right\} = \sum_{hkl} w\Delta \frac{\partial |Fc|}{\partial p_i}$$

There are n of these equations for j=1,....,n to determine the n unknowns:

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

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

$$\ldots \quad \ldots \quad \ldots \qquad \ldots \quad \ldots \quad \ldots \qquad \ldots \quad \ldots \quad \ldots$$

Alternatively, the normal equations may be expressed in matrix form:

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

where $a_{ij} = \sum_{hkl} w \frac{\partial|Fc|}{\partial p_i}.\frac{\partial|Fc|}{\partial p_j}$ and $b_j = \sum_{hkl} w\Delta \frac{\partial|Fc|}{\partial p_j}$

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

In the case of a structure which involves a large number of atoms it is impracticable to calculate all the terms of the normal equation matrix a_{ij}. However, by making certain assumptions, i.e. if the atoms are well resolved, then some of the off-diagonal terms in the full matrix can be neglected (Cruickshank et alii, 1961). With three-dimensional data the "block-diagonal approximation" is useful. The S.F.L.S. programme used to carry out the refinements which will be described

(Appendix I) uses a chain of 9× 9 matrices for the coordinates and anisotropic temperature parameters of each atom, with a 2× 2 matrix for the scale and overall isotropic vibration. This takes into account interaction between the positional and thermal parameters of any one atom but not general interatomic interaction.

1.14 Accuracy of parameters obtained from least-squares refinement

In matrix notation the normal equations are of form:

$$\sum_{i=1}^{n} a_{ij}\epsilon_i = b_j$$

The best choice of weights is $w = \frac{1}{\sigma^2}$ and in this case the variance of the parameter p_i is given by:

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

where $(a^{-1})_{ii}$ is a diagonal term of the matrix which is the inverse of the matrix whose elements are a_{ij}.

If the relative weights only are known, so that $w = \frac{k}{\sigma^2}$, the experimental standard deviation (e.s.d.) is given by:

$$\sigma^2(p_i) = \frac{1}{a_{ii}} \frac{\Sigma w\Delta^2}{(m-n)}$$

where (m-n) is the number of degrees of freedom of the system, i.e. the excess of the number of independent hkl observations over the number of parameters.

In the block-diagonal approximation variances may be estimated using the appropriate diagonal terms from the inverse of the block matrices. Such estimates somewhat underestimate the true variances because of neglect of the interatomic interactions in the full matrix (Hodgson and Rollett, 1963).

Bibliography

"Elementary Crystallography" by M.J. Buerger, Wiley (1956).

"Mathematical Crystallography" by M.A. Jaswon, Longmans (1965).

"The Crystalline State, Volume III" by H. Lipson and W. Cochran, Bell (1966).

"Crystal Structure Analysis" by M.J. Buerger, Wiley (1960).

"International Tables for X-ray Crystallography", Volume I (1952),
Volume II(1959), Volume III (1962), Kynoch Press, Birmingham.

CHAPTER TWO

"INTERNAL" COORDINATION COMPLEXES
OF
GROUP II METAL ALKYLS

2.1 Introduction

The crystal structure analyses presented in this thesis were undertaken principally to provide information about the factors which determine the degree of association of so-called "internal coordination complexes". The term is applied to the type of compound commonly produced when an organometallic compound reacts with a ligand containing reactive hydrogen:

$$Me_2Zn \ + \ t\text{-}BuSH \longrightarrow MeZnSBu^t \ + \ CH_4$$

The product, if monomeric, would contain a coordinatively unsaturated metal atom attached to a donor atom which because of the dipole $\overset{\delta+}{\text{Metal}}\text{——}\overset{\delta-}{\text{Ligand}}$, would have increased donor properties. The compounds do, of course, generally associate and degrees of association of 2,3,4, 5,6 and infinity have been proposed for the complexes of zinc.

Several factors have been considered to influence the degree of association which is observed:

a) The Nature of the Donor Atom

Boron as the acceptor is unique in being able to expand its covalency by internal coordination as well as by association. Thus if the donor is a first row element, p_π-p_π bonding is often sufficiently strong to obviate polymerisation and many B-O and B-N derivatives are monomeric, e.g. $Me_2B.OMe$, $MeB(OMe)_2$ and $B(OMe)_3$. If, however, boron is attached to a donor atom from the second or later rows of the Periodic

Table, conditions for orbital overlap are unfavourable and polymers result; $(Me_2B.PMe_2)_3$ is a cyclic trimer (Burg and Wagner, 1953). Halogen atom as donor is a noteable exception to this, BCl_3 being monomeric. The monomeric compound $Me_2B.SMe$ appears anomalous, but the σ-bonding power of sulphur to boron is weak and, it is suggested, insufficient to hold a polymer together (Stone, 1958). In the later rows of the periodic system it is suggested that d_π-d_π interaction may strengthen internal coordination, thus $(Me_2Al.SMe)_2$ and $(Me_2Ga.SMe)_2$ are depolymerised by trimethylamine whereas $(Me_2In.SMe)_2$ and $(Me_2Tl.SMe)_2$ are not (Bradley, 1962).

b) Steric Influence of Bulky Substituents on the Donor Atom

There is less steric interference between bulky substituents in a dimer than in the corresponding trimer. Thus $(Et_2Al.OMe)_3$ is trimeric whereas diethylaluminium ethoxide and t-butoxide are dimers (Hoffmann, 1960).

c) Valence Angle Deformation

Atoms of high atomic number undergo valence angle deformation more easily than lighter elements. Valence angle deformation is gradually relieved with the formation of larger cyclic oligomers and polymers.

Clearly these last two factors will tend to work in opposition. Dimers will be favoured by complexes with bulky substituents on the donor atoms. On the other hand dimers necessarily involve considerable valence angle strain in a four-membered ring. Large oligomers will relieve valence angle strain but will bring bulky substituents into greater proximity.

These three factors are generally held to be the most important. However, a more fundamental consideration would be to examine in greater detail, the nature of the reaction intermediate and this might be most important of all (Beachley and Coates, 1965). The isolation of polymeric, tetrameric or trimeric species from intermolecular condensations involving polymeric intermediates is expected. Intramolecular condensations going through monomeric intermediates favour the dimer as the associated species.

The entropy effect will always favour the formation of dimers relative to that of trimers, tetramers or more associated species since this gives the greater number of independent molecules per unit mass.

The products of reactions between bases containing acidic hydrogen and the dialkyls of Group II metals are of particular interest here. Much attention has recently been given to the coordination complexes of beryllium (Coates and Tranah, 1967; Coates and Fishwick, 1967), magnesium (Coates and Heslop, 1966; Coates and Ridley, 1966; Coates and Ridley, 1967), zinc (Coates and Ridley, 1965; Coates and Ridley, 1966) and cadmium (Coates and Lauder, 1966).

2.2 Complexes with 1-atom donor groups:

a) From reactions with amines

Since with secondary amines as ligands, only one lone-pair is available on the nitrogen for coordination, compounds of the type $RMNR'_2$ can only associate to form open ring structures or polymers in which the metal atoms are necessarily three-coordinate. Only from the reaction of a metal alkyl with a primary amine where two acidic hydrogen atoms can cause the cleavage of two metal-carbon bonds, can an associated organometallic complex with a "cubane" structure be envisaged.

$$Ph_3Al + PhNH_2 \longrightarrow (PhAlNPh)_4 + C_6H_6$$

The "cubane" structure of the phenylaluminium anilide tetramer $(PhAlNPh)_4$ has been confirmed by X-ray analysis (MacDonald and MacDonald, 1963). Such complexes are however inaccessible to Group II elements and in fact very little study has been made of the reactions of the dialkyls of Group II with primary amines.

TABLE 2.1

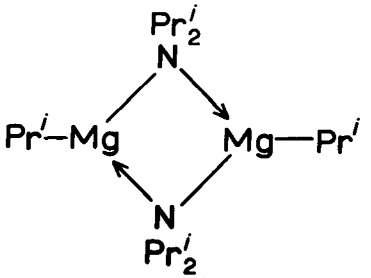
Aminoberyllium Dimers and Trimers in Benzene Solution

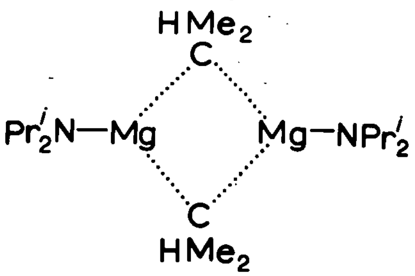
Trimers	$(MeBeNMe_2)_3$	$(MeBeNEt_2)_3$	$(PhBeNMe_2)_3$	$(EtBeNMe_2)_3$
Dimers	$(MeBeNPr^n_2)_2$	$(MeBeNPh_2)_2$	$(EtBeNEt_2)_2$	$(PhBeNPh_2)_2$

In the case of the aminoberyllium alkyls the ring size appears to be determined by steric effects. The strain energy of a dimer is expected to make trimers more favourable unless prevented by steric hindrance. From Table 2.1 it appears that the borderline may be drawn between $(MeBeNEt_2)_3$ and $(EtBeNEt_2)_2$.

In the case of aminozinc alkyls, no trimers have yet been reported since the reaction of dimethylamine with dimethylzinc results in disproportionation products and only bisdimethylaminozinc $[(Me_2N)_2Zn]_x$ has been isolated. Methyl and ethyl(diphenylamino)zinc however, have been isolated and are dimeric in benzene solution. An X-ray structure analysis of methyl(diphenylamino)zinc, $(MeZnNPh_2)_2$, has confirmed that as well as in solution, the molecule is a dimer in the crystal. The structure incorporates a four-membered zinc-nitrogen ring in which the zinc atoms are three-coordinate.

The tendency for alkyl groups, bound to magnesium, to form alkyl bridges is very high, so compounds of the type $RMgNR'_2$ are in general likely to be polymeric. In addition, the necessity of working with R_2Mg in solution in donor solvents like diethyl ether and tetrahydrofuran, THF, means that the associated complexes formed nearly always contain ether, which, in many cases, it is impossible to remove. But two examples of ether-free aminomagnesium alkyls which are dimeric in benzene, and have to be formulated with three-coordinate magnesium are $(Pr^iMgNPr^i_2)_2$ and $(EtMgNEtCH_2Ph)_2$, the latter being formed from diethylmagnesium and benzalanil, PhCH:NPh. Isopropyl(di-isopropylamino)magnesium may be formulated with either of the two structures shown,





although a structure containing one nitrogen and one carbon bridge cannot be ruled out.

The reactions of dialkylzinc with diphenylketimine produce

$$R_2Zn \;+\; Ph_2C{:}NH \longrightarrow RZnN{:}CPh_2 \;+\; RH$$

compounds exemplified by methyl(α-phenylbenzylideneamino)zinc, $(MeZnN{:}CPh_2)_2$. All the compounds which have been made (Pattison and Wade, 1967) where R = Me, Et, Ph have been dimeric in benzene and they too probably have structures with a planar four-membered zinc-nitrogen ring.

b) From reactions with alcohols

The vigorous reactions between zinc alkyls and water or alcohols have been known since the first preparations of zinc alkyls by Frankland in 1853.

The oxygen atom with a second lone-pair available for coordination enables compounds of the type RMOR' to associate to form cage structures in which the oxygen becomes four-coordinate and the metal atom achieves a preferred coordination number of four.

The molecular weight of methylzinc methoxide determined cryoscopically in benzene shows that the molecule is tetrameric, $(MeZnOMe)_4$. X-ray structure analysis now shows that methylzinc methoxide is also tetrameric in the crystal, with zinc and oxygen atoms near the corners of a distorted cube. The X-ray powder diffraction patterns of $(MeZnOMe)_4$ and $(MeCdOMe)_4$ are similar and crystals of the compounds are probably isomorphous. The methoxide, ethoxide and t-butoxides of methylberyllium and also $(Bu^tBeOMe)_4$ and $(PhBeOMe)_4$ are all tetrameric in benzene solution as are the alkylmagnesium alkoxides in which there is chain branching at the carbon α to oxygen; $(EtMgOPr^i)_4$, $(EtMgOBu^t)_4$ and $(Pr^iMgOPr^i)_4$. It is possible that all these tetrameric alkoxides are isostructural.

In contrast, ebullioscopic molecular weight determinations using a differential thermocouple, have shown that in ether solution the beryllium alkoxides, MeBeOR, where R = Me, Et, Pr^n, Pr^i and Bu^t, are dimeric. Evidently the ether oxygen competes successfully with the second lone-pair of the alkoxy oxygen, for the fourth coordination position about beryllium.

The alkoxides of magnesium show differing degrees of association. Ethylmagnesium n-propoxide, isopropylmagnesium methoxide and ethoxide are oligomers which have degrees of association in benzene in the range 7-8·4. It is probable that these alkoxides are polymeric in the solid state.

An X-ray analysis (Matsui et alii, 1966) has shown that $(EtZnOBu^t)_4$ is a tetramer in the crystal. However, in this series, $(MeCdOBu^t)_2$ is a dimer and might appear anomalous. The energy separation of s- and p-orbitals for cadmium is very much larger than that in zinc and so for cadmium, hybrid orbitals with large 's' character are to be expected. In accordance with this, a dimeric structure for methylcadmium t-butoxide would involve cadmium in utilising sp^2 hybrids as opposed to the sp^3 hybrid orbitals used in a "cubane" arrangement.

The only other alkoxides of Group II which are not tetrameric in benzene solution have organic groups present which are sufficiently bulky to make smaller oligomers more favourable. $(EtZnOCHPh_2)_3$ is trimeric in benzene solution. A trimeric organomagnesium species, n-butylmagnesium isopropoxide, has also been reported (Bryce-Smith and

Graham, 1966). $(PhZnOCPh_3)_2$ and $(EtZnOCPh_3)_2$ are dimeric as is the beryllium analogue of the latter. As would be expected the Group II alkoxides of formula $(Bu^tMOBu^t)_2$ are all dimeric and probably have structures analogous to $(MeZnNPh_2)_2$.

The reactions of dimethylzinc and dimethylcadmium with trimethylsilanol give compounds, $(MeMOSiMe_3)_4$, which are

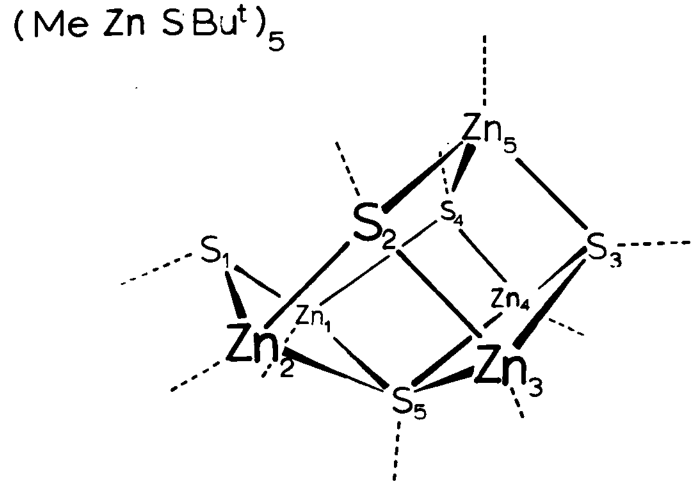
$$Me_2M + HOSiMe_3 \longrightarrow CH_4 + MeMOSiMe_3$$

tetrameric in inert organic solvents. These tetramethylsiloxanes also, are assumed to have the cubane structure of methylzinc methoxide (Schindler, Schmidbaur and Kruger, 1965).

c) From reactions with thiols

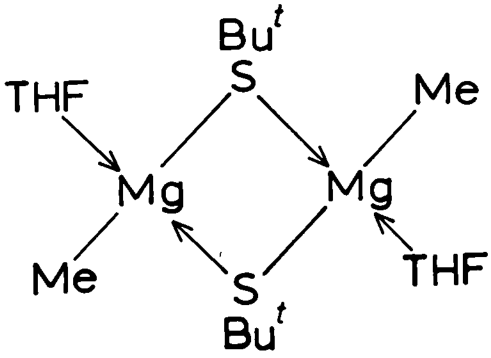
The products of reactions with thiols show differing degrees of association. $(MeBeSBu^t)_4$, $(EtBeSEt)_4$, $(EtBeSPr^i)_4$ and $(EtBeSBu^t)_4$ as indicated are all tetrameric and presumably have the structure shown by the tetrameric alkoxides. Ethylberyllium methylsulphide and methylzinc methylsulphide are however insoluble in benzene and are assumed to be polymeric in the solid state. The thio- derivatives of methylzinc and methylcadmium are somewhat anomalous. Methylzinc isopropylsulphide and its cadmium analogue were found to be hexameric in benzene solution. A preliminary X-ray investigation of methylzinc isopropylsulphide is consistent with the existence of octamers in the crystal (Adamson and Shearer, 1967). And whereas methylzinc t-butylsulphide is a pentamer, methylcadmium t-butylsulphide is tetrameric.

A crystal structure analysis of methylzinc t-butylsulphide (Adamson and Shearer, 1966) has confirmed that the molecule is a pentamer, $(MeZnSBu^t)_5$, in the crystal. The zinc atoms lie near the



corners of a square-based pyramid with the apical atom, Zn(5), closer to Zn(3) and Zn(4). The sulphurs S(2), S(3), S(4) lie above the centres of the triangular faces, S(1) above the face defined by Zn(1), Zn(2) and Zn(5), but is much further away from Zn(5). S(5) lies below the basal plane and is somewhat closer to Zn(3) and Zn(4). The arrangement results in the three zinc atoms Zn(3), Zn(4), Zn(5) and the four sulphur atoms S(2), S(3), S(4), S(5) lying near the corners of a cube. With one methyl bonded to each zinc and one t-butyl to each sulphur, all the zinc atoms and three of the sulphurs are four-coordinate whereas S(1) is three-coordinate and S(5) five-coordinate. That $(MeZnSBu^t)_5$ prefers to the "cubane" structure of methylzinc methoxide, a pentameric arrangement in which one sulphur atom is only three-coordinate is very puzzling. There is no evidence of significant steric interactions between organic groups in $(MeZnSBu^t)_5$. The seven atoms Zn(3), Zn(4), Zn(5), S(2), S(3), S(4) and S(5) lie near the corners of a cube and on steric grounds there seems to be no reason why a MeZn unit should not be accommodated at the eigth corner of the cube.

In the thio-derivatives of alkylmagnesium, the second lone-pair on the sulphur atom competes unsuccessfully with ether (present as solvent during the preparation) for the fourth coordination position about the metal. All the complexes of this type which have been made, are etherates, and are dimers with structures similar to that shown for $(MeMgSBu^t.THF)_2$.



The t-butylmagnesium isopropylsulphide diethyl ether complex, $(Bu^tMgSPr^i.OEt_2)_2$, is a further example.

The diethyl ether complex of t-butylmagnesium chloride, $(Bu^tMgCl.OEt_2)_2$ is also a dimer and is expected to have a structure similar to that described above, the monomers linking through chlorine bridges. X-ray structure analysis has established that the diethyl ether complex of t-butoxymagnesium bromide is a centrosymmetric dimer in the crystal, with a four-membered magnesium-oxygen ring (Moseley and Shearer, 1967). An unexpected feature of this structure is that in both cases the oxygen atoms appear to be very nearly coplanar with the three atoms to which they are bonded.

d) Alkylzinc halides

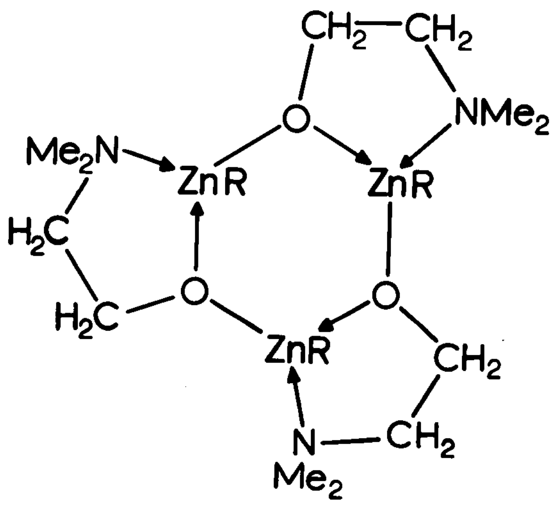
The degrees of association of the alkylzinc halides are also of interest in this context. Molecular weight measurements in benzene have established that unsolvated ethylzinc chloride and bromide are tetrameric (Boersma and Noltes, 1966), and it is suggested that the tetramers have a "cubane" structure in which the molecule associates through halogen bridging as in $(Me_3PtCl)_4$ (Rundle and Sturdivant, 1947). In contrast, X-ray structure analysis (Moseley and Shearer, 1966) has shown that in the crystal ethylzinc iodide is a coordination polymer, the iodine-zinc linkages giving rise to a layer structure. The "cubane" arrangement presumably breaks down owing to the difficulty of forming a four-membered ring containing an atom as large as iodine.

2.3 Complexes with 2-atom donor groups

Here the position is more complex. In some cases both donor atoms are involved in coordination, in other cases only one. Consequently it is more difficult to make predictions about the nature of the association.

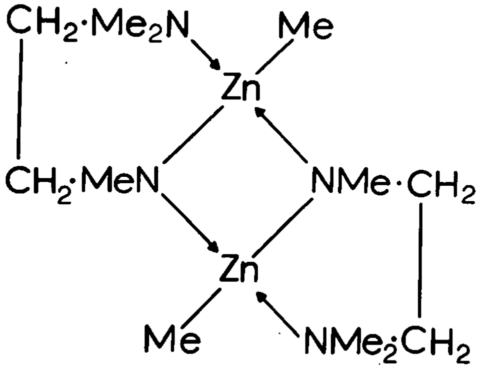
The tetrameric 2-methoxy-ethoxy complex, $(MeZnOCH_2.CH_2OMe)_4$, is thought to be like the other alkoxides because the donor strength of the oxygen bound to zinc is greater (on account of the electropositive character of the metal) than that of the ether oxygen. The ether side chains will protrude from the corners of the cube resulting in a molecule of low symmetry and this is probably responsible for the fact that methylzinc 2-methoxy-ethoxide is a liquid.

The 2-dimethylaminoethoxy derivatives of dimethyl- and diethylzinc are however trimers. If this seems inconsistent with the 2-methoxy-ethoxy derivative mentioned above, it must be remembered that in

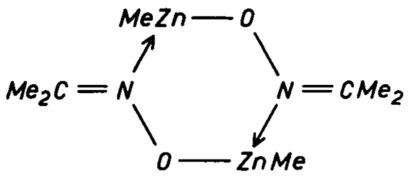


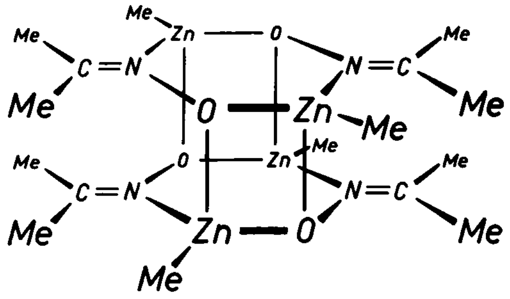
$(RZnOCH_2.CH_2NMe_2)_3$ the nitrogen lone-pair is in competition for a coordination position about the metal, not with three-coordinate oxygen but with the fourth valency of the relatively rarely encountered four-coordinate oxygen. Although the beryllium compound $(MeBeSCH_2.CH_2NMe_2)_3$ is also trimeric and presumably has a similar structure, the position is confused by the fact that $(Bu^tMgSCH_2.CH_2NMe_2)_2$ is a dimer and $MeBeOCH_2.CH_2NMe_2$ is polymeric. The situation is even more complicated than this however, the magnesium analogue of the trimer illustrated above, $(MeMgOCH_2.CH_2NMe_2)_4$ is tetrameric in solution.

The complexes formed from Me_2Be, Me_2Mg and Me_2Zn with NNN'-trimethylethylenediamine are all dimeric in benzene solution and are thought to have structures similar to that illustrated below for $(MeZnN(Me)CH_2.CH_2NMe_2)_2$.



Methylzinc dimethylketoximate $(MeZnON:CMe_2)_4$ is tetrameric in solution and could conceivably have a structure analogous to that of the tetrameric alkoxides. It seems more likely, however, that the nitrogen also is coordinated to the metal. It was proposed that methylzinc acetoximate consisted of two parallel six-membered rings and that that coordination number of zinc was made up to four by zinc-oxygen interactions between the rings.





This structure however, like the alkoxide structures,involved several four-membered rings. We have now examined the structure of $(MeZnON:CMe_2)_4$ in the crystal. Coordination does indeed take place through both oxygen and nitrogen but a "cage" structure results in which there are four five-membered rings and two adjacent six-membered rings but no four-membered rings. A further outcome of the arrangement is that the four zinc atoms are in three different kinds of environment.

2.4 Complexes with 3-atom donor groups

Carboxylates, phosphinates, isocyanates and carbodiimides will come into this category. Methylzinc acetate from dimethylzinc and acetic acid, and methylzinc dimethylphosphinate, are insoluble and are probably polymerised by interaction between the metal of one ring and an oxygen of another. An X-ray diffraction study of $[Zn(Bu^n_2PO_2)_2]_x$, a complex which is representative of a class of zinc(II) and cobalt(II) di-n-alkylphosphinate coordination polymers, has revealed a structure with alternate single and triple bridging phosphinate groups along chains of tetrahedrally coordinated zinc atoms (Giordana et alii, 1967).

Although methyl and ethyl isocyanates are trimerised by the action of zinc alkyls, phenyl isocyanate adds diethyl- or diphenylzinc to give tetrameric products, $(EtZnNPh.COEt)_4$ and $(PhZnNPh.CO.Ph)_4$. Structures involving zinc-oxygen interactions between two parallel eight-membered rings were suggested (c.f. the acetoximate). This arrangement would involve four-membered zinc-oxygen rings however and in view of the crystal structure of methylzinc acetoximate presented, this is now regarded as unlikely.

Evidence has recently been presented to show that the catalytic species, active in the trimerisation of methyl and ethyl isocyanates, are organozinc ureas, $(EtZnNPh.CO.NPh_2)_3$ and organozinc carbamates, $(EtZnNPh.CO.OMe)_3$. These ureas and carbamates are trimeric in benzene and are formulated with a six-membered zinc-nitrogen ring which acts as a "template" for the trimerisation of isocyanate (Noltes and Boersma, 1967).

CHAPTER THREE

THE CRYSTAL STRUCTURE OF TETRAMERIC METHYLZINC METHOXIDE

3.1 Preparation, Chemical and Spectroscopic Characteristics

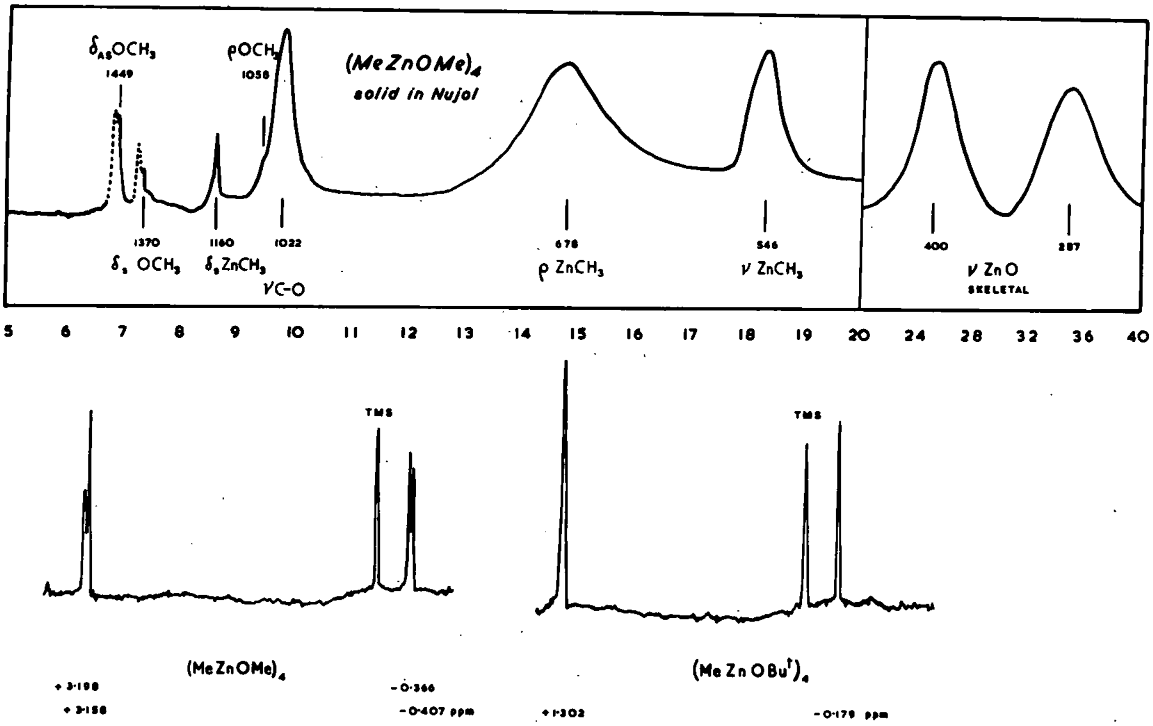
It was a remarkable achievement, considering the spontaneously inflammable and air-sensitive nature of zinc alkyls, when Butlerow first prepared methylzinc methoxide over a hundred years ago in 1864. Using carbon dioxide as a protective atmosphere, Butlerow obtained a colourless crystalline solid from the reaction of dimethylzinc with an excess of methanol. The methoxide for the present work was prepared under a dry nitrogen atmosphere by the slow addition of methanol to a solution of dimethylzinc in hexane at -70°, one mole of methane being evolved.

$$Me_2Zn + MeOH \longrightarrow MeZnOMe + CH_4$$

The compound crystallised as short needles of rectangular cross-section. It has a melting point of 190-191°. Cryoscopic measurements have shown that the molecule is tetrameric in benzene solution.

The infrared spectrum of a solution in cyclohexane is virtually identical with that of the solid examined as a Nujol mull and is relatively simple. Nine of the ten absorption bands between 200 and 2000 $cm.^{-1}$ have been assigned (Coates and Ridley, 1965).

The proton magnetic resonance spectrum of methylzinc methoxide in benzene solution consists of two double peaks, a methoxy doublet and a Zn-Me doublet. The Zn-Me doublet collapses over a range of about 10° becoming a sharp singlet at 45°. The methoxy doublet, in contrast, remains at such even at 100°. Since the corresponding spectrum of



$(MeZnOBu^t)_4$ consists of only two single sharp peaks, it was suggested that isomeric forms are accessible to the methoxy compound, but denied to the t-butoxy derivative on account of steric hindrance (Coates and Ridley, 1965). However, subsequent to the appearance of a preliminary report on the crystal structure of $(MeZnOMe)_4$ (Shearer and Spencer, 1966), further investigation (Allen, Bruce et alii, 1966) showed that the spectrum of a freshly prepared solution of the methoxide at 40° shows only one methoxyl resonance and is thus in agreement with the structure proposed for the crystal. The existence of the methoxy doublet in the earlier spectrum has been explained by Bruce and co-workers, in terms of equilibrium mixtures in solutions of methylzinc methoxide which have been allowed to age.

3.2 Crystals

Crystals suitable for the structure analysis were obtained by re-crystallisation from hexane and were sealed individually in pyrex glass capillary tubes in the dry nitrogen atmosphere of a glove box. The compound crystallised as translucent needles, however in spite of the elaborate precautions taken to exclude oxygen and moisture, after sealing in capillaries the crystals had a white opaque appearance. However, this did not seem to affect the quality of the X-ray reflections obtained and could only have been due to a surface layer of zinc oxide.

3.3 Crystal Data

Methylzinc methoxide, $(MeZnOMe)_4$, M.W. = 445·80

Orthorhombic: needles elongated along b,

well developed {100} and {001} faces.

$a = 7{\cdot}481$, $b = 7{\cdot}673$, $c = 29{\cdot}41$ Å;

$U = 1688$ Å^3; $Z = 4$ units of $(MeZnOMe)_4$;

$D_m = 1{\cdot}75$; $D_x = 1{\cdot}754$ gm.cm.$^{-2}$

Absorption Coefficient for Cu Kα radiation, $\mu = 67$ cm.$^{-1}$

Conditions limiting the observed reflections:

h00: h=2n

0k0: k=2n

00l: l=2n

The space group is therefore uniquely determined as, Number 19, $P2_12_12_1$.

The unit cell dimensions were obtained from precession photographs of the hk0 and 0kl reciprocal lattice nets using Cu Kα radiation (λ = 1·5418 Å). The statistical standard deviations in unit cell lengths were 0·006 Å in a, 0·005 Å in b, and 0·008 Å in c. However, if systematic errors are included, the uncertainty is probably of the order of 0·2%.

3.4 Data Collection and Correction

Three-dimensional intensity data were recorded photographically by the equi-inclination Weissenberg technique using nickel-filtered copper radiation. The multiple film technique was used in recording the hnl nets where n=0 to 7. The intensities were estimated visually by comparison with a calibrated scale and were placed on a common scale using photographs on which timed exposures of different nets had been made.

In the case of high order reflections which were split owing to the resolution of the Kα_1, Kα_2 doublet, the intensity of the reflection due to the Kα_1 component alone was estimated and was multiplied by an empirical correcting factor of 1·32.

The usual Lorentz and polarisation factors were applied and in the case of upper layers the intensities were also corrected for spot length (Phillips, 1956). On upper layers the intensities of the contracted spots were not estimated.

The crystal used in data collection had the following dimensions (expressed in cm.):

along $\underline{a}$, 0·026; along $\underline{b}$, 0·090; along $\underline{c}$, 0·019

In view of the size of the crystal and the value of $\mu = 67$ cm.$^{-1}$ for the linear absorption coefficient, it seemed necessary to correct the intensities for absorption. This was done using the method of Busing and Levy (1957).

3.5 The Patterson Function

The intensities were multiplied by a weighting function w, where $w = \exp(12\sin^2\theta/\lambda^2)$. The "sharpened" Patterson function was then evaluated:

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

'u' was calculated at intervals of 0·25 Å, a/40;

'v' was calculated at intervals of 0·26 Å, b/40;

'w' was calculated at intervals of 0·25 Å, c/120.

The symmetry of the vector set is Pmmm and the Patterson function was computed over one eigth of the unit cell.

The three two-fold screw axes in the crystal result in three Harker sections in the Patterson function: $P(\frac{1}{2},v,w)$, $P(u,\frac{1}{2},w)$ and $P(u,v,\frac{1}{2})$. Four Zn-Zn vectors between symmetry related atoms are expected in each Harker section. The Harker sections at $(\frac{1}{2},v,w)$ and $(u,\frac{1}{2},w)$ both contain more than four peaks large enough to be due to Zn-Zn vectors. However, the section at $(u,v,\frac{1}{2})$ is extremely simple, containing only three resolved peaks, one of which is large enough to arise from the coincidence of two vectors. Starting from $P(u,v,\frac{1}{2})$ the simplest of the Harker sections, and then finding consistent vectors on $P(\frac{1}{2},v,w)$ and $P(u,\frac{1}{2},w)$, sets of coordinates for all four zinc atoms were found. These positions were confirmed by finding suitable peaks in the Patterson map for the four vectors between each pair of atoms and those atoms related by the symmetry operations of the space group. The 24 vectors of this type, together with the 12 Harker peaks, accounted for all the major features of the Patterson function.

An attempt was now made to find the positions of the oxygen atoms by superposition methods but this was unsuccessful.

At this stage the heavy atom coordinates were:

Zn(1)	-0•100	0•200	0•175
Zn(2)	0•083	0•200	0•083
Zn(3)	0•083	-0•117	0•142
Zn(4)	-0•275	0•000	0•096

3.6 Light Atom Positions

A first set of structure factors was calculated using the coordinates of the four zinc atoms. The value of the residual, R, was 0•32.

$$\text{where } R = \frac{\Sigma||Fo| - |Fc||}{\Sigma|Fo|}$$

A three-dimensional Fo synthesis, was then computed using the phase angles deduced from the heavy atom positions.

The electron density map showed peaks at the position of the zinc atoms with heights of 48 ± 2 e.Å^{-3}. Four peaks with heights between 4•3 and 5•7 e.Å^{-3} were attributed to oxygen atoms. Peaks in positions compatible with the four carbon atoms attached to zinc and also the four attached to oxygen had heights ranging from 2·6 to 3·7 e.Å^{-3}. There were two further peaks with heights of ∼ 4 e.Å^{-3} and six of ∼ 3 e.Å^{-3}.

A new set of structure factors were calculated on the basis of the four zinc, the four oxygen and the eight carbon atoms. Agreement with the observed structure factors improved to R = 0·27. The calculated phases were used to compute a second Fo synthesis. The peak heights of the oxygen atoms now ranged from 8·0 to 10·6 e.Å^{-3}, those of the carbon atoms from 5·6 to 6·4 e.Å^{-3}. There were no unassigned peaks greater than 3 e.Å^{-3}.

3.7 Structure Refinement

The positional and thermal parameters of the atoms were then refined by the method of least squares using the block diagonal approximation. After three cycles with isotropic temperature parameters for all atoms, followed by three cycles with anisotropic temperature parameters throughout, the residual had improved to 0·12. At this stage many of the intense low order planes were giving poor agreement between observed and calculated values, so bearing in mind the possibility of finding hydrogen atoms an (Fo-Fc) synthesis was calculated. The features of the map were:

4 peaks of 4 e.Å^{-3} corresponding to the Zn atoms,
4 peaks of 1 e.Å^{-3} corresponding to the O atoms,
8 peaks of 0·6-0·7 e.Å^{-3} corresponding to the C atoms.

No other significant peaks were found. The expected positions of certain hydrogen atoms were estimated but suitable peaks on the difference map were not found.

It was noted that most of the planes which gave poor agreement were on the $0k\ell$ and $1k\ell$ lattice lines and further, that Fo was always proportionally greater than Fc. Due to the shape of the crystal, these reflections were narrower than the norm, with the result that their intensities had been overestimated. An attempt was made to correct for this by an empirical method.

After five more cycles of least-squares refinement the R factor had converged to a value of 0·098. At this point, in only 12 out of the 145 parameters being refined, did the shifts exceed 1/3 of the corresponding e.s.d. As the refinement seemed complete, structure factors were calculated and used to compute a final electron density difference synthesis. The map showed the following features:

4 peaks of +3·5 e.Å^{-3} corresponding to the Zn atoms,
4 peaks of +0·75 e.Å^{-3} corresponding to the O atoms,
8 peaks of +0·45 e.Å^{-3} corresponding to the C atoms.

The map showed no other pronounced features.

Structure factors were calculated for the 341 unobserved reflections, none of them were significantly greater than the expected maximum value, Fmin. The unobserved planes were not included in the refinement.

Finally, three cycles of least-squares refinement were applied, in which all atoms had anisotropic temperature parameters, and, in addition individual scale factors for the reciprocal lattice nets h01 to h71 were refined. Lingafelter (1966) has pointed out that if data is collected about one axis only, i, then there is complete degeneracy between the U_{ii} and the scale factors κ_i, and it is impossible to evaluate them individually. However, in this instance, before introducing individual scale factors, the refinement was almost complete using experimentally derived values of κ_i. That we were allowing for random errors in the scaling was confirmed by the fact that half the κ_i values increased while the rest decreased. The maximum change in scale factor obtained was 7·7% and the mean difference between the observed and refined values was 4·3%. The treatment had no noticeable effect on the anisotropic vibration tensor elements U_{22} although the nets were collected up the b axis.

Towards the end of the refinement the structure factors were weighted by a function $\sqrt{w}$, given by:

$$\sqrt{w} = \frac{1 - \exp(-p_1 \sin^2\theta/\lambda^2)}{(1 + p_2|Fo| + p_3|Fo|^2 + p_4|Fo|^3)^{\frac{1}{2}}}$$

where p_1=35, p_2=0·143, p_3=0·00286 and p_4=0·0000429.

The least squares totals and the variation of $w\Delta^2$ with $|Fo|$ and with $\sin\theta/\lambda$ are given in Table 3.1.

In the final cycle of refinement the largest parameter shift was only 0·31 of its e.s.d. The final values of the positional and thermal parameters together with their e.s.d.'s are given in Tables 3.2 and 3.3.

The observed and calculated structure factors are given in Table 3.10. The residual, calculated over the observed reflections only, was 0·091.

In this case and with the other structure to be described, the atomic scattering factors used were those given in International Tables (1962) Volume III. The real part of the dispersion correction was applied in the case of zinc.

$(\mathrm{MeZnOMe})_4$ TABLE 3.1

Least-Squares Totals

Number of Observed Planes 1287

$\Sigma\lvert\Delta\rvert$	3271·4	$\Sigma\lvert Fo\rvert$	36053·2	$\Sigma\lvert Fc\rvert$	35203·1	R	0·091
$\Sigma w\lvert\Delta\rvert^2$	1173·5	$\Sigma w\lvert Fo\rvert^2$	84942·1	$\Sigma w\lvert Fc\rvert^2$	83781·3	R'	0·014

Weighting Analysis

$w.\Delta^2$ averaged in batches and the number of planes per batch

			$\sin\theta/\lambda$		
	0·0-0·2	0·2-0·4	0·4-0·6	0·6-0·8	TOTALS
$\lvert Fo\rvert$					
0-12	1·27/5	0·62/32	0·83/311	0·96/40	0·83/388
12-24	2·58/9	0·80/103	0·94/318	3·56/1	0·95/431
24-48	2·55/12	0·66/168	1·56/84	0·00/0	1·03/264
48-97	0·70/27	0·66/132	4·12/2	0·00/0	0·71/161
97-193	1·61/17	1·15/23	0·00/0	0·00/0	1·34/40
193-UP	1·18/2	0·46/1	0·00/0	0·00/0	0·94/3
TOTALS	1·51/72	0·71/459	0·97/715	1·02/41	0·91/1287

(MeZnOMe)$_4$ TABLE 3.2

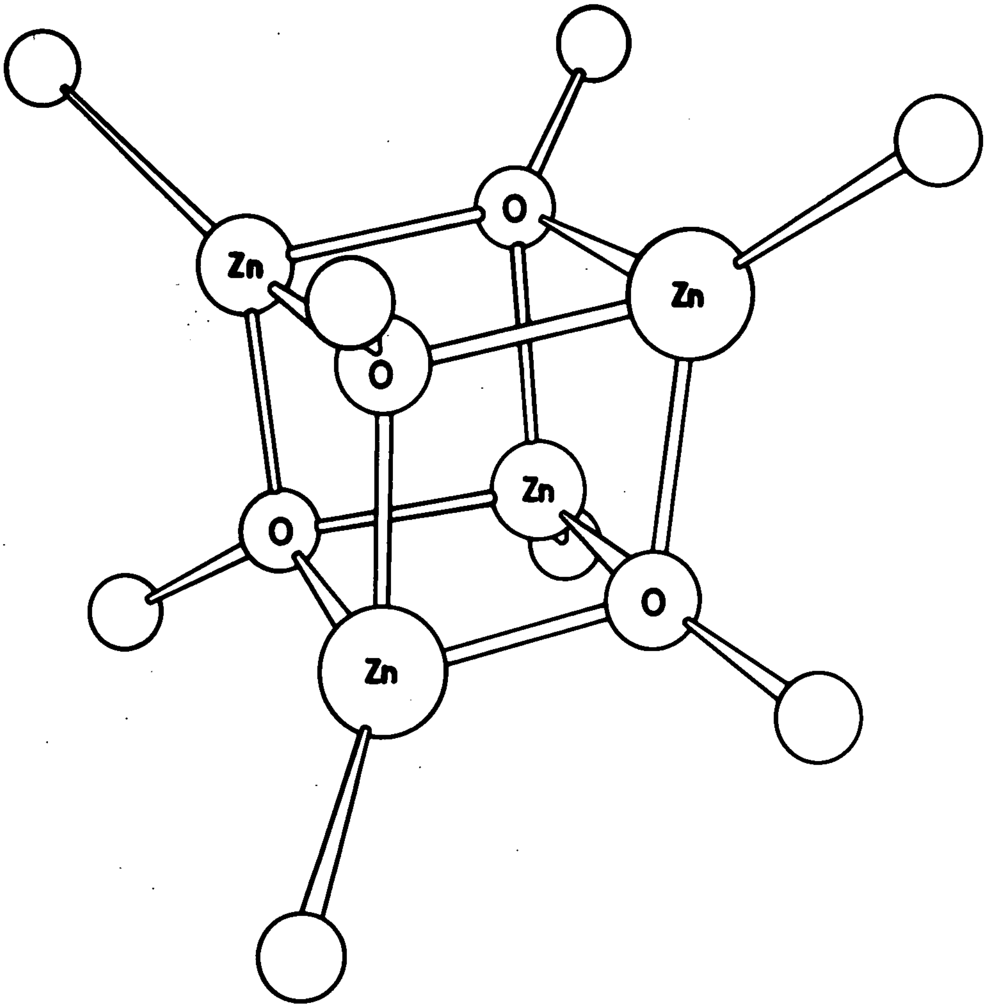
Final Values of Atomic Cordinates and their Standard Deviations

Atom	x/a	y/b	z/c	σ(x/a)	σ(y/b)	σ(z/c)
Zn(1)	0·06488	-0·13218	0·14018	0.00036	0·00033	0·00008
Zn(2)	-0·11056	0·20635	0·17505	0·00036	0·00036	0·00008
Zn(3)	0·07638	0·20216	0·08147	0·00033	0·00033	0·00008
Zn(4)	-0·27936	0.00391	0.09552	0.00034	0.00037	0.00009
O(1)	-0·18888	-0·04370	0·16082	0·00158	0·00177	0·00035
O(2)	0·13480	0·12551	0·14838	0·00139	0·00165	0·00032
O(3)	-0·17406	0·25165	0·10674	0·00165	0·00193	0·00037
O(4)	-0·02347	-0·05070	0·07633	0·00146	0·00178	0·00034
C(1)	0·18486	-0·35667	0·15084	0·00346	0·00349	0·00091
C(2)	-0·18706	0·34069	0·22772	0·00478	0·00328	0·00064
C(3)	0·21041	0·33805	0·03824	0·00301	0·00294	0·00066
C(4)	-0·50146	-0·09036	0·07069	0·00291	0·00357	0·00060
C(5)	-0·28915	-0·14623	0·19221	0·00287	0·00345	0·00066
C(6)	0·29546	0·17668	0·17051	0·00253	0·00349	0·00074
C(7)	-0·27796	0·40778	0.09405	0·00475	0·00346	0·00074
C(8)	0·01720	-0·15176	0·03684	0·00379	0·00319	0·00075

$(MeZnOMe)_4$ TABLE 3.3

Final Values of Anisotropic Temperature Parameters ($\mathring{A}^2$) and their Standard Deviations ($\mathring{A}^2$ x 10^4 for zinc and oxygen, $\mathring{A}^2$ x 10^3 for carbon)

Atom	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Zn(1)	0·0829(15)	0·0612(12)	0·0717(12)	0·0067(23)	-0·0052(24)	0·0142(26)
Zn(2)	0·0911(16)	0·0728(14)	0·0590(11)	-0·0030(23)	0·0118(22)	0·0177(29)
Zn(3)	0·0764(13)	0·0689(13)	0·0639(11)	0·0138(23)	0·0073(21)	0·0020(27)
Zn(4)	0·0686(13)	0·0773(14)	0·0750(13)	-0·0001(25)	0·0011(23)	-0·0009(27)
O(1)	0·0670(67)	0·0753(73)	0·0586(58)	0·0015(114)	-0·0184(106)	0·0157(129)
O(2)	0·0538(52)	0·0782(70)	0·0482(50)	0·0165(106)	-0·0147(86)	-0·0010(119)
O(3)	0·0667(65)	0·0948(92)	0·0568(57)	-0·0211(122)	-0·0067(102)	-0·0002(138)
O(4)	0·0585(58)	0·0845(80)	0·0485(51)	0·0028(110)	-0·0034(94)	0·0118(119)
C(1)	0·098(15)	0·095(15)	0·123(17)	0·065(31)	-0·010(27)	0·040(29)
C(2)	0·206(29)	0·089(14)	0·069(11)	-0·038(22)	0·117(32)	0·075(37)
C(3)	0·091(13)	0·081(12)	0·078(10)	0·023(19)	0·052(21)	-0·014(24)
C(4)	0·084(12)	0·111(16)	0·063(10)	-0·008(21)	-0·050(19)	-0·034(24)
C(5)	0·079(11)	0·104(15)	0·083(11)	0·053(24)	0·023(20)	0·046(26)
C(6)	0·059(10)	0·108(17)	0·107(14)	0·041(26)	-0·045(21)	0·024(23)
C(7)	0·185(28)	0·093(16)	0·074(12)	0·006(23)	-0·060(33)	0·124(38)
C(8)	0·124(18)	0·071(12)	0·091(13)	-0·005(21)	-0·018(27)	-0·000(27)



(MeZnOMe)$_4$

Figure 3·1

3.8 Description and Discussion of Structure

The molecular arrangement is shown in Figure 3.1.

The zinc atoms lie at the corners of a tetrahedron and the oxygen atoms at the corners of an interpenetrating but smaller tetrahedron. Thus the zinc and oxygen atoms are four coordinate and are situated on alternate corners of a distorted cube. The distortion can be described in terms of an inward movement of the oxygen atoms along the threefold axes of the cube, resulting in the Zn-O-Zn angles being greater than 90°, and as would be expected the deviation of the angles at zinc from the tetrahedral are greater than those at oxygen.

The zinc-zinc distances vary from 3•073 to 3•093 Å with a mean value of 3•085 Å. The standard deviations obtained directly from coordinate e.s.d.'s are 0•003 Å. After allowance has been made for uncertainties in unit cell dimensions the standard deviations are increased to 0•007 Å and on this basis the differences in the zinc-zinc distances are not significant. The oxygen-oxygen distances vary from 2•729 to 2•788 Å. These values do not differ significantly from one another or from the mean of 2•769 Å. Within the limits of experimental error then, the interpenetrating tetrahedra of zinc and oxygen atoms are regular.

Table 3.5 gives the bond lengths and their standard deviations. The Zn-O distances are also shown on Figure 3.2.

The mean Zn-C distance of 1·95 Å is less than the sum (2·08 Å) of the Pauling tetrahedral covalent radii but agrees closely with the length of 1·94 Å in dimethylzinc (Rundle, 1963). A shortening of the Zn-C bond in dimethylzinc was explained by invoking hyperconjugation involving the empty 4p orbitals on zinc. None of the Zn-C distances in methylzinc methoxide differs significantly from the mean value. Similarly the O-C distances may be taken to be the same with a mean of 1·44 Å. This compares closely with the value of 1·427 Å in methanol (Venkateswarlu and Gordy, 1955) in spite of the change in coordination number and in the character of bonding at oxygen.

The Zn-O distances vary from 2·039 to 2·105 Å with e.s.d.'s of 0·012 Å. Considering the two extreme lengths, the value of t_o is 3·9, where t_o is a value of the random variable t having a Student distribution with ν degrees of freedom, and is defined by:

$$t_o = \frac{x_1 - x_2}{\sqrt{(\sigma_{x_1}^2 - \sigma_{x_2}^2)}}$$

Since the number of planes greatly exceeds the number of refined parameters, ν is large and the t distribution is normal. For the extreme Zn-O distances, the difference is therefore significant at the 0·01% probability level. The lengths of four Zn-O bonds are significantly shorter than 2·105 Å, namely:

Zn(1)-O(2) 2·059 Å; Zn(2)-O(1) 2·049 Å;
Zn(3)-O(3) 2·051 Å; Zn(4)-O(4) 2·039 Å.

It is noticed that each zinc and each oxygen atom participates in one of these four short bonds and further that the four short bonds are related by a fourfold inversion axis. The mean of the other eight Zn-O bonds is 2·089 Å, none of the individual values differing significantly from this. The mean Zn-O distance taken over all twelve values is 2·076 Å. A satisfactory explanation for the existence of these four short bonds has not been forthcoming and it is difficult to understand why there should be two kinds of Zn-O bond in this compound.

TABLE 3.4

Zinc-Oxygen Distances

Experimental Value from:		Semi-Empirical Estimate from:	
$Zn_4O(CH_3COO)_6$ Oxyacetate complex (Koyama and Saito, 1954)	1·98	Pauling tetrahedral covalent radii	1·97
$ZnCl_2(H_2NCONHCONH_2)_2$ Biuret zinc chloride complex (Nardelli et alii, 1963)	2·04	Tetrahedral covalent radii with Schomaker Stevenson correction	1·90
		Pauling crystal radii	2·14
$Zn(C_9H_6ON)_2(H_2O)_2$ 8-hydroxyquinoline complex (Merritt et alii, 1954)	2·05	Crystal radii corrected for change from octahedral to tetrahedral coordination	1·99

Table 3.4 gives some experimental and some semi-empirical zinc-oxygen distances. The Zn-O distances observed in methylzinc methoxide are significantly greater than the value of 1•98 observed in the zinc oxyacetate complex, where zinc has a tetrahedral environment, this latter distance agreeing closely with the sum of the Pauling tetrahedral covalent radii (1•97 Å). However, some increase in Zn-O distance over that expected for atoms in a tetrahedral environment might be expected since both the zinc and oxygen atoms have three valence angles near 90°, the atomic orbitals used in bond formation having increased 'p' character. There is indeed better agreement with zinc-oxygen distances measured in complexes where zinc is octahedrally coordinated as in the other two compounds shown in Table 3.4.

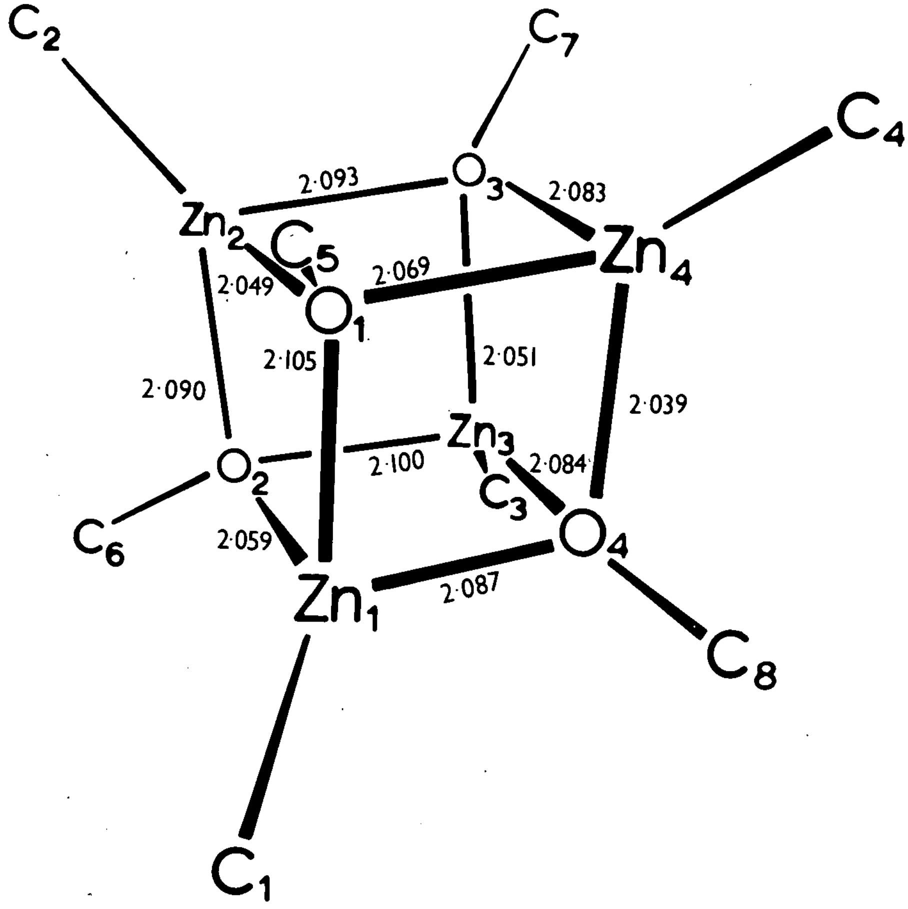
In the case of zinc-oxygen bonds, comparisons of interatomic distances are not very informative about the nature of the bonding. There is agreement between the observed Zn-O distances in zincite (1•95, 1•98 Å) with the sum of the Pauling tetrahedral covalent radii, but the issue is confused by the fact that the observed distances also fit reasonably well with the sums of the standard ionic radii corrected for fourfold coordination. Nevertheless, the Zn-O bond is expected to have considerable polar character. However, if an electronegativity correction is applied, it leads to a shortening of the simple covalent radii sum, and an even bigger discrepancy from the observed bond length in methylzinc methoxide.

In general, the use of these semi-empirical estimations gives Zn-O distances which are shorter than the distances observed in methylzinc methoxide. However, the use of tetrahedral radii is not entirely satisfactory, since the valence angles at both zinc and oxygen depart considerably from the tetrahedral.

Table 3.7 gives the bond angles with their standard deviations.

The Zn-O-Zn angles vary from 94·8° to 97·2°. The value of t_o between these extreme values is 3·3 and the difference is significant. The average O-Zn-O angle is 83·7° but again t_o for the extreme values of 82·6° and 85·0° is greater than 3·8 and the difference is significant at the 0·01% probability level. The differences between the observed values within these two sets of angles are, of course, essentially connected with the variation in the Zn-O bond lengths already discussed.

The Zn-O-C angles can be taken to be the same with a mean value of 120·9°. However, the O-Zn-C angles vary between 123·4° and 135·9° with an e.s.d. of about 1°. The three such angles associated with each zinc show a tendency for one to fall at the lower end of this range, one at the upper and one with an intermediate value.



(Me Zn O Me)$_4$

Zinc–Oxygen Distances

Figure 3·2

$(MeZnOMe)_4$ TABLE 3.5

Bond Lengths (Å) and their Standard Deviations (Å x 10^3)

Zn(1)-Zn(2)	3·085(4)
Zn(1)-Zn(3)	3·093(4)
Zn(2)-Zn(3)	3·087(3)
Zn(2)-Zn(4)	3·078(4)
Zn(3)-Zn(4)	3·093(4)
Zn(4)-Zn(1)	3·073(4)
O(1)-O(2)	2·771(16)
O(1)-O(3)	2·770(19)
O(2)-O(3)	2·788(16)
O(2)-O(4)	2·778(15)
O(3)-O(4)	2·729(19)
O(4)-O(1)	2·776(15)
Zn(1)-C(1)	1·967(27)
Zn(2)-C(2)	1·946(23)
Zn(3)-C(3)	1·926(21)
Zn(4)-C(4)	1·954(22)
O(1)-C(5)	1·426(25)
O(2)-C(6)	1·422(23)
O(3)-C(7)	1·476(32)
O(4)-C(8)	1·429(26)
Zn(1)-O(1)	2·105(12)
Zn(1)-O(2)	2·059(13)
Zn(1)-O(4)	2·087(11)
Zn(2)-O(1)	2·049(14)
Zn(2)-O(2)	2·090(11)
Zn(2)-O(3)	2·093(11)
Zn(3)-O(2)	2·100(10)
Zn(3)-O(3)	2·051(13)
Zn(3)-O(4)	2·084(14)
Zn(4)-O(1)	2·069(11)
Zn(4)-O(3)	2·083(15)
Zn(4)-O(4)	2·039(11)

$(MeZnOMe)_4$ TABLE 3.7

Bond Angles with their Standard Deviations

	Angle	e.s.d.
Zn(1)-O(1)-Zn(2)	95.9°	0·5°
Zn(1)-O(1)-Zn(4)	94·8	0·4
Zn(2)-O(1)-Zn(4)	96·8	0·5
Zn(1)-O(2)-Zn(2)	96·1	0·5
Zn(1)-O(2)-Zn(3)	96·1	0·4
Zn(2)-O(2)-Zn(3)	94·9	0·4
Zn(2)-O(3)-Zn(3)	96·3	0·5
Zn(2)-O(3)-Zn(4)	95·0	0·6
Zn(3)-O(3)-Zn(4)	96·8	0·6
Zn(3)-O(4)-Zn(4)	97·2	0·6
Zn(3)-O(4)-Zn(1)	95·7	0·5
Zn(4)-O(4)-Zn(1)	96·3	0·4
O(1)-Zn(1)-O(2)	83·4	0·5
O(1)-Zn(1)-O(4)	83·0	0·4
O(2)-Zn(1)-O(4)	84·2	0·5
O(1)-Zn(2)-O(2)	84·1	0·5
O(1)-Zn(2)-O(3)	83·9	0·5
O(2)-Zn(2)-O(3)	83·6	0·4
O(2)-Zn(3)-O(3)	84·4	0·4
O(2)-Zn(3)-O(4)	83·2	0·5
O(3)-Zn(3)-O(4)	82·6	0·5
O(3)-Zn(4)-O(4)	82·9	0·5
O(3)-Zn(4)-O(1)	83·7	0·5
O(4)-Zn(4)-O(1)	85·0	0·4

$(MeZnOMe)_4$ TABLE 3.7 (continued)

	Angle	e.s.d.
O(1)-Zn(1)-C(1)	130·4°	0·9°
O(2)-Zn(1)-C(1)	134·9	0·8
O(4)-Zn(1)-C(1)	123·4	0·9
O(1)-Zn(2)-C(2)	125·0	0·9
O(2)-Zn(2)-C(2)	135·6	1·1
O(3)-Zn(2)-C(2)	127·5	0·9
O(2)-Zn(3)-C(3)	131·5	0·7
O(3)-Zn(3)-C(3)	127·9	0·8
O(4)-Zn(3)-C(3)	130·0	0·7
O(1)-Zn(4)-C(4)	124·1	0·7
O(3)-Zn(4)-C(4)	135·9	0·9
O(4)-Zn(4)-C(4)	128·2	0·7
Zn(1)-O(1)-C(5)	118·9	1·2
Zn(2)-O(1)-C(5)	122·3	1·2
Zn(4)-O(1)-C(5)	121·8	1·1
Zn(1)-O(2)-C(6)	122·2	1·3
Zn(2)-O(2)-C(6)	119·2	1·1
Zn(3)-O(2)-C(6)	121·8	1·1
Zn(2)-O(3)-C(7)	119·8	1·1
Zn(3)-O(3)-C(7)	122·7	1·4
Zn(4)-O(3)-C(7)	120·1	1·4
Zn(1)-O(4)-C(8)	120·1	1·3
Zn(3)-O(4)-C(8)	119·2	1·2
Zn(4)-O(4)-C(8)	122·4	1·3

TABLE 3.6

Non-bonding Intramolecular Distances (Å)

between peripheral carbons

C(1).....C(5)	4·08	C(2).....C(6)	4·18
C(3).....C(7)	4·04	C(4).....C(8)	4·03
C(3).....C(8)	4·03	C(1).....C(8)	3·91
C(1).....C(6)	4·21	C(3).....C(6)	4·13
C(4).....C(7)	4·23	C(4).....C(5)	3·93
C(2).....C(5)	3·95	C(2).....C(7)	4·02

Shown in Table 3.6 are the intramolecular contacts, between peripheral carbons, ranging from 3·91 Å to 4·23 Å. The variation in these contacts appears to follow the trend in O-Zn-C angles which has been mentioned.

The variation in the O-Zn-C angles is explained to some extent, in terms of short intermolecular contacts. The positions of the carbon atoms involved in these angles appear to be displaced in such a way as to alleviate the strain arising from short non-bonding distances. The non-bonding intermolecular contacts less than 4 Å are shown in Table 3.8.

The short contacts of 3·72 Å between C(1) and C(6) and of 3·88 Å between C(1) and C(2) in the molecule at $-x$, $y-\frac{1}{2}$, $\frac{1}{2}-z$ are consistent with the bond angles observed at Zn(1), namely:

O(2)-Zn(1)-C(1)	134·9°;
O(1)-Zn(1)-C(1)	130·4°;
O(4)-Zn(1)-C(1)	123·4°.

The distance C(1).....C(2) of 3·88 Å already mentioned is the only short contact involving C(2). Displacement of C(2) away from C(1) is indeed in such a direction as to make O(2)-Zn(2)-C(2) the largest of the three angles at Zn(2).

Displacment of C(4) to make O(3)-Zn(4)-C(4) the largest of the three O-Zn-C angles at Zn(4) is in such a direction as to increase the two short contacts of 3·73 Å and 3·77 Å between C(4) and atoms related to C(8) in two adjacent molecules. The other six contacts involving C(4) are also consistent with the observed order:

$$O(3)\text{-}Zn(4)\text{-}C(4) > O(4)\text{-}Zn(4)\text{-}C(4) > O(1)\text{-}Zn(4)\text{-}C(4)$$

C(3) is involved in only one contact less than 4 Å, and that, with C(8) in the molecule at $\frac{1}{2}+x$, $\frac{1}{2}-y$, $-z$ is at a distance of 3·99 Å. Consistently, the range of angles at Zn(3) is only $3\frac{1}{2}^{\circ}$ whereas it is more than 10° at the other three zincs.

Figure3.3shows the packing of the tetramers viewed in projection along the a axis.

The molecular symmetry is very nearly $\bar{4}3m$. The greatest deviations from this are found for the methyl carbon atoms attached to zinc. Table 3.9 gives the equations of the six planes which would be required as mirror planes in a molecule of $\bar{4}3m$ symmetry. The planes have been calculated for the pairs of zinc and oxygen atoms both with and without the appropriate methyl carbons.

The inclusion of the eight methyl carbons in the calculations had the effect of displacing the mean planes such that, with one exception only, the two zinc atoms and one oxygen atom lie to one side of the plane, with the remaining oxygen atom to the other. In these cases, the deviations of the atoms from the plane are significant as are the differences between atoms which would be related by the plane.

When the carbon atoms are left out of the calculations, each of the six sets of atoms, within the limits of experimental error, is found to be coplanar. In four cases the deviations from the planes are similar, with a value of about 0·010 Å. For the remaining two planes the deviations are 0·003 and 0·018 Å. These planes have Zn(3) and O(1) in common.

The temperature parameters of the zinc atoms are slightly larger than those of the oxygen atoms. The form factors used for zinc and oxygen were those for neutral atoms. The temperature parameters obtained from refinement will tend to allow for the fact that in this compound the zinc atoms are expected to carry a small positive charge and the oxygen atoms will be negatively charged. As might be expected, the temperature parameters for the carbon atoms, which occupy positions around the periphery of the molecule, are fairly large, with B values of about 8 Å^2. There is little difference between the temperature parameters of the carbon atoms attached to zinc and those attached to oxygen.

$(MeZnOMe)_4$ TABLE 3.8

Non-bonding Intermolecular Contacts less than 4 Å

Equivalent Position Number 1	x,	y,	z;
Equivalent Position Number 2	$\frac{1}{2}-x$,	$-y$,	$\frac{1}{2}+z$;
Equivalent Position Number 3	$\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$-z$;
Equivalent Position Number 4	$-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$;

Atom A	Atom B	Equivalent Position	Cell	A-B Angstroms
C(1)	O(2)	1	(0, -1, 0)	3·99
C(1)	C(2)	4	(0, -1, 0)	3·88
C(1)	C(4)	1	(1, 0, 0)	3·90
C(1)	C(6)	1	(0, -1, 0)	3·72
C(3)	C(8)	3	(0, 0, 0)	3·99
C(4)	Zn(1)	1	(-1, 0, 0)	3·85
C(4)	Zn(3)	1	(-1, 0, 0)	3·89
C(4)	O(2)	1	(-1, 0, 0)	3·92
C(4)	O(4)	1	(-1, 0, 0)	3·92
C(4)	C(6)	1	(-1, 0, 0)	3·89
C(4)	C(8)	1	(-1, 0, 0)	3·77
C(4)	C(8)	3	(-1, -1, 0)	3·73

$(MeZnOMe)_4$ TABLE 3·9

Equations of Least-Squares Planes referred to the Crystal Axes

	$0{\cdot}8682x + 0{\cdot}4862y - 0{\cdot}0995z = -0{\cdot}5392$								$0{\cdot}8661x + 0{\cdot}4820y - 0{\cdot}1325z = -0{\cdot}6250$			
Out-of-Plane deviations (Å) for atoms defining plane	Zn(1)	Zn(2)	O(3)	O(4)	C(1)	C(2)	C(7)	C(8)	Zn(1)	Zn(2)	O(3)	O(4)
	0·058	0·079	0·035	-0·026	-0·032	-0·071	-0·020	-0·023	0·011	-0·010	0·012	-0·012
Out-of-plane deviations (Å) for other atoms	Zn(3)	Zn(4)	O(1)	O(2)	C(3)	C(4)	C(5)	C(6)	Zn(3)	Zn(4)	O(1)	O(2)
	1·551	-1·540	-1·321	1·449	3·054	-3·261	-2·446	2·618	1.550	-1.543	-1.387	1·384

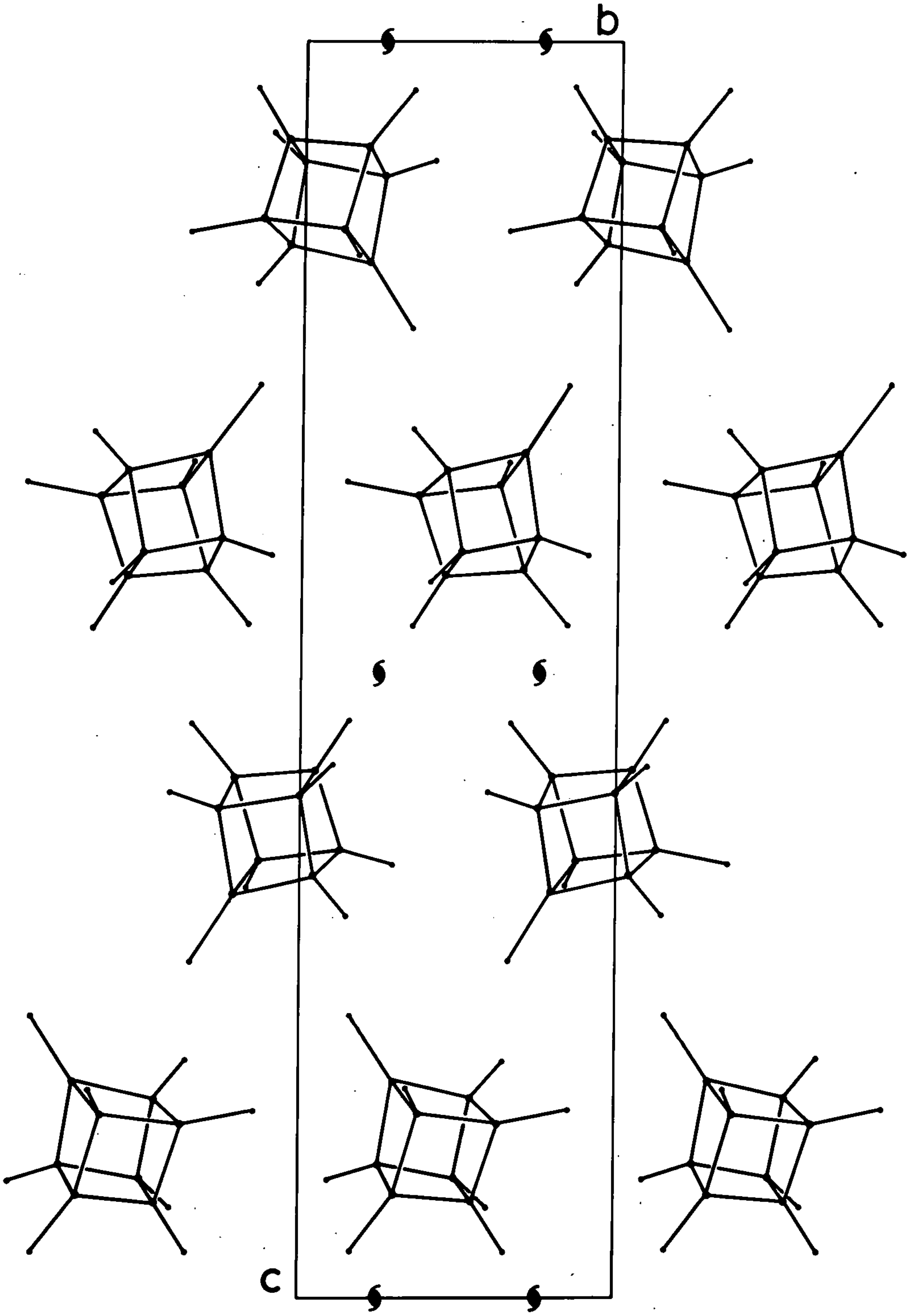
	$-0{\cdot}8404x + 0{\cdot}3201y - 0{\cdot}4373z = -0{\cdot}9871$								$-0{\cdot}8340x + 0{\cdot}3510y - 0{\cdot}4256z = -0{\cdot}9489$			
Out-of-Plane deviations (Å) for atoms defining plane	Zn(2)	Zn(3)	O(1)	O(4)	C(2)	C(3)	C(5)	C(8)	Zn(2)	Zn(3)	O(1)	O(4)
	-0·063	-0·045	-0·001	0·029	0·071	0·003	-0·026	0·033	0·003	-0·003	-0·003	0·003
Out-of-plane deviations (Å) for other atoms	Zn(1)	Zn(4)	O(2)	O(3)	C(1)	C(4)	C(6)	C(7)	Zn(1)	Zn(4)	O(2)	O(3)
	-1·548	1·524	-1·461	1·326	-2·991	3·009	-2·629	2·526	-1·566	1·507	-1·411	1·376

	$0{\cdot}4406x - 0{\cdot}8382y - 0{\cdot}3215z = -1{\cdot}8102$								$0{\cdot}4199x - 0{\cdot}8464y - 0{\cdot}3278z = -1{\cdot}8409$			
Out-of-Plane deviations (Å) for atoms defining plane	Zn(3)	Zn(4)	O(1)	O(2)	C(3)	C(4)	C(5)	C(6)	Zn(3)	Zn(4)	O(1)	O(2)
	-0·008	-0·039	-0·052	0·045	-0·031	0·070	-0·020	0·036	-0·017	0·017	-0·019	0·019
Out-of-Plane deviations (Å) for other atoms	Zn(1)	Zn(2)	O(3)	O(4)	C(1)	C(2)	C(7)	C(8)	Zn(1)	Zn(2)	O(3)	O(4)
	1·548	-1·536	-1·391	1·337	3·286	-3·150	-2·617	2·494	1·551	-1·534	-1·368	1·360

	$0{\cdot}4422x - 0{\cdot}0006y - 0{\cdot}8969z = -3{\cdot}4499$								$0{\cdot}4534x - 0{\cdot}0221y - 0{\cdot}8910z = -3{\cdot}4412$			
Out-of-Plane deviations (Å) for atoms defining plane	Zn(1)	Zn(4)	O(2)	O(3)	C(1)	C(4)	C(6)	C(7)	Zn(1)	Zn(4)	O(2)	O(3)
	-0·033	0·006	-0·019	0·058	0·084	-0·073	-0·071	0·048	0·010	-0·010	-0·011	0·011
Out-of-Plane deviations (Å) for other atoms	Zn(2)	Zn(3)	O(1)	O(4)	C(2)	C(3)	C(5)	C(8)	Zn(2)	Zn(3)	O(1)	O(4)
	-1·534	1·553	-1·417	1·359	-3·177	3·136	-2·576	2·536	-1·556	1·531	-1·406	1·370

	$-0{\cdot}0021x + 0{\cdot}8282y - 0{\cdot}5604z = -1{\cdot}6162$								$0{\cdot}0296x + 0{\cdot}8298y - 0{\cdot}5573z = -1{\cdot}5914$			
Out-of-Plane deviations (Å) for atoms defining plane	Zn(2)	Zn(4)	O(2)	O(4)	C(2)	C(4)	C(6)	C(8)	Zn(2)	Zn(4)	O(2)	O(4)
	0·044	0·071	-0·034	0·036	0·030	-0·115	-0·077	0·045	0·011	-0·011	-0·012	0·012
Out-of-Plane deviations (Å) for other atoms	Zn(1)	Zn(3)	O(1)	O(3)	C(1)	C(3)	C(5)	C(7)	Zn(1)	Zn(3)	O(1)	O(3)
	-1·535	1·556	-1·309	1·458	-3·139	3·130	-2·476	2·661	-1·533	1·560	-1·365	1·405

	$-0{\cdot}4383x - 0{\cdot}4816y - 0{\cdot}7589z = -2{\cdot}7703$								$-0{\cdot}4131x - 0{\cdot}5038y - 0{\cdot}7586z = -2{\cdot}8260$			
Out-of-Plane deviations (Å) for atoms defining plane	Zn(1)	Zn(3)	O(1)	O(3)	C(1)	C(3)	C(5)	C(7)	Zn(1)	Zn(3)	O(1)	O(3)
	-0·083	-0·045	-0·039	0·029	0·115	-0·022	-0·032	0·076	0·009	-0·009	-0·010	0·010
Out-of-Plane deviations (Å) for other atoms	Zn(2)	Zn(4)	O(2)	O(4)	C(2)	C(4)	C(6)	C(8)	Zn(2)	Zn(4)	O(2)	O(4)
	-1·537	1·540	-1·447	1·331	-2·958	3·170	-2·657	2·452	-1·535	1·543	-1·386	1·391



(MeZnOMe)$_4$ projection on the [100] plane

Figure 3·3

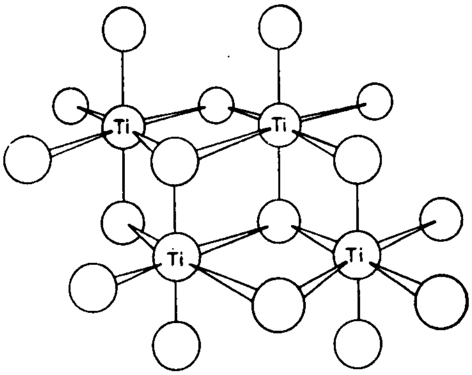
3.9 The Association of Metal Alkoxides

Polymerisation in alkoxides is a manifestation of the tendency of the metal to expand its covalency by coordination with oxygen. The most stable structure formed will be the one containing most intermolecular bonds between adjacent units. This criterion requires that the metal alkoxide adopts the smallest possible structural unit which is consistent with all the metal atoms attaining a higher coordination number while the coordination number of oxygen must not exceed four (Bradley, 1958).

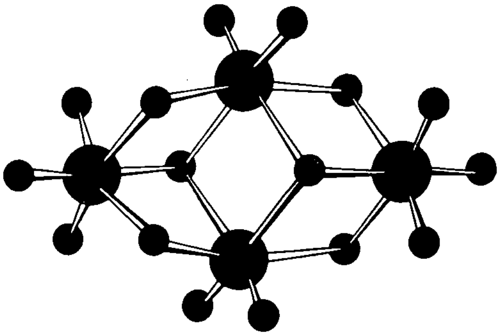
The application of this rule to alkali metal alkoxides would limit the coordination number of the alkali metal to 3, with a coordination number of 4 for oxygen. The only example in Group I, for which the structure is known, is lithium methoxide and with four-coordinate lithium and five-coordinate oxygen this provides a noteable exception to the rule. In lithium methoxide the oxygen atoms are bonded to a methyl group on one side and coordinated to four lithium ions on the other to form a square pyramid with oxygen at the centre. The lithium ions are surrounded by a distorted tetrahedron of oxygen atoms. If the structure is viewed normal to the four-fold axis, it is seen to consist of layers ABCBA ABCBA ... with A=Me, B=O, C=Li. Wheatley (1960) has suggested that this feature reflects some degree of covalent character.

The structures of the alkoxides of titanium have received most attention. Monoethyltriethyl titanate $[Ti(OMe)(OEt)_3]_4$ and titanium(IV) ethoxide $[Ti(OEt)_4]_4$ are both tetramers and adopt structures in the crystal whereby the titanium atoms achieve an octahedral environment.

Monomethyltriethyl titanate has an arrangement in which the titanium atoms in each tetramer form a planar diamond-shaped pattern with three oxygens above and below the plane of the titaniums. Each tetramer is nearly centrosymmetric and there are three types of oxygen (Witters and Caughlin, 1965).



The tetrameric structure of crystalline $Ti(OC_2H_5)_4$.



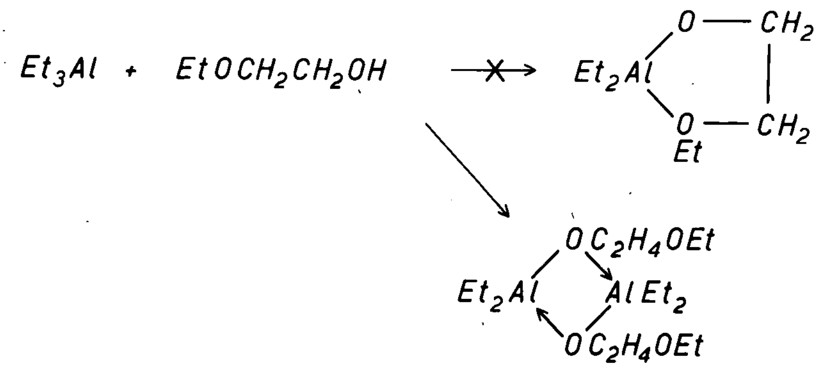
Structure of $Ti(OCH_3)(OC_2H_5)_3$ tetramer. Large circles are titanium atoms; small circles are oxygen atoms; carbons not shown

In crystalline $[Ti(OEt)_4]_4$ titanium is again six-coordinate, four TiO_6 octahedra sharing five common edges. There are two kinds of ethoxide bridging groups and in addition, five independent terminal oxygen atoms in each centrosymmetric tetramer (Ibers, 1963). Titanium methoxide is also tetrameric and has a similar structure (Wright and Williams, 1966).

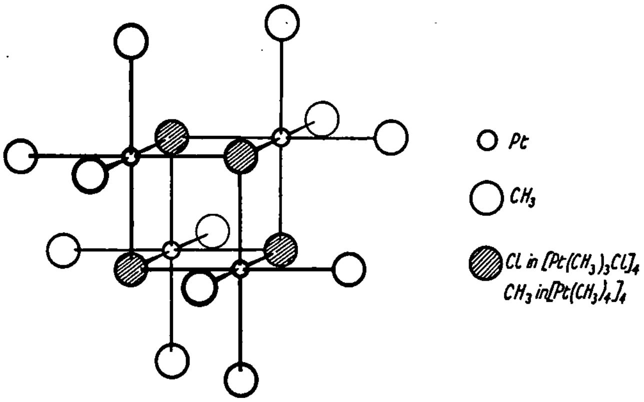
The crystal structure of the first hydrolysis product, $Ti_7O_{24}Et_{19}$, of titanium ethoxide has also been examined (Watenpaugh, 1967). A central TiO_6 octahedron shares six of its twelve edges with other TiO_6 units to form Ti_7O_{24} and all titanium atoms are octahedrally coordinated.

An X-ray structure analysis of thallium methoxide $(TlOMe)_4$ revealed an arrangement of four thallium atoms at the corners of a tetrahedron (Dahl et alii, 1962). Although it was not possible to locate the positions of the oxygen and carbon atoms, it was proposed that the thallium atoms and the methoxide groups occupy the alternate corners of a distorted cube in an arrangement similar to that shown by methylzinc methoxide. The coordination number of the thallium atoms is three.

Replacing a methyl group in dimethylzinc by an alkoxy group is expected greatly to increase the acceptor or Lewis-acid character of the zinc. And in a similar way the donor or Lewis-base character of a



metal alkoxide is greater than either that of an alcohol or ether oxygen. The contrast between the donor character of the two kinds of oxygen atoms is clearly demonstrated by the reaction between 2-ethoxyethanol and triethylaluminium whereby the chelate complex is not formed but a four-membered ring dimer instead (Hofmann, 1960).



The structure of the tetrameric molecules $[Pt(CH_3)_3Cl]_4$ and $[Pt(CH_3)_4]_4$ (idealized).

The chief problem concerned with the structure of methylzinc methoxide centres on the apparent existence of two kinds of Zn-O bond. There can be no 'prima facie' reason why all these bond lengths should not be equal. The phenylaluminium anilide tetramer (MacDonald and MacDonald, 1963) already mentioned, trimethylplatinum chloride and tetramethylplatinum (Rundle and Sturdivant, 1947) are all required to have twelve equal bonds in the 'cube'. A similar situation exists in ethylzinc iodide where there are two long Zn-I bonds of 2·91 Å and one shorter value of 2·64 Å (Moseley and Shearer, 1966). However, the steric problem involved in packing together iodine and zinc atoms is so different from a situation with zinc and oxygens that the comparison is perhaps not very meaningful.

With the exception of the alkali metal alkoxides, where the bonding is essentially ionic or may be of an electron deficient nature, the degree of association in metal alkoxides is then limited by a maximum coordination number for oxygen of 4. This criterion no longer applies in the case of metal alkylsulphides. A sulphur atom has empty low lying d orbitals, and it is large enough to accommodate five groups in its coordination sphere. This fact is probably responsible for the unusually varied structures shown by the methylzinc alkylsulphides, in contrast to the more coherent picture for zinc alkoxides.

Perhaps the most puzzling question in this context is why methylzinc t-butylsulphide should in such large part have the "cubane" structure of the methoxide and yet, at the eigth corner of the 'cube', instead of a fourth MeZn unit, a fifth $MeZnSBu^t$ unit distorts the structure into the curious pentameric arrangement described in §2.2(c).

$(MeZnOMe)_4$ TABLE 3.10

Final Values of the Observed and Calculated Structure Factors

h	k	l	|Fo|	|Fc|
0	0	4	233	338
0	0	6	108	32
0	0	8	117	94
0	0	10	10	10
0	0	12	197	180
0	0	14	8	9
0	0	16	106	88
0	0	18	74	70
0	0	20	21	22
0	0	22	70	70
0	0	26	18	18
0	0	28	29	26
0	0	32	24	21
1	0	1	247	228
1	0	2	78	92
1	0	3	151	143
1	0	4	18	19
1	0	5	92	94
1	0	6	5	4
1	0	7	46	46
1	0	8	144	123
1	0	9	23	13
1	0	10	59	62
1	0	11	106	98
1	0	12	152	136
1	0	13	13	12
1	0	14	57	55
1	0	15	69	62
1	0	16	104	100
1	0	17	51	47
1	0	18	13	14
1	0	19	17	16
1	0	20	17	19
1	0	21	69	66
1	0	22	12	13
1	0	24	31	32
1	0	27	10	9
1	0	28	29	25
1	0	29	32	28
1	0	30	11	10
1	0	31	13	12
1	0	33	23	22
2	0	0	21	13
2	0	1	86	95
2	0	2	35	31
2	0	3	23	26
2	0	5	135	148
2	0	6	14	14
2	0	8	23	24
2	0	9	52	52
2	0	10	92	88
2	0	11	54	57
2	0	12	5	6
2	0	13	67	68
2	0	14	94	98
2	0	15	71	71
2	0	16	57	59
2	0	17	127	123
2	0	18	56	55
2	0	19	23	24
2	0	20	47	54
2	0	21	49	51
2	0	24	13	12
2	0	25	10	9
2	0	26	19	16
2	0	27	8	8
2	0	28	20	21
2	0	29	13	13
2	0	30	10	12
2	0	32	21	19
3	0	1	17	17
3	0	2	135	147
3	0	3	45	49
3	0	4	110	113
3	0	5	39	44
3	0	6	95	96
3	0	7	47	53
3	0	8	95	95
3	0	9	31	33
3	0	10	15	17
3	0	11	18	22
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0	4	23	22	22
0	4	24	21	18
0	4	25	12	12
0	4	26	9	10
0	4	28	12	10
0	4	29	13	12
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1	4	6	60	53
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1	4	19	32	32
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1	4	22	14	15
1	4	23	27	22
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1	4	27	10	9
1	4	28	13	11
1	4	29	9	9
1	4	30	12	10
1	4	32	7	8
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2	4	2	23	24
2	4	3	80	71
2	4	4	102	89
2	4	5	42	44
2	4	6	15	19
2	4	7	66	66
2	4	8	68	66
2	4	9	54	52
2	4	10	12	11
2	4	11	32	36
2	4	12	18	21
2	4	13	8	8
2	4	14	7	9
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2	4	18	14	15
2	4	20	26	23
2	4	21	13	16
2	4	22	15	13
2	4	23	6	7
2	4	24	22	19
2	4	25	12	13
2	4	26	17	15
2	4	27	9	8
2	4	28	15	12
2	4	29	12	13
2	4	30	9	9
2	4	31	6	6
3	4	0	18	20
3	4	1	13	13
3	4	2	18	19
3	4	3	39	39
3	4	4	68	65
3	4	5	46	49
3	4	6	34	33
3	4	7	33	38
3	4	8	71	68
3	4	9	22	22
3	4	10	20	21
3	4	12	34	36
3	4	13	22	25

h	k	l	|Fo|	|Fc|
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3	4	15	14	17
3	4	16	12	13
3	4	17	30	29
3	4	18	19	18
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3	4	30	11	9
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4	4	2	17	18
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4	4	6	17	20
4	4	7	27	29
4	4	8	21	24
4	4	9	7	9
4	4	10	20	21
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6	6	1	18	16
6	6	2	14	15
6	6	3	13	11
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6	6	6	8	7
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0	7	2	7	6
0	7	3	9	9
0	7	4	6	4
0	7	6	27	26
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2	7	6	10	9
2	7	7	11	12
2	7	8	28	27
2	7	9	11	11
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2	7	14	17	16
2	7	15	7	8
2	7	18	6	6
2	7	23	6	8
3	7	0	23	24
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4	7	3	11	8
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4	7	12	9	10
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4	7	14	10	10
4	7	16	6	5
5	7	1	7	4
5	7	2	9	10
5	7	5	6	5
5	7	6	10	10
5	7	8	6	6
5	7	9	6	7
5	7	10	10	10
5	7	11	6	7
5	7	12	8	8

CHAPTER FOUR

THE CRYSTAL STRUCTURE
OF
DIMERIC METHYL(DIPHENYLAMINO)ZINC

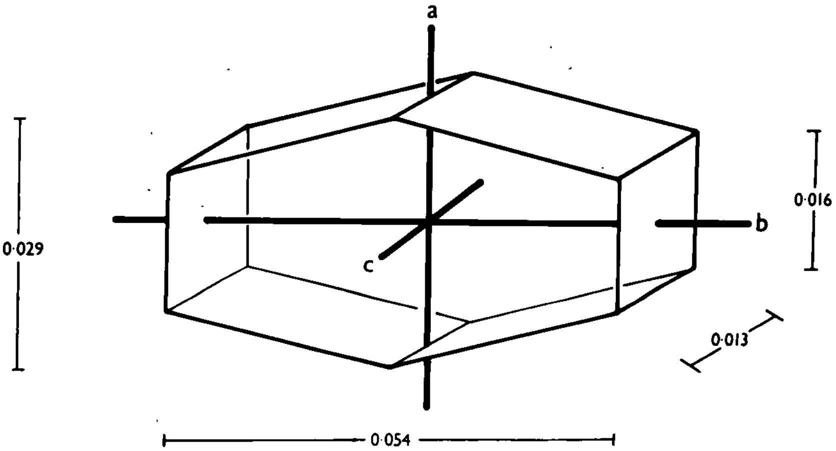
4.1 Introduction

Methyl(diphenylamino)zinc is prepared by heating freshly sublimed diphenylamine and dimethylzinc in a sealed tube at 70°. The white crystalline solid obtained is recrystallised from benzene as small colourless plates, melting point 185°-195°. Molecular weight measurements indicate that in benzene solution the molecule is a dimer and has to be formulated with three-coordinate zinc as a part of a four-membered ring (Coates and Ridley, 1965).

Although several associated alkylzinc complexes were dimeric in solution, the existence of three-coordinate zinc in the solid state had yet to be confirmed. In the crystal, the alternative to a structure incorporating three-coordinate zinc, was an unlikely arrangement in which association through methyl bridges allowed the zinc to become four-coordinate.

4.2 Crystals

The crystals obtained from benzene solution were in the form of irregular hexagonal plates. The dimensions (expressed in cm.) of the crystal used for data collection are shown below:



As before, the crystals were sealed individually in glass capillary tubes under a dry nitrogen atmosphere.

4.3 Crystal Data

Zero level precession photographs, using Mo-K_α radiation ($\lambda = 0{\cdot}7107$ Å) gave the following unit cell dimensions:

Orthorhombic $P2_12_12_1$;

$a = 7{\cdot}57$, $b = 14{\cdot}95$, $c = 20{\cdot}43$ Å;

$Z = 4$ units of $(MeZnNPh_2)_2$;

$U = 2313$ Å; Molecular weight of dimer = 497·27;

$D_m = 1{\cdot}43$ gm.cm^{-1}; $D_m = 1{\cdot}426$ gm.cm^{-1};

Absorption Coefficient for Cu-K_α radiation, $\mu = 27$ $cm.^{-1}$

The statistical standard deviations in unit cell lengths were 0·004 Å in a, 0·008 Å in b, and 0·006 Å in c. However, the uncertainty is probably of the order of 0·2%.

4.4 Data Collection and Correction

The equi-inclination Weissenberg technique was used to record photographically the hnl nets where n=0 to 13. The intensities were estimated, corrected for Lorentz and polarisation factors and the correlation was carried out as in the previous chapter.

In addition, the intensities were corrected for absorption using the method of Busing and Levy, but, in view of the value of μ and the small cross-section of the crystal, these corrections were small.

4.5 The Patterson Function

The Patterson function was calculated using "sharpened" intensities as coefficients.

The Patterson function is extremely simple since there are only eight zinc atoms in the unit cell. Superficially the Harker section at $(u,\frac{1}{2},w)$ contains only one large peak, considerably greater in height than that expected of Zn-Zn vector. On closer inspection however, this could be interpreted as containing two peaks about 0·5 Å apart. Using one of these peaks, x- and z-coordinates were assigned to one zinc atom. Consistent vectors of similar peak height on the other two Harker sections confirmed these parameters and also fixed the y-coordinate. The coordinates of the atom giving rise to the second Harker peak on each section were then assigned, choosing the appropriate peak to give Zn_1 -Zn_2 type vectors consistent with those observed.

Initial inspection of the $P(\frac{1}{2},v,w)$ and $P(u,v,\frac{1}{2})$ Harker sections was confused by the presence on each, of a third vector with peak height much larger than that expected for a vector between zinc atoms. The x-coordinates of the two zinc atoms are almost X and $\frac{1}{2}$-X, and similarly the z-coordinates, Z and $\frac{1}{2}$-Z. Thus Zn(1)-Zn(2) vectors at x=0·48 and z=0·49, repeat across the mirror planes at $x=\frac{1}{2}$ and $z=\frac{1}{2}$, resulting in very large non-Harker peaks on the $P(\frac{1}{2},v,w)$ and $P(u,v,\frac{1}{2})$ sections.

The six Harker peaks together with the four Zn(1)-Zn(2) vectors accounted for all the major features of this very simple Patterson function. The coordinates of the zinc atoms obtained were as follows:

Zn(1)	0·125	0·189	0·234
Zn(2)	0·400	0·054	0·253

4.6 Light Atom Positions

As a preliminary to the computation of an electron density map, the parameters for the zinc atoms obtained from the Patteron function were improved through two cycles of least-squares refinement. Structure factors were then calculated and gave a residual of 0·40. A three-dimensional Fo synthesis was then calculated.

Positions for all 28 light atoms other than hydrogen were obtained from this first Fo synthesis. Peaks at the positions of the zinc atoms came up to 58 e.Å^{-3}. The minimum peak height shown by a carbon atom was 2·8 e.Å^{-3} and there was only one false peak (3·4 e.Å^{-3}) greater than this. There were only half a dozen unassigned peaks greater than 2 e.Å^{-3}. A structure factors calculation based on the two zinc, the two nitrogen, and the twenty six carbon atoms gave an R value of 0·28.

4.7 Structure Refinement

The atomic parameters were then refined by the method of least-squares, first through two cycles with isotropic temperature parameters, to an R value of 0•15. Then, after four cycles with anisotropic temperature parameters for all atoms, the refinement had converged to an R value of 0•095.

Finally, as with the methoxide, four cycles of least-squares refinement were applied in which individual scale factors for the reciprocal lattice nets h01 to h131 were refined. As before, this treatment had no noticeable effect on the vibration tensor elements U_{22}, but the residual improved to 0•086 and there was marked improvement in several of the carbon-carbon bond lengths. The mean difference between observed and refined κ_i values was 3•7%.

In the final cycle of refinement the largest parameter shift was only 0•27 of its corresponding e.s.d. The final values of the positional and thermal parameters together with their e.s.d.'s are given in Tables 4.2 and 4.3.

After the last cycle of refinement an (Fo-Fc) synthesis was calculated as a check against any gross errors in the structure. It is rather puzzling that once again there were positive peaks on the map at atomic positions. In the case of the zinc, nitrogen and carbon atoms respectively, there were peaks of height ~3•0, ~0•5 and ~0•4 e.$\mathring{A}^{-3}$. The map showed no other pronounced features.

Towards the end of the refinement the structure factors were weighted by the same function as for methylzinc methoxide. For methyl-(diphenylamino)zinc the coefficients used were:

$$p_1 = 20, \quad p_2 = 0{\cdot}2, \quad p_3 = 0{\cdot}0012, \quad p_4 = 0{\cdot}00003.$$

The least-squares totals and the variation of $w.\Delta^2$ with $|Fo|$ and with $\sin\theta/\lambda$ are given in Table 4.1.

The observed and calculated structure factors are listed in Table 4.9. The 277 unobserved reflections were given zero weight in the refinement but few have calculated values greater than the minimum observable values.

$(MeZnNPh_2)_2$ TABLE 4.1

Least-Squares Totals

Number of Observed Planes 2110

$\Sigma\|\Delta\|$	3410·8	$\Sigma\|Fo\|$	39868·4	$\Sigma\|Fc\|$	39147·4	R 0·086
$\Sigma w\|\Delta\|^2$	1240·5	$\Sigma w\|Fo\|^2$	96761·9	$\Sigma w\|Fc\|^2$	95492·5	R' 0·013

Weighting Analysis

$w.\Delta^2$ averaged in batches and the number of planes per batch.

	sinθ/λ				
	0·0-0·2	0·2-0·4	0·40-0·6	0·6-0·8	TOTALS
Fo					
0-14	0·59/20	0·60/162	0·52/894	0·59/169	0·54/1245
14-28	0·70/14	0·58/185	0·61/274	0·00/0	0·60/473
28-57	0·74/26	0·75/201	0·89/54	0·00/0	0·77/281
57-113	0·67/27	0·60/68	0·00/0	0·00/0	0·62/95
113-227	0·33/8	1·48/7	0·00/0	0·00/0	0·86/15
227 UP	0·00/1	0·00/0	0·00/0	0·00/0	0·00/1
TOTALS	0·64/96	0·65/623	0·55/1222	0·59/169	0·59/2110

(MeZnNPh$_2$)$_2$ TABLE 4.2

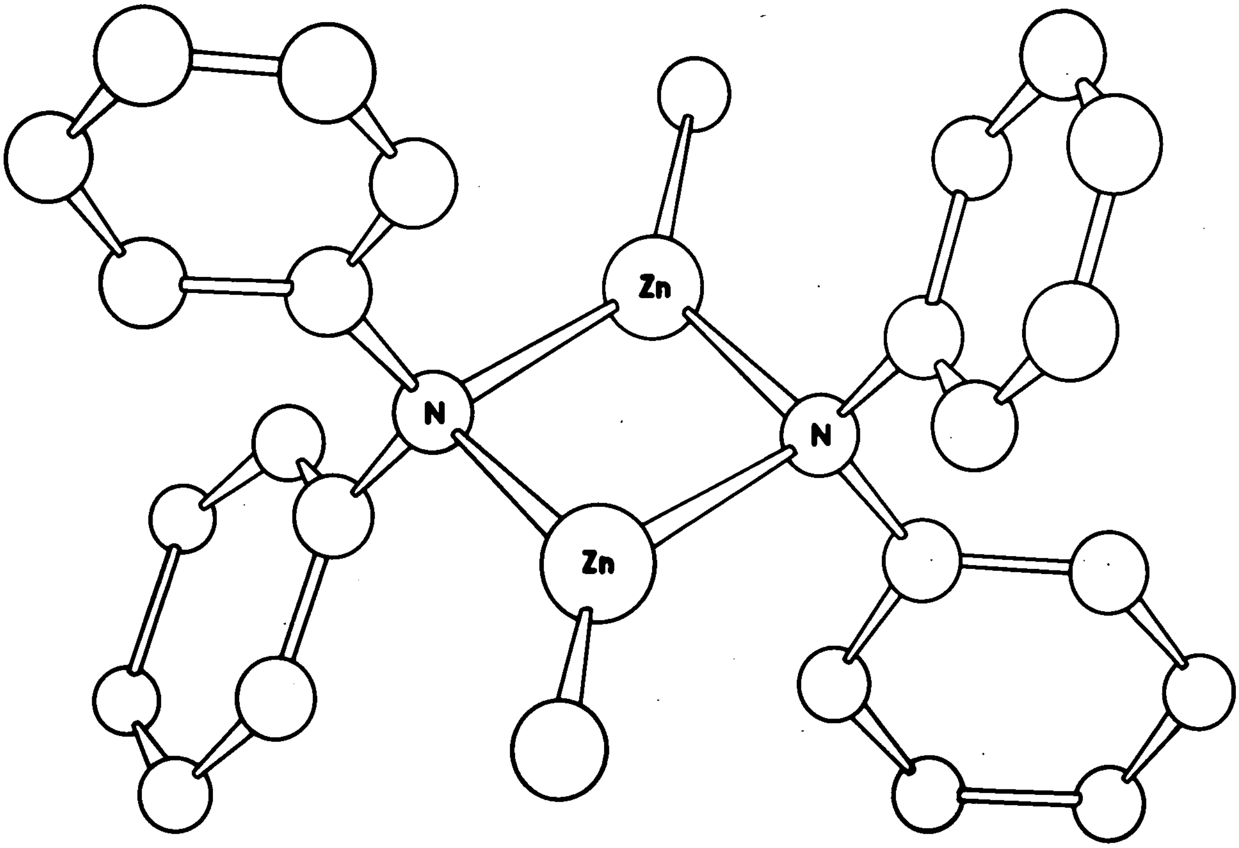
Final Values of Atomic Coordinates and their Standard Deviations

Atom	x/a	y/b	z/c	σ(x/a)	σ(y/b)	σ(z/c)
Zn(1)	0·39073	0·05280	0·25768	0·00018	0·00010	0·00006
Zn(2)	0·12508	0·18927	0·23172	0·00018	0·00010	0·00006
N(1)	0·28735	0·10959	0·17377	0·00120	0·00060	0·00039
N(2)	0·22954	0·13318	0·31541	0·00114	0·00055	0·00038
C(1)	0·17599	0·04806	0·13845	0·00129	0·00070	0·00046
C(2)	0·18420	0·03864	0·07007	0·00139	0·00078	0·00050
C(3)	0·07511	-0·02130	0·03851	0·00172	0·00093	0·00057
C(4)	-0·04685	-0·07356	0·07341	0·00175	0·00097	0·00070
C(5)	-0·05330	-0·06485	0·14033	0·00159	0·00096	0·00071
C(6)	0·05685	-0·00703	0·17233	0·00153	0·00086	0·00054
C(7)	0·41594	0·15581	0·13451	0·00144	0·00075	0·00045
C(8)	0·39258	0·24200	0·11505	0·00164	0·00089	0·00059
C(9)	0·51798	0·28802	0·07721	0·00207	0·00107	0·00077
C(10)	0·67352	0·24209	0·06032	0·00187	0·00102	0·00062
C(11)	0·70066	0·15535	0·07940	0·00176	0·00100	0·00066
C(12)	0·57037	0·11114	0·11752	0·00165	0·00089	0·00060
C(13)	0·33515	0·19499	0·35095	0·00123	0·00073	0·00045
C(14)	0·32628	0·20445	0·41936	0·00147	0·00081	0·00051
C(15)	0·43727	0·26616	0·45032	0·00176	0·00101	0·00062
C(16)	0·55806	0·31541	0·41524	0·00185	0·00104	0·00073
C(17)	0·56852	0·30361	0·34909	0·00174	0·00112	0·00080
C(18)	0·46098	0·24519	0·31778	0·00148	0·00081	0·00059
C(19)	0·09744	0·08580	0·35367	0·00128	0·00074	0·00043
C(20)	0·12413	0·00151	0·37731	0·00168	0·00088	0·00054
C(21)	0·00052	-0·04237	0·41665	0·00191	0·00087	0·00062
C(22)	-0·15477	0·00304	0·43248	0·00167	0·00101	0·00061
C(23)	-0·18484	0·08738	0·40890	0·00174	0·00102	0·00063
C(24)	-0·06017	0·12946	0·36924	0·00153	0·00089	0·00067
C(25)	0·57974	-0·03121	0·27561	0·00221	0·00109	0·00088
C(26)	-0·05819	0·27879	0·21510	0·00227	0·00129	0·00089

$(MeZnNPh_2)_2$ TABLE 4.3

Final Values of Anisotropic Temperature Parameters ($Å^2$) and their Standard Deviations ($Å^2 \times 10^4$)

Atom	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Zn(1)	0·0582(7)	0·0777(9)	0·0570(6)	-0·0084(11)	-0·0009(12)	0·0127(13)
Zn(2)	0·0597(7)	0·0760(8)	0·0574(6)	-0·0015(11)	0·0010(12)	0·0132(13)
N(1)	0·0607(46)	0·0705(53)	0·0526(39)	-0·0026(75)	0·0114(74)	0·0138(86)
N(2)	0·0604(47)	0·0638(50)	0·0482(36)	0·0035(66)	-0·0080(71)	0·0084(78)
C(1)	0·0535(49)	0·0639(60)	0·0583(46)	-0·0031(86)	-0·0020(81)	0·0186(90)
C(2)	0·0572(55)	0·0815(73)	0·0598(51)	-0·0121(96)	-0·0179(90)	0·0184(103)
C(3)	0·0734(71)	0·0969(89)	0·0686(62)	-0·0166(110)	-0·0354(111)	0·0208(126)
C(4)	0·0690(66)	0·0957(90)	0·0932(81)	-0·0132(143)	-0·0279(128)	-0·0017(131)
C(5)	0·0559(56)	0·0951(87)	0·0997(84)	-0·0019(146)	0·0054(117)	-0·0106(120)
C(6)	0·0612(58)	0·0895(79)	0·0643(56)	-0·0182(106)	0·0104(95)	0·0100(113)
C(7)	0·0618(58)	0·0767(65)	0·0489(42)	-0·0092(82)	-0·0044(84)	-0·0007(101)
C(8)	0·0666(66)	0·0953(85)	0·0767(64)	0·0166(117)	-0·0078(120)	0·0094(134)
C(9)	0·0907(90)	0·1109(106)	0·0909(85)	0·0147(158)	0·0424(156)	-0·0422(169)
C(10)	0·0839(80)	0·1120(103)	0·0735(66)	-0·0134(137)	0·0290(126)	-0·0637(158)
C(11)	0·0674(69)	0·1066(95)	0·0809(70)	-0·0093(140)	0·0221(124)	0·0013(139)
C(12)	0·0678(64)	0·0936(83)	0·0744(65)	-0·0316(119)	0·0305(111)	-0·0055(123)
C(13)	0·0493(47)	0·0784(65)	0·0509(42)	0·0008(85)	-0·0096(73)	0·0256(93)
C(14)	0·0641(59)	0·0876(78)	0·0588(50)	-0·0303(103)	-0·0058(94)	0·0041(113)
C(15)	0·0726(70)	0·1060(96)	0·0747(68)	-0·0279(130)	-0·0152(113)	0·0103(136)
C(16)	0·0762(73)	0·1048(98)	0·0912(84)	-0·0148(147)	-0·0437(135)	-0·0038(146)
C(17)	0·0612(64)	0·1170(106)	0·1068(98)	0·0204(168)	0·0050(134)	-0·0227(142)
C(18)	0·0594(56)	0·0794(75)	0·0753(62)	0·0107(112)	0·0123(102)	-0·0268(112)
C(19)	0·0519(49)	0·0822(67)	0·0493(41)	-0·0033(83)	0·0134(80)	-0·0093(97)
C(20)	0·0697(66)	0·0922(77)	0·0666(54)	0·0135(104)	-0·0129(117)	-0·0082(134)
C(21)	0·0860(80)	0·0815(79)	0·0781(67)	0·0136(122)	0·0082(133)	-0·0025(137)
C(22)	0·0647(67)	0·1182(100)	0·0728(63)	-0·0006(134)	0·0099(112)	-0·0349(143)
C(23)	0·0672(66)	0·1064(95)	0·0812(71)	0·0038(136)	0·0224(120)	0·0007(136)
C(24)	0·0508(54)	0·0950(85)	0·0878(74)	0·0135(123)	0·0380(108)	0·0129(108)
C(25)	0·0997(101)	0·1057(104)	0·1178(108)	-0·0344(174)	-0·0347(178)	0·0764(174)
C(26)	0·0950(99)	0·1382(131)	0·1113(113)	-0·0548(201)	-0·0225(175)	0·0801(195)



$(MeZnNPh_2)_2$

Figure 4·1

4.8 Description and Discussion of Structure

The arrangement of atoms in the molecule is shown in Figure 4.1.

As in solution the molecule is a dimer and contains a four-membered zinc-nitrogen ring. The nitrogen atoms are four-coordinate but the zinc atoms are each bonded to two nitrogens and to a methyl carbon and are three-coordinate. It is thought that this is the first example of three-coordinate zinc to have been established by X-ray structure analysis.

The bond lengths and angles are tablulated in Tables 4.4 and 4.5 and mean values are illustrated in Figure 4.2.

The two Zn-C lengths are the same within experimental error with a mean value of 1·95 Å. This distance is the same as that observed in methylzinc methoxide where zinc is sp^3 hybridised. One might expect a change in bond distance on going from an sp^3 to an sp^2 hybrid state at the metal, however it is noted that the Zn-C lengths in:

Me_2Zn - two-coordinate zinc,
$(MeZnNPh_2)_2$ - three-coordinate zinc,
$(MeZnOMe)_4$ - four-coordinate,

are all the same within experimental error. In dimethylzinc, zinc is sp hybridised. However, although in $(MeZnNPh_2)_2$ and $(MeZnOMe)_4$, zinc formally uses sp^2 and sp^3 hybrid orbitals respectively, in practice the distinction is not so clearcut. In these compounds the necessary bond angles in the four-membered rings involve the use by zinc of orbitals with large 'p' character, and consequently, the orbitals for bonding with carbon have greater 's' character than their formal hybrid states suggest.

The four Zn-N lengths are the same within experimental error with a mean value of 2·07 Å. This distance is significantly greater than the value of 2·01 Å observed in di-imidazole-zinc(II) dichloride, $Zn(C_3H_4N_2)_2Cl_2$, where the environment at zinc is tetrahedral (Lundberg, 1966), this value being the same as the sum of the Pauling tetrahedral covalent radii. The length of 2·07 Å does not however, differ significantly from the distance of 2·09 Å in mono-thiosemicarbazide zinc chloride where zinc is four-coordinate but zinc and nitrogen are part of a five-membered ring (Cavalca et alii, 1960). The distance also agrees closely with the Zn-O distance observed in methylzinc methoxide. As a net result of the difference in size of the two donor atoms and the change in hybrid state of the metal, the two bond lengths become equal.

As with methylzinc methoxide it is very difficult to correlate the observed bond lengths with the tetrahedral covalent radii. The Zn-C length is very much shorter than the covalent radii sum, the Zn-N length much longer; similar to the effect noticed in methylzinc methoxide. Although some increase in Zn-N and Zn-O lengths over the predicted values is expected, in view of the valence angles in the rings, it is not clear why the Zn-C length should be so much shorter than the value derived from the covalent radii.

Purely covalent bonding places formal charges of +1 on nitrogen and -1 on zinc, however the bond would be expected to have enough ionic character to give the zinc atoms small positive charges and small negative charges to the nitrogens. The observed Zn-N distance is consistent with the Zn-N bonds having appreciable polar character.

All four N-C lengths may be taken to be the same within experimental error with a mean value of 1·44 Å. This distance is similar to the value of 1·426 Å in acetanilide (Interatomic Distances, 1958).

The mean bond angle in the phenyl groups is 120·0° and the mean C-C bond length, 1·39 Å, none of the individual values differing significantly from the mean. This distance can be compared with the value of 1·397 Å found in benzene. If the individual values of the bond lengths and bond angles in the phenyl groups are regarded as estimates of the same quantity, statistical standard deviations of 0·021 Å in bond length and 1·5° in bond angle can be deduced. The average values of the standard deviations for these bond lengths and angles obtained from the least-squares estimates of the coordinate errors are 0·018 Å and 1·2°; 15% and 20% less than the above values. Standard deviations obtained using the method of least squares with the block diagonal approximation are indeed often thought to be somewhat optimistic (Hodgson and Rollett, 1963). However unless otherwise stated the e.s.d.'s used here for significance tests were unmodified values obtained by inversion of the block-diagonal least-squares matrix.

The mean Zn-N-Zn and N-Zn-N angles are respectively 89·4° and 90·6°, the individual values agreeing very closely. The difference between these two mean values is considered significant. In methylzinc methoxide the angles at zinc deviate more from the tetrahedral value than those at oxygen, however in the methyl(diphenylamino)zinc dimer, zinc is formally sp^2 hybridized, nitrogen sp^3, and the combined effect appears to result in a situation in which the angles at zinc are slightly greater.

Since the Zn-N-Zn angles are approximately 90°, the other angles at nitrogen are considerably greater than tetrahedral. This increase is greatest in the case of the C-N-C angles which have a mean value of 115·2°. In this way the separations between atoms in adjacent phenyl groups are made as large as possible. The Zn-N-C angles vary from 107·7° to 116·2° and will be discussed later.

Of the eight N-C-C angles, N(2)-C(13)-C(14) had a value of 123·1° and this is formally greater than the expected value of 120°. Increase in this angle increases the separation of C(14) from the phenyl group C(19) to C(24). The related angle N(1)-C(1)-C(2) has a value of 122·4° but in this case the difference from 120° is not significant.

Although none of the C-C-C angles differ significantly from the mean value of 120°, in each of the four cases, the value of the ring angle at carbon bonded to nitrogen calculates at less than 120°. In triphenylaluminium (Malone and MacDonald, 1967) the corresponding angles <u>are</u> less than 120° and similar steric factors may operate in the two cases.

The equations of the mean planes through the four C_6H_5N groups are as follows:

$$-0{\cdot}6951x + 0{\cdot}7126y - 0{\cdot}0950z = -0{\cdot}6897$$

Out-of-Plane	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	N(1)
deviations (Å)	0·007	-0·004	-0·007	0·010	0·007	-0·019	0·007

$$-0{\cdot}4414x - 0{\cdot}3261y - 0{\cdot}8360z = -4{\cdot}4561$$

Out-of-Plane	C(7)	C(8)	C(9)	C(10)	C(11)	C(12)	N(1)
deviations (Å)	0·009	-0·001	0·002	-0·006	0·001	0·001	-0·006

$$-0{\cdot}6810x + 0{\cdot}7211y - 0{\cdot}1276z = -0{\cdot}5624$$

Out-of-Plane	C(13)	C(14)	C(15)	C(16)	C(17)	C(18)	N(2)
deviations (Å)	0·021	-0·010	0·002	0·002	-0·007	-0·000	-0·008

$$-0{\cdot}4258x - 0{\cdot}3782y - 0{\cdot}8220z = -6{\cdot}7595$$

Out-of-Plane	C(19)	C(20)	C(21)	C(22)	C(23)	C(24)	N(2)
deviations (Å)	0·021	0·015	0·001	-0·021	-0·005	0·021	-0·030

With the exception of the group C(19) to C(24), N(2), the values of χ^2 are all less than 6·6, and these three phenylamine groups are considered to be planar. For the best plane through C(19) to C(24), and N(2), $\chi^2 = 25{\cdot}7$ and for $\nu=4$ the deviation from planarity must be considered significant at the 0·1% probability level. The phenyl group C(19) to C(24) alone is strictly planar, χ^2 being only 0·8.

The planes of the two phenyl rings bonded to the <u>same</u> nitrogen atom are in both cases almost perpendicular to each other. The dihedral angle between the mean planes through C(1) to C(6) and C(7) to C(12) is 81·3°. The corresponding value for the phenyl groups attached to N(2) is 83·1°. The two cis phenyl rings which are bonded to <u>different</u> nitrogen atoms are also approximately perpendicular. Values of these dihedral angles are:

C(1) to C(6) and C(19) to C(24), 84·7°;
C(7) to C(12) and C(13) to C(18), 80·3°.

These angles are similar to those found between phenyl rings attached to phosphorus in phenyltriphosphonitriles where the environment of phosphorus is similar to that of nitrogen in methyl(diphenylamino)zinc. In the two phenyltriphosphonitriles which have been studied the mean dihedral angle between phenyl rings is 86·7° (Mani, Ahmed and Barnes, 1966).

The dihedral angles between the best plane through the zinc-nitrogen ring and the planes of the phenyl groups C(1) to C(6) and C(13) to C(18) are 90° within experimental error. This equalises the contacts between the two zinc atoms and C(6), and similarly those with C(18). The dihedral angles between the plane of the ring and the planes of phenyl groups C(7) to C(12) and C(19) to C(24) are 56·1° and 53·3° respectively.

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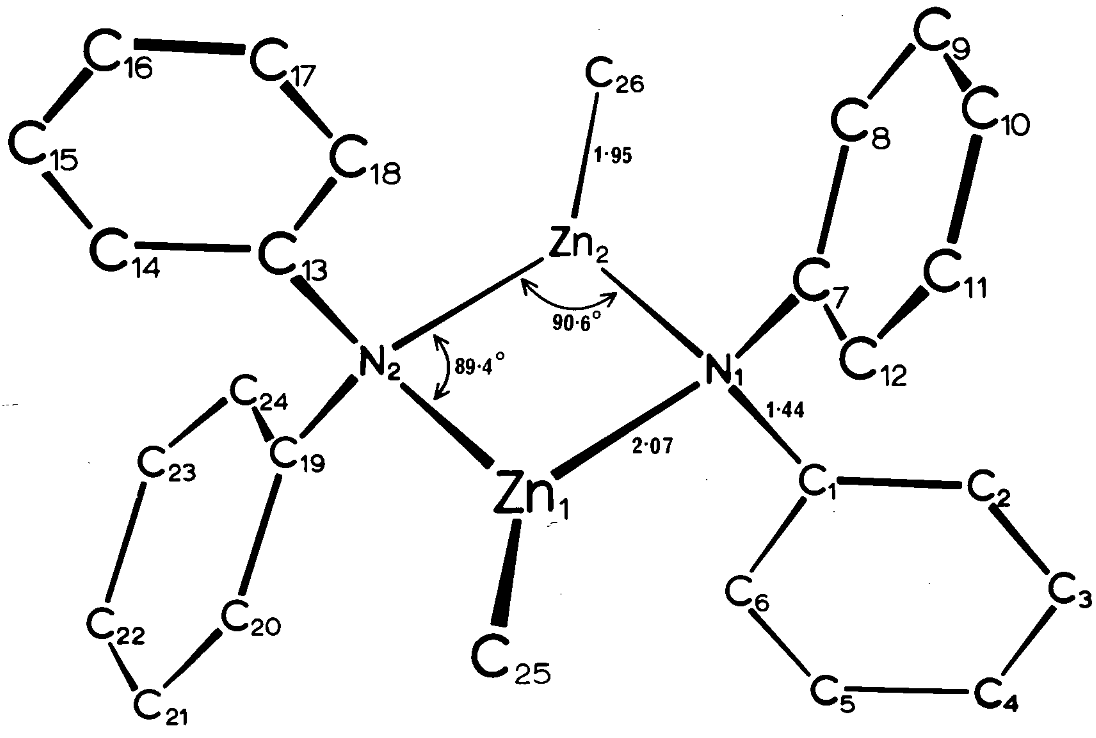


$(MeZnNPh_2)_2$

Some Mean Bond Lengths and Angles

Figure 4·2

$(MeZnNPh_2)_2$ TABLE 4.4

Bond Lengths (Å) and their Standard Deviations (Å x 10^3)

Zn(1)-C(25)	1·939(17)
Zn(2)-C(26)	1·958(18)
Zn(1)-N(1)	2·067(8)
Zn(1)-N(2)	2·080(8)
Zn(2)-N(1)	2·081(9)
Zn(2)-N(2)	2·062(8)
N(1)-C(1)	1·442(13)
N(1)-C(7)	1·438(14)
N(2)-C(13)	1·422(13)
N(2)-C(19)	1·454(13)
C(1)-C(2)	1·406(14)
C(2)-C(3)	1·379(17)
C(3)-C(4)	1·404(19)
C(4)-C(5)	1·374(20)
C(5)-C(6)	1·368(18)
C(6)-C(1)	1·404(16)
C(7)-C(8)	1·360(17)
C(8)-C(9)	1·405(20)
C(9)-C(10)	1·406(21)
C(10)-C(11)	1·370(21)
C(11)-C(12)	1·420(19)
C(12)-C(7)	1·391(17)
C(13)-C(14)	1·406(14)
C(14)-C(15)	1·399(18)
C(15)-C(16)	1·376(20)
C(16)-C(17)	1·365(22)
C(17)-C(18)	1·355(19)
C(18)-C(13)	1·389(15)
C(19)-C(20)	1·365(17)
C(20)-C(21)	1·397(18)
C(21)-C(22)	1·396(19)
C(22)-C(23)	1·369(21)
C(23)-C(24)	1·394(19)
C(24)-C(19)	1·397(16)

$(MeZnNPh_2)_2$ TABLE 4.5

Bond Angles with their Standard Deviations

	Angle	e.s.d.
Zn(2)-N(2)-Zn(1)	89·4°	0·3°
Zn(2)-N(1)-Zn(1)	89·3	0·3
N(1)-Zn(2)-N(2)	90·7	0·3
N(1)-Zn(1)-N(2)	90·6	0·3
C(26)-Zn(2)-N(2)	133·9	0·6
C(26)-Zn(2)-N(1)	135·3	0·6
C(25)-Zn(1)-N(1)	134·6	0·6
C(25)-Zn(1)-N(2)	134·5	0·6
Zn(2)-N(2)-C(19)	112·3	0·6
Zn(1)-N(2)-C(13)	109·6	0·6
Zn(2)-N(1)-C(1)	107·7	0·6
Zn(1)-N(1)-C(7)	113·8	0·7
Zn(2)-N(2)-C(13)	112·0	0·6
Zn(1)-N(2)-C(19)	115·3	0·6
Zn(2)-N(1)-C(7)	116·2	0·7
Zn(1)-N(1)-C(1)	112·0	0·6
C(19)-N(2)-C(13)	115·4	0·8
C(1)-N(1)-C(7)	115·1	0·8
N(1)-C(1)-C(2)	122·4	0·9
N(1)-C(1)-C(6)	120·2	0·9
N(1)-C(7)-C(8)	122·0	1·0
N(1)-C(7)-C(12)	118·5	1·0
N(2)-C(13)-C(14)	123·1	0·9
N(2)-C(13)-C(18)	119·2	0·9
N(2)-C(19)-C(20)	122·5	0·9
N(2)-C(19)-C(24)	118·9	1·0

(MeZnNPh$_2$)$_2$ TABLE 4.5 (continued)

	Angle	e.s.d.
C(1)-C(2)-C(3)	120·2°	1·0°
C(2)-C(3)-C(4)	121·2	1·1
C(3)-C(4)-C(5)	118·4	1·2
C(4)-C(5)-C(6)	120·9	1·2
C(5)-C(6)-C(1)	121·8	1·1
C(6)-C(1)-C(2)	117·4	1·0
C(7)-C(8)-C(9)	122·5	1·2
C(8)-C(9)-C(10)	117·5	1·4
C(9)-C(10)-C(11)	121·2	1·3
C(10)-C(11)-C(12)	119·5	1·3
C(11)-C(12)-C(7)	119·8	1·2
C(12)-C(7)-C(8)	119·4	1·1
C(13)-C(14)-C(15)	119·9	1·0
C(14)-C(15)-C(16)	121·1	1·2
C(15)-C(16)-C(17)	119·0	1·4
C(16)-C(17)-C(18)	121·1	1·4
C(17)-C(18)-C(13)	122·0	1·2
C(18)-C(13)-C(14)	117·6	1·0
C(19)-C(20)-C(21)	122·5	1·2
C(20)-C(21)-C(22)	118·0	1·2
C(21)-C(22)-C(23)	120·4	1·2
C(22)-C(23)-C(24)	120·5	1·2
C(23)-C(24)-C(19)	120·0	1·2
C(24)-C(19)-C(20)	118·5	1·0

Although the space group does not impose any symmetry on this molecule, the molecular symmetry is nearly 2/m. In addition to a centre of symmetry at the centre of the four-membered ring, this symmetry would require the molecule to possess a twofold axis along the direction:

C(25)-Zn(1)-Zn(2)-C(26),

and a mirror plane containing the atoms:

C(1) to C(6), C(7), C(10), N(1), N(2), C(19), C(22), C(13) to C(18).

A superficial examination of the Zn-N-C angles, which vary from 107·7° to 116·2° shows that the latter two symmetry relationships apply to only a very rough extent.

The equation of the best plane through the four ring atoms, together with the distances of atoms from the plane are given below:

$$-0{\cdot}7091x - 0{\cdot}7048y - 0{\cdot}0214z = -2{\cdot}7705$$

Deviations (Å) of atoms defining the plane	Zn(1)	Zn(2)	N(1)	N(2)
	0·003	0·003	-0·003	-0·003

Deviations (Å) of other atoms	C(1)	C(7)	C(13)	C(19)	C(25)	C(26)
	1·259	-1·164	-1·237	1·189	-0·134	0·052

The distances of the methyl carbon atoms C(25), C(26) from this plane show that these atoms are non-coplanar with the ring. C(25) and C(26) lie on opposite sides of the ring but at significantly different distances from it.

The atoms C(25), Zn(1), Zn(2), C(26) required by a molecule of symmetry 2, to lie on a twofold axis, are clearly not colinear. The distances from the plane, of the phenyl carbon atoms bound to nitrogen, also differ significantly from each other.

Shown below is the equation of the best plane through the group of atoms required to lie on a mirror plane in a molecule of symmetry m. The out-of-plane deviations indicate the way in which the molecule deviates from this symmetry.

$$-0{\cdot}6571x + 0{\cdot}7320y - 0{\cdot}1798z = -0{\cdot}8538$$

C(6)	C(5)	C(1)	C(4)	C(2)	C(3)	C(7)	C(10)	N(1)
-0·139	-0·107	-0·005	0·012	0·102	0·105	-0·005	-0·071	-0·016

C(15)	C(14)	C(16)	C(13)	C(17)	C(18)	C(19)	C(22)	N(2)
-0·064	-0·073	0·003	0·030	0·065	0·075	0·008	0·068	0·010

The phenyl groups C(1) to C(6) and C(13) to C(18) are twisted out of this plane along the directions N(1)-C(1)-C(4) and N(2)-C(13)-C(16) respectively. The two rotations are in the same direction however and the resulting dihedral angle between these two phenyl groups is only $2{\cdot}1^{\circ}$.

The deviations from 2 and m symmetry are then quite easily demonstrated as being significant. To check the validity of the centre of symmetry is however a different matter.

We have seen that the Zn-N-C angles vary from 107·7° to 116·2°, however the pairs of Zn-N-C angles related by the molecular centre are equal within experimental error:

Zn(1)-N(2)-C(13)	109·6°	Zn(2)-N(2)-C(13)	112·0°
Zn(2)-N(1)-C(1)	107·7°	Zn(1)-N(1)-C(1)	112·0°
Zn(1)-N(2)-C(19)	115·3°	Zn(2)-N(2)-C(19)	112·3°
Zn(2)-N(1)-C(7)	116·3°	Zn(1)-N(1)-C(7)	113·8°

Table 4.6 shows the atomic coordinates referred to an origin at 0·2575, 0·1214, 0·2449 (nearly $\frac{1}{4},\frac{1}{8},\frac{1}{4}$) obtained by averaging the positional parameters with equal weights for all atoms.

TABLE 4.6

Atomic Coordinates (Å) referred to the crystal axes, molecular centre as origin

Zn(1)	1·009	-1·026	0·260	N(1)	0·226	-0·177	-1·454
Zn(2)	-1·003	1·015	-0·270	N(2)	-0·212	0·176	1·440
C(1)	-0·617	-1·097	-2·175	C(7)	1·200	0·514	-2·256
C(13)	0·588	1·100	2·166	C(19)	-1·212	-0·532	2·221
C(2)	-0·555	-1·237	-3·572	C(8)	1·023	1·803	-2·654
C(14)	0·521	1·242	3·564	C(20)	-1·010	-1·792	2·704
C(3)	-1·381	-2·133	-4·217	C(9)	1·973	2·491	-3·427
C(15)	1·361	2·164	4·196	C(21)	-1·946	-2·448	3·508
C(4)	-2·305	-2·915	-3·504	C(10)	3·151	1·804	-3·772
C(16)	2·276	2·900	3·479	C(22)	-3·122	-1·770	3·832
C(5)	-2·354	-2·785	-2·137	C(11)	3·356	0·507	-3·382
C(17)	2·355	2·724	2·128	C(23)	-3·350	-0·509	3·350
C(6)	-1·519	-1·920	-1·483	C(12)	2·369	-0·153	-2·603
C(18)	1·541	1·851	1·488	C(24)	-2·406	0·120	2·540
C(25)	2·440	-2·282	0·627	C(26)	-2·391	2·353	-0·610

In only 7 out of the 45 pairs of parameters related by this centre does the difference in coordinates differ by more than 0·05 Å, the greatest difference being 0·081 Å. The greatest differences are associated with the carbon atoms. The differences in coordinates between the phenyl groups C(13) to C(18) and C(19) to C(24) and those related to C(1) to C(6) and C(7) to C(12) respectively by inversion through this centre appear to be systematic. The two sets of coordinates may be made almost the same by rotation of the phenyl group C(13) to C(18) about an axis passing through the midpoints of the bonds C(13)-C(18) and C(15)-C(16). In the case of the phenyl group C(19) to C(24) the rotation is about an axis through the midpoints of C(19)-C(20) and C(22)-C(23).

Since in only a small number of cases were the differences between related atoms considered significant, it was thought desirable to make a more systematic examination of this apparent symmetry. A detailed statistical treatment (Appendix II)shows that the function

$$\sum_{x,y,z}\left(\sum\frac{(x_1 + x_2)^2}{\sigma_1^2 + \sigma_2^2} - \frac{\left(\sum\frac{x_1 + x_2}{\sigma_1^2+\sigma_2^2}\right)^2}{\sum\frac{1}{\sigma_1^2+\sigma_2^2}}\right)$$

where x_1 , x_2 are the x-coordinates, referred to the crystal origin, of atoms approximately related by the centre under discussion, and σ_1 , σ_2 are the associated e.s.d.'s,

distributes as χ^2.

The summations were carried out independently along the three axial directions and resulted in values for χ^2 of 33 along x, 46 along y, and 66 along z, each value associated with 14 degrees of freedom. The overall value of χ^2 for the apparent centring is 146 and for $\nu = 42$ this corresponds to a probability of less than 0·1%. The structure is not therefore regarded as possessing a centre of symmetry. Even using values of the e.s.d.'s increased by 15%, as suggested from analysis of the dimensions of the phenyl groups, this conclusion is not altered.

It seems likely that with less bulky substituents on the nitrogen atoms, the resulting compound would have been able to retain the inherent symmetry in this dimeric arrangement and that such a structure would be centric.

——oOo——

TABLE 4.7

Short Non-bonding Intramolecular Distances

C(2)..... C(7)	2·81	C(14)..... C(19)	2·82
C(1)..... C(12)	3·16	C(13)..... C(24)	3·17
C(2)..... C(12)	3·27	C(14)..... C(24)	3·30
C(1)..... C(8)	3·37	C(13)..... C(20)	3·35
C(2)..... C(8)	3·55	C(14)..... C(20)	3·51
C(6)..... C(7)	3·73	C(18)..... C(19)	3·71
C(25)..... C(12)	3·87	C(26)..... C(24)	3·86

Shown in Table 4.7 are the non-bonding contacts shorter than 4 Å. Contacts between carbons bonded to a common atom are not included. The two methyl carbon atoms are each involved in only one contact less than 4 Å, of which that between C(25) and C(12) has a value of 3·87 Å. The contact involving C(26) is seen to be given by inverting C(25)..... C(12) through the molecular centre and has a similar value.

All other short intramolecular contacts are between carbon atoms in adjacent phenyl groups. There are several contacts less than 3·7 Å and two have values of 2·8 Å. Although this latter distance is less than the sum of the van der Waals radii of two carbon atoms, it is not considered unusual in a molecule which contains two phenyl groups bonded to a common atom. Again, the pairs of contacts between atoms approximately related to each other by inversion through the molecular centre are very similar in value.

$(MeZnNPh_2)_2$ TABLE 4.8

Non-bonding Intermolecular Contacts less than 4 Å

Equivalent Position Number 1	x,	y,	z;
Equivalent Position Number 2	$\frac{1}{2}-x$,	$-y$,	$\frac{1}{2}+z$;
Equivalent Position Number 3	$\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$-z$;
Equivalent Position Number 4	$-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$;

Atom A	Atom B	Equivalent Position	Cell	A-B Angstroms
C(10)	C(26)	1	(1, 0, 0)	3·80
C(10)	C(9)	3	(0, 0, 0)	3·86
C(10)	C(8)	3	(0, 0, 0)	3·96
C(11)	C(26)	1	(1, 0, 0)	3·80
C(11)	C(4)	1	(1, 0, 0)	3·92
C(11)	C(3)	1	(1, 0, 0)	3·96
C(11)	C(5)	1	(1, 0, 0)	3·98
C(12)	C(5)	1	(1, 0, 0)	3·91
C(14)	C(3)	2	(0, 0, 0)	3·74
C(14)	C(4)	4	(0, 0, 0)	3·94
C(15)	C(23)	3	(0, 0, 1)	3·73
C(15)	C(4)	4	(0, 0, 0)	3·84
C(15)	C(4)	2	(0, 0, 0)	3·91
C(15)	C(14)	3	(0, 0, 1)	3·96
C(16)	C(3)	4	(1, 0, 0)	3·82
C(16)	C(2)	4	(1, 0, 0)	3·88
C(16)	C(23)	1	(1, 0, 0)	3·93
C(16)	C(14)	3	(0, 0, 1)	3·95
C(17)	C(25)	4	(1, 0, 0)	3·72
C(17)	C(24)	1	(1, 0, 0)	3·85
C(17)	C(23)	1	(1, 0, 0)	3·93
C(17)	C(26)	1	(1, 0, 0)	3·95
C(18)	C(25)	4	(1, 0, 0)	3·86
C(21)	C(2)	2	(0, 0, 0)	3·94
C(22)	C(4)	2	(-1, 0, 0)	3·81
C(22)	C(11)	2	(0, 0, 0)	3·84
C(22)	C(3)	2	(-1, 0, 0)	3·86
C(23)	C(4)	2	(-1, 0, 0)	3·93
C(25)	C(23)	1	(1, 0, 0)	3·71
C(25)	C(22)	1	(1, 0, 0)	3·82
C(25)	C(5)	1	(1, 0, 0)	3·95
C(26)	C(21)	4	(0, 0, 0)	3·82
C(26)	C(20)	4	(0, 0, 0)	3·86
C(26)	C(5)	4	(0, 0, 0)	3·86
C(26)	C(6)	4	(0, 0, 0)	3·94

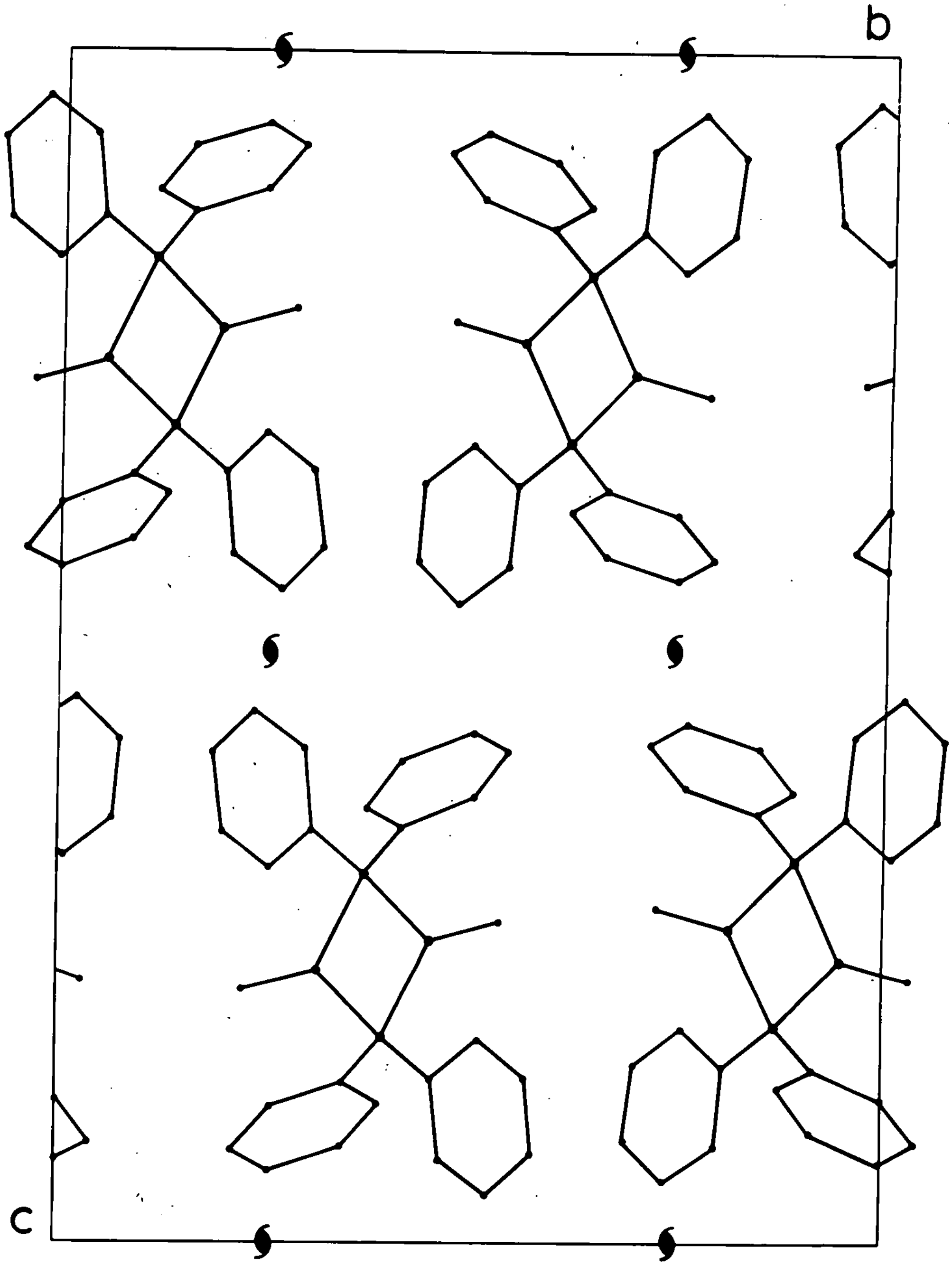
The packing in the crystal is shown in Figure 4.3, where the structure is projected along the a axis. Only four of the approach distances are less than 3·8 Å and all are greater than 3·7 Å so that there does not appear to be any significant interaction between molecules. Although the van der Waals forces on opposite sides of the molecule are slightly different, it is very difficult to account for any of the detailed deviations from 2/m symmetry in terms of either intra- or inter-molecular contacts.

The temperature parameters of the zinc and nitrogen atoms are much alike and, with B values of about 4 Å^2, are similar to those normally encountered. The temperature factors for the phenyl carbon atoms increase with the distance from the centre of the molecule. As would be expected, the largest temperature parameters found are those of the methyl carbon atoms with B values of around 8 Å^2.

4.9 Four-membered rings with three-coordinate zinc

In contrast to oxygen, nitrogen ligands have only one lone-pair of electrons for coordination. In the case of the methyl(diphenylamino)-zinc dimer, if we assume that the methyl groups do not take part in the association, then only open cyclic structures need be considered. All such structures would involve three-coordinate zinc. The formation of a dimer will be favoured by both steric and entropy considerations. The advantage of a trimer is that the considerable valence angle strain connected with a four-membered ring would be averted. The present structure analysis shows that zinc and nitrogen are prepared to tolerate this angle strain in order to retain the advantages of a dimeric arrangement. Four-membered zinc-oxygen rings are present in methylzinc methoxide and structures similar to methyl(diphenylamino)zinc have been postulated for several dimeric complexes containing oxygen, e.g. $(EtZnOCPh_3)_2$ and $(Bu^tZnOBu^t)_2$.

In the crystal, a structure for methyl(diphenylamino)zinc which was further associated through methyl bridges was considered to be a possibility. The structural evidence available indicates that methyl bridging normally involves very sharp bridge angles of about 70°. In the case of zinc with a tetrahedral covalent radius of 1·31 Å,this would force the metal atoms closer together than the Zn-Zn single bond distance and would lead to serious inner-core repulsions (Rundle, 1963). So for the same reason that dimethylzinc does not form a polymer, like dimethylberyllium, methyl(diphenylamino)zinc remains a dimer in the crystal and zinc forfeits the coordination number of four, preferred in its organic chemistry.



(MeZnNPh$_2$)$_2$ projection on the [100] plane

Figure 4·3

h	k	l	|Fo|	|Fc|
2	0	0	100	94
4	0	0	142	122
6	0	0	29	26
1	0	1	9	10
2	0	1	66	68
3	0	1	14	13
4	0	1	47	42
5	0	1	13	13
7	0	1	13	14
8	0	1	7	8
0	0	2	184	179
1	0	2	10	12
2	0	2	28	18
3	0	2	9	10
4	0	2	121	102
5	0	2	8	7
6	0	2	31	31
8	0	2	28	24
1	0	3	10	11
2	0	3	18	16
3	0	3	11	11
4	0	3	6	8
5	0	3	6	9
6	0	3	12	12
7	0	3	5	6
8	0	3	9	10
0	0	4	35	34
1	0	4	20	18
2	0	4	6	3
3	0	4	15	13
4	0	4	85	83
5	0	4	5	4
6	0	4	13	14
8	0	4	29	28
1	0	5	25	23
2	0	5	37	39
3	0	5	13	12
4	0	5	56	51
5	0	5	13	15
6	0	5	34	34
7	0	5	12	11
0	0	6	207	197
1	0	6	8	10
2	0	6	21	23
3	0	6	14	15
4	0	6	84	84
5	0	6	24	25
8	0	6	14	15
1	0	7	27	27
2	0	7	106	115
3	0	7	7	7
4	0	7	8	11
5	0	7	29	30
6	0	7	28	26
7	0	7	12	12
0	0	8	57	63
1	0	8	19	19
2	0	8	35	34
3	0	8	13	13
4	0	8	102	97
5	0	8	26	27
6	0	8	27	25
8	0	8	14	15
1	0	9	10	12
2	0	9	43	37
3	0	9	4	5
5	0	9	16	16
6	0	9	21	21
8	0	9	7	7
0	0	10	129	115
1	0	10	26	28
2	0	10	16	17
3	0	10	12	13
4	0	10	62	62
5	0	10	7	8
6	0	10	10	11
8	0	10	5	5
1	0	11	21	24
2	0	11	64	64
3	0	11	13	15
4	0	11	5	6
5	0	11	7	8
6	0	11	25	23
0	0	12	67	70
1	0	12	15	17
2	0	12	9	10
4	0	12	13	13
5	0	12	9	9
6	0	12	6	4
8	0	12	5	5
1	0	13	31	32
2	0	13	70	70
3	0	13	14	15
4	0	13	29	32
5	0	13	11	13
6	0	13	31	27
1	0	14	16	18
2	0	14	7	2
3	0	14	7	7
4	0	14	9	9
5	0	14	5	5
6	0	14	17	16
8	0	14	5	7
1	0	15	30	33
2	0	15	47	50
3	0	15	7	8
4	0	15	21	23
5	0	15	19	18
6	0	15	22	21
0	0	16	26	27
1	0	16	11	13
4	0	16	7	6
5	0	16	5	5
1	0	17	16	19
2	0	17	39	40
3	0	17	7	7
4	0	17	25	22
5	0	17	14	13
6	0	17	15	13
0	0	18	14	17
1	0	18	5	5
5	0	18	9	8
1	0	19	14	15
2	0	19	30	30
3	0	19	13	11
5	0	19	11	10
6	0	19	12	11
0	0	20	14	15
1	0	21	14	16
2	0	21	22	20
3	0	21	10	9
5	0	21	8	8
0	0	22	12	11
1	0	22	5	6
3	0	22	6	6
4	0	22	4	1
1	0	23	9	9
2	0	23	16	14
3	0	23	9	9
1	0	24	5	5
3	0	24	5	5
2	0	25	9	9
1	1	0	149	151
2	1	0	27	27
3	1	0	86	75
4	1	0	19	13
5	1	0	29	27
6	1	0	22	17
7	1	0	32	30
1	1	1	139	135
2	1	1	35	36
3	1	1	62	59
4	1	1	18	18
5	1	1	37	36
6	1	1	12	10
7	1	1	21	21
8	1	1	7	8
9	1	1	6	7
0	1	2	31	28
1	1	2	108	116
2	1	2	33	36
3	1	2	66	63
4	1	2	15	15
5	1	2	25	21
6	1	2	27	26
7	1	2	26	24
8	1	2	9	10
1	1	3	97	90
2	1	3	33	36
3	1	3	50	48
4	1	3	25	22
5	1	3	25	21
6	1	3	16	18
7	1	3	18	17
8	1	3	12	13
0	1	4	7	7
1	1	4	83	77
2	1	4	44	46
3	1	4	73	70
4	1	4	31	28
5	1	4	12	11
6	1	4	27	26
7	1	4	21	21
0	1	5	19	19
1	1	5	88	84
2	1	5	52	51
3	1	5	71	64
4	1	5	31	29
5	1	5	34	31
6	1	5	24	21
7	1	5	17	17
8	1	5	4	5
1	1	6	99	91
2	1	6	41	40
3	1	6	61	57
4	1	6	9	8
5	1	6	51	43
6	1	6	6	5
7	1	6	21	21
8	1	6	5	6
0	1	7	82	73
1	1	7	54	55
2	1	7	45	49
3	1	7	50	49
4	1	7	41	37
5	1	7	55	50
6	1	7	6	8
7	1	7	15	17
8	1	7	7	9
9	1	7	3	6
0	1	8	54	53
1	1	8	64	62
2	1	8	16	18
3	1	8	65	64
5	1	8	41	41
6	1	8	5	6
7	1	8	20	20
0	1	9	91	83
1	1	9	44	46
2	1	9	30	34
3	1	9	51	51
4	1	9	40	37
5	1	9	25	24
6	1	9	8	9
7	1	9	8	10
8	1	9	8	8
9	1	9	4	7
0	1	10	16	15
1	1	10	59	60
2	1	10	10	11
3	1	10	63	60
4	1	10	6	7
5	1	10	14	13
6	1	10	8	9
7	1	10	15	14
0	1	11	55	52
1	1	11	43	46
2	1	11	44	47
3	1	11	33	35
4	1	11	31	30
5	1	11	7	7
6	1	11	12	12
8	1	11	6	8
0	1	12	5	5
1	1	12	41	46
2	1	12	13	14
3	1	12	46	47
4	1	12	18	20
5	1	12	17	16
6	1	12	10	9
7	1	12	11	10
0	1	13	25	28
1	1	13	34	37
2	1	13	35	34
3	1	13	22	23
4	1	13	9	9
5	1	13	13	15
6	1	13	9	10
8	1	13	9	8
0	1	14	11	12
1	1	14	42	48
2	1	14	18	18
3	1	14	34	36
4	1	14	7	8
5	1	14	20	20
7	1	14	9	10
0	1	15	21	21
1	1	15	32	35
2	1	15	16	18
3	1	15	10	13
4	1	15	14	13
5	1	15	34	28
6	1	15	12	10
1	1	16	29	31
2	1	16	13	13
3	1	16	9	9
4	1	16	14	15
5	1	16	19	17
6	1	16	7	5
7	1	16	7	6
0	1	17	25	29
1	1	17	19	21
2	1	17	23	22
3	1	17	5	6
4	1	17	31	25
5	1	17	15	14
6	1	17	6	6
1	1	18	12	14
2	1	18	13	14
3	1	18	15	14
4	1	18	5	6
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0	1	20	9	10
1	1	20	12	13
2	1	20	9	12
3	1	20	13	12
5	1	20	5	5
6	1	20	5	5
1	1	21	14	14
2	1	21	12	11
3	1	21	9	8
4	1	21	5	4
5	1	21	8	7
0	1	22	12	13
1	1	22	9	9
2	1	22	8	8
4	1	22	7	5
5	1	22	3	4
1	1	23	11	11
2	1	23	6	6
3	1	23	8	8
2	1	24	11	10
3	1	24	5	6
2	1	25	6	6
1	2	0	15	14
2	2	0	5	2
3	2	0	17	17
4	2	0	12	9
5	2	0	14	12
7	2	0	7	8
1	2	1	5	5
2	2	1	66	58
3	2	1	55	47
4	2	1	85	73
5	2	1	66	56
6	2	1	14	13
7	2	1	14	13
8	2	1	12	12
9	2	1	12	14
1	2	2	49	46
2	2	2	79	68
3	2	2	47	44
4	2	2	9	7
6	2	2	18	18
7	2	2	24	22
0	2	3	87	78
1	2	3	266	269
2	2	3	59	52
3	2	3	94	90
4	2	3	52	48
5	2	3	46	43
6	2	3	14	15
7	2	3	7	9
8	2	3	18	19
9	2	3	7	6
1	2	4	77	70
2	2	4	17	15
3	2	4	13	16
4	2	4	27	27
5	2	4	31	28
6	2	4	30	28
7	2	4	4	3
0	2	5	19	24
1	2	5	89	96
2	2	5	27	21
3	2	5	55	49
4	2	5	58	57
5	2	5	66	61
6	2	5	7	8
7	2	5	7	8
8	2	5	11	12
9	2	5	7	8
0	2	6	13	12
1	2	6	29	22
2	2	6	30	32
3	2	6	26	27
4	2	6	9	8
5	2	6	35	30
6	2	6	25	24
7	2	6	8	10
9	2	6	4	4
0	2	7	86	81
1	2	7	92	92
2	2	7	38	38
3	2	7	26	29
4	2	7	66	58
5	2	7	44	42
6	2	7	6	8
7	2	7	4	4
9	2	7	4	5
0	2	8	35	39
1	2	8	42	41
2	2	8	68	74
3	2	8	36	40
4	2	8	8	8
5	2	8	21	21
6	2	8	14	13
7	2	8	11	12
8	2	8	5	6
0	2	9	70	70
1	2	9	63	63
2	2	9	53	50
3	2	9	24	25
4	2	9	45	44
5	2	9	19	17
6	2	9	16	14
7	2	9	9	8
8	2	9	5	7
0	2	10	33	35
1	2	10	74	75
2	2	10	44	47
3	2	10	40	39
4	2	10	16	16
5	2	10	24	22
6	2	10	16	16
7	2	10	6	7
0	2	11	39	42
1	2	11	20	21
2	2	11	25	27
3	2	11	20	20
4	2	11	30	29
5	2	11	33	33
6	2	11	8	9
8	2	11	4	5
0	2	12	21	25
1	2	12	22	22
2	2	12	50	53
3	2	12	35	39
4	2	12	14	13
6	2	12	12	11
7	2	12	15	13
0	2	13	23	26
1	2	13	26	27
2	2	13	15	17
3	2	13	25	28
5	2	13	13	12
7	2	13	5	4
8	2	13	4	4
0	2	14	22	24
1	2	14	30	32
2	2	14	40	43
3	2	14	26	27
4	2	14	13	13
5	2	14	15	15
6	2	14	14	15
7	2	14	7	8
0	2	15	19	20
1	2	15	13	15
2	2	15	10	11
3	2	15	12	14
4	2	15	11	12
5	2	15	9	10
6	2	15	9	9
0	2	16	20	24
1	2	16	41	36
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3	12	2	12	13
4	12	2	11	12
5	12	2	18	20
0	12	3	4	4
1	12	3	10	11
2	12	3	10	10
4	12	3	4	4
5	12	3	6	6
6	12	3	6	7
0	12	4	15	18
1	12	4	24	23
2	12	4	5	6
3	12	4	19	19
4	12	4	13	13
5	12	4	11	12
6	12	4	6	6
1	12	5	17	16
2	12	5	7	6
3	12	5	12	10
4	12	5	6	5
5	12	5	6	5
6	12	5	6	6
0	12	6	13	16
1	12	6	26	26
2	12	6	11	11
3	12	6	21	19
4	12	6	8	7
5	12	6	10	9
6	12	6	5	4
1	12	7	20	19
2	12	7	4	3
3	12	7	13	11
5	12	7	8	7
0	12	8	10	9
1	12	8	20	20
2	12	8	12	12
3	12	8	11	10
4	12	8	7	8
5	12	8	14	12
1	12	9	12	11
2	12	9	14	12
3	12	9	15	13
5	12	9	8	7
0	12	10	7	8
1	12	10	10	11
2	12	10	9	10
3	12	10	5	6
4	12	10	8	7
5	12	10	8	8
1	12	11	10	10
2	12	11	14	13
3	12	11	11	10
5	12	11	12	9
0	12	12	13	10
1	12	12	11	11
2	12	12	9	9
3	12	12	5	4
4	12	12	7	6
5	12	12	6	5
0	12	13	6	7
1	12	13	13	11
2	12	13	8	9
3	12	13	13	12
4	12	13	3	4
5	12	13	5	5
0	12	14	4	2
1	12	14	6	4
2	12	14	6	6
3	12	14	6	5
4	12	14	5	4
0	12	15	7	9
1	12	15	12	11
3	12	15	11	8
4	12	15	5	4
2	12	16	5	4

h	k	l	|Fo|	|Fc|
3	12	16	5	4
0	12	17	10	9
1	12	17	11	10
3	12	17	2	5
0	12	18	5	4
1	12	18	4	3
3	12	18	4	3
0	12	19	8	8
1	12	19	7	6
2	12	19	5	5
1	13	0	21	27
2	13	0	12	15
3	13	0	4	5
4	13	0	5	5
5	13	0	11	12
6	13	0	8	10
0	13	1	2	1
1	13	1	8	11
2	13	1	8	9
3	13	1	13	13
6	13	1	4	4
0	13	2	4	3
1	13	2	13	13
2	13	2	17	17
3	13	2	10	12
4	13	2	8	9
5	13	2	9	10
6	13	2	6	7
0	13	3	6	8
1	13	3	5	6
2	13	3	7	7
3	13	3	10	11
5	13	3	5	5
6	13	3	5	5
0	13	4	7	9
1	13	4	12	13
2	13	4	16	16
3	13	4	16	17
5	13	4	6	6
6	13	4	5	4
0	13	5	5	6
1	13	5	12	11
2	13	5	11	11
3	13	5	10	10
5	13	5	6	7
6	13	5	3	3
0	13	6	5	6
1	13	6	16	14
2	13	6	19	17
3	13	6	13	12
4	13	6	6	5
5	13	6	6	6
0	13	7	5	6
1	13	7	10	9
2	13	7	9	9
3	13	7	11	11
4	13	7	8	6
5	13	7	4	4
0	13	8	7	8
2	13	8	14	13
3	13	8	5	5
4	13	8	12	10
5	13	8	7	5
0	13	9	8	9
1	13	9	12	12
2	13	9	6	6
3	13	9	10	10
4	13	9	7	6
5	13	9	6	6
0	13	10	7	9
1	13	10	11	10
2	13	10	14	10
3	13	10	8	6
4	13	10	7	6
5	13	10	5	4
0	13	11	8	8
1	13	11	18	17
2	13	11	9	8
3	13	11	15	10
4	13	11	6	6
5	13	11	7	5
0	13	12	5	5
1	13	12	10	9
2	13	12	12	9
3	13	12	6	5
4	13	12	7	6
0	13	13	6	6
1	13	13	9	10
2	13	13	5	4
3	13	13	16	12
4	13	13	7	6
0	13	14	5	5
1	13	14	4	3
4	13	14	4	3
0	13	15	6	5
1	13	15	6	6
3	13	15	4	4
4	13	15	5	4
0	13	16	5	6
1	13	16	3	2
2	13	16	4	3
0	13	17	11	8
1	13	17	7	7
0	13	18	4	4

$(MeZnNPh_2)_2$ TABLE 4.9

Final Values of the Observed and Calculated Structure Factors

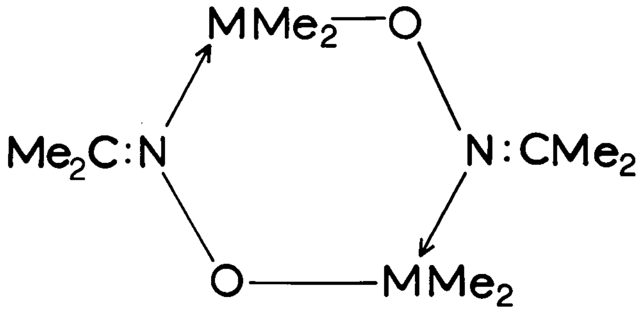
CHAPTER FIVE

THE CRYSTAL STRUCTURE
OF
TETRAMERIC METHYLZINC ACETOXIMATE

5.1 Introduction

Methylzinc dimethylketoximate is prepared by the slow addition of a diethyl ether solution of acetoxime to dimethylzinc in ether at about -100°. Gas evolution is apparent when the mixture warms to about -80°. A small amount of white solid, probably $(Me_2C{:}NO)_2Zn$, present when the mixture reaches room temperature, is filtered off and the product obtained by concentrating the filtrate, followed by cooling to -70°. The white solid product decomposed at 170° without melting. On recrystallisation from pentane, beautifully formed, colourless needles of rectangular cross-section are obtained. Crystals for X-ray examination were sealed in pyrex capillaries under a dry nitrogen atmosphere.

Cryoscopic measurements showed that methylzinc acetoximate is tetrameric in benzene solution, $(MeZnON{:}CMe_2)_4$, (Coates and Ridley, 1966). Dimeric compounds $(Me_2C{:}NOMMe_2)_2$, (M = Al, Ga, In) had been prepared and were considered to have cyclic structures (Jennings and Wade, 1967).



However, replacement of MMe_2 in the above structure by ZnMe would result in only three-coordinate zinc. The present structure analysis was undertaken to establish the degree of association in the solid state and to investigate the manner in which the association takes place. The infrared spectrum of $(MeZnON:CMe_2)_4$ contains an absorption of medium intensity at 1629 $cm.^{-1}$, 40 $cm.^{-1}$ lower than that due to ν(C:N) in acetoxime.

5.2. Crystal Data

Zero level precession photographs, with Mo-K_α radiation, gave the following unit cell dimensions:

Monoclinic: needles elongated along a.
a = 9·258, b = 13·58, c = 24·10 Å;
β = 105°27';
U = 2920 Å^3; Z = 4 units of $(MeZnON:CMe_2)_4$.
D_x = 1·387 $gm.cm.^{-1}$; M.W. of $(MeZnON:CMe_2)_4$ = 610·02.
Absorption Coefficient for Cu-K_α radiation, μ = 41 $cm.^{-1}$.

At the time the compound was prepared, a density of 1·50 $gm.cm.^{-1}$ was reported, measured by flotation in a mixture of orthobromotoluene (ρ=1·41) and bromobenzene (ρ=1·52). Owing to shortage of sample it has not been possible to repeat this measurement.

The space group was uniquely determined by the conditions limiting the observed reflections:

0k0: k=2n,
h0l: l=2n,

as Number 14, $P2_1/c$ (C_{2h}^5).

The statistical standard deviations in unit cell lengths were 0·005 Å in *a*, 0·006 in Å in *b*, 0·007 Å in *c*. Including systematic errors the uncertainty is probably of the order of 0·2%. The uncertainty in β is of the order of 10'.

5.3 Data Collection and Corrections

Three-dimensional data were obtained on layers with h=0 to 8 using the equi-inclination Weissenberg and multiple film techniques.

The crystals deteriorated slowly on exposure to X-radiation, turning from colourless, through yellow to dark brown after an exposure time of about a fortnight. Three crystals were used in data collection (Table 5.1).

TABLE 5.1

Crystals Used To Record The Data

Crystal 1 Cross-Section: 0·013 cm. square	0kl; 1kl; 2kl;
Crystal 2 Cross-Section: 0·015×0·024 cm.^{2}	3kl; 4kl; 5kl; 6kl;
Crystal 3 Cross-Section: 0·021 cm. square	7kl; 8kl; 0,1,2,3kl; 0,4,5,6kl.

Although crystal 1 was abandoned before it showed visible signs of decomposition, there was a marked deterioration in the shape of the reflections after the 2kl net. The rest of the data was collected using the second crystal, however the 7kl and 8kl nets were repeated after the reflections from crystal 2 showed deterioration in quality. The third crystal sufficed to put the nets 0kl to 6kl on to the same relative scale by taking timed Weissenberg photographs of four levels, on different parts of the same film.

The intensities were estimated as before and the usual Lorentz and polarisation corrections were applied, together with length corrections for the upper level data.

All three crystals were needle-like and were elongated along $\underline{a}$. Crystal 2 was seen to have well-developed $\{011\}$ faces. However, in the case of the two crystals with square cross-section, although there was some difficulty in recognising individual crystal faces optically, it appeared that it was the $\{010\}$ and $\{001\}$ faces which were developed. In view of this uncertainty, together with the relatively small size of the crystals and the almost square cross-section in two cases, no corrections for absorption were applied.

5.4 The Patterson Function

The observed structure factors were multiplied by a weighting function w, where $w = \exp(4\sin^2\theta/\lambda^2)$. The weighting function was not allowed to become greater than 2·718, the value of e^1. This means that the weighting function takes a constant value for reflections with $\sin\theta/\lambda \geqslant 0{\cdot}5$. The Patterson function was then calculated using the squares of these weighted structure factors as coefficients:

$$P(u,v,w) = \frac{4}{V}\sum_{0}^{h}\sum_{0}^{k}\sum_{-1}^{1}\Big(w(hk1)|F(hk1)|\Big)^2$$
$$\Big(\cos2\pi hu.\cos2\pi kv.\cos2\pi 1w - \sin2\pi hu.\cos2\pi kv.\sin2\pi 1w\Big)$$

The symmetry of the vector set is P2/m. The Patterson function was calculated over one quarter of the unit cell, 'u' at intervals of 0·232 Å to a, 'v' at intervals of 0·226 Å to b/2 and 'w' at intervals of 0·241 Å to c/2.

The Patterson function includes a Harker section at $(u,\frac{1}{2},w)$ which contains vectors between atoms related by the 2_1 screw axis, and a Harker line $P(0,v,\frac{1}{2})$ containing vectors between atoms related by the axial glide plane.

Four double weight Zn-Zn vectors are expected on each Harker section. The Harker line $P(0,v,\frac{1}{2})$ contained only three resolved peaks, one of which was large enough to accommodate two vectors of the expected peak height. On the Harker section $P(u,\frac{1}{2},w)$ there were six peaks large enough to be Zn-Zn double weight vectors. One of these peaks was large enough to arise from the coincidence of two such vectors. From the occurrence of multiple peaks along $P(0,\frac{1}{2},w)$ and of extra peaks on $P(u,\frac{1}{2},w)$ it was expected that two unrelated zinc atoms would have similar y-coordinates. This was supported by the presence of large peaks on the section $P(u,0,w)$.

Using one of the peaks on the Harker line, a value of 2y for the first zinc atom was chosen. This leads to the section at 2y where a single weight peak (2x,2y,2z) is expected between this atom and that related to it by the centre. The x- and z-coordinates found were consistent with one of the vectors on the $P(u,\frac{1}{2},w)$ Harker section.

In a similar manner, three single weight vectors for the other zinc atoms were found, consistent with the peaks observed on the two Harker sections. The four sets of coordinates were then confirmed by finding suitable peaks on the Patterson function, corresponding to the 24 vectors between zinc atoms unrelated by symmetry.

The heavy atom coordinates found were:

Zn(1)	0·163	0·346	0·135
Zn(2)	0·419	0·206	0·233
Zn(3)	0·358	0·196	0·068
Zn(4)	0·106	0·104	0·130

The four zinc atoms occupied positions at the corners of a slightly distorted tetrahedron.

5.5 Light Atom Positions

The coordinates of the zinc atoms were refined through two cycles of least-squares refinement, using arbitrary initial values for scale and temperature factors. Structure factors were calculated on the basis of the refined parameters (R=0·45) and were used to calculate an Fo synthesis. The function was evaluated at the same intervals as the Patterson map.

The positions of all the light atoms, other than hydrogen, were clearly indicated. The mean peak heights were as follows: zinc 56·9 e.Å^{-3}; oxygen 10·7 e.Å^{-3}; nitrogen 9·0 e.Å^{-3}; carbon 5·3 e.Å^{-3}. Only five spurious peaks were of height greater than peaks attributed to atoms. The greatest unassigned peak had a height of 6·1 e.Å^{-3}.

On the introduction of the light atom contributions, the agreement with the observed structure factors was still only R=0·37. However, the scaling was still considerably in error, $\Sigma|Fo|$ was greater than $\Sigma|Fc|$ by a factor of 3:2.

5.6 Refinement

The structure was refined through one cycle of least-squares using isotropic temperature parameters throughout. R improved to 0·30.

Structure factors were then calculated and were used to compute a second Fo synthesis. The peak heights of the oxygen atoms now ranged from 11·3 to 13·4 e.Å^{-3}, those of the nitrogen from 9·0 to 10·3 e.Å^{-3}

and the mean peak height of carbon was 7·1 e.Å^{-3}. Only one (5·6 e.Å^{-3}) unassigned peak was greater than 3·1 e.Å^{-3}.

The structure was then refined by the method of least squares, using the block diagonal approximation, to an R value of 0·106. For three cycles, isotropic temperature parameters were used, followed by four cycles with anisotropic temperature factors throughout. At this stage refinement was nearing completion but the distance C(8)-C(9) was 1·63 Å. The error appeared to be in the position C(9) since the length of C(8)-C(10) and the angles at C(8) were normal.

To guard against the possibility of the structure refining to a false minimum or that the rate of refinement was unduly slow, the position of C(9) was adjusted to make the length of the C(8)-C(9) bond normal. This involved giving to C(9) a y-coordinate of $\frac{1}{4}$. Individual layer-scales for the reciprocal lattice nets 0kl to 6kl were also now introduced although these nets had originally been correlated experimentally. In only one cycle, C(9) moved back to its original position. A further cycle improved R to 0·102.

Up to this stage 2660 observed planes on the 0kl to 6kl nets had been used in the refinement. More intensity data was available from the reciprocal lattice nets 7kl and 8kl ($\nu = 35^{\circ}39'$ and $41^{\circ}46'$ respectively). The relative scaling of these two nets was not known but their structure factors were placed on to an absolute scale simply by a comparison of $\Sigma|Fo|$ and $\Sigma|Fc|$ for each net. In the final stages of least-squares refinement, structure factors were calculated for 3081 planes on nine reciprocal lattice nets each with its own layer-scale κ_i.

After five more cycles the structure converged to R=0·101 and during this refinement the position of C(9) slowly improved. In the last two cycles the shifts were still such that the length C(8)-C(9) improved from 1·60 to 1·58 Å. This late improvement in the position of C(9) may be related to C(9) being situated very near to y = $\frac{1}{4}$.

In the final cycle of refinement the biggest parameter shift was only 0·12 of the corresponding e.s.d. The final values of the positional and thermal parameters together with their e.s.d.'s are given in Tables 5.3 and 5.4.

Structure factors were calculated and used to compute a final (Fo-Fc) synthesis as a check on the structure. Small positive peaks were again observed on the atomic sites. Peaks of about 3 e.Å^{-3} came up at the zinc positions and of about 0·5 e.Å^{-3} in the positions of the oxygen and nitrogen atoms. At the sites of the carbon atoms were peaks of about 0·4 e.Å^{-3}. On the whole the background was small and only in a few other regions did it reach values greater than 0·4 e.Å^{-3}.

In the last nine cycles of refinement the structure factors were weighted by the same function used in the refinement of methylzinc methoxide. For methylzinc acetoximate the coefficients used were:

$$p_1 = 4, \qquad p_2 = 0{\cdot}05, \qquad p_3 = 0{\cdot}0004, \qquad p_4 = 0{\cdot}000003.$$

The least-squares totals and the variation of $w.\Delta^2$ with $|Fo|$ and with $\sin\theta/\lambda$ are given in Table 5.3.

The observed and calculated structure factors are listed in Table 5.9. Unobserved reflexions were given zero weight in the refinement but none of those on the nets 0kl to 6kl were significantly greater than their minimum observable value, Fmin.

$(MeZnON{:}CMe_2)_4$ TABLE 5.2

Least-Squares Totals

Number of Observed Planes 3081

$\Sigma\lvert\Delta\rvert$	9336·9	$\Sigma\lvert Fo\rvert$	92250·1	$\Sigma\lvert Fc\rvert$	90214·0	R	0·101
$\Sigma w\lvert\Delta\rvert^2$	4331·2	$\Sigma w\lvert Fo\rvert^2$	293661·0	$\Sigma w\lvert Fc\rvert^2$	289270·7	R'	0·015

Weighting Analysis

$w.\Delta^2$ averaged in batches and the number of planes per batch.

	$\sin\theta/\lambda$				
	0·0-0·2	0·2-0·4	0·4-0·6	0·6-0·8	TOTALS
$\lvert Fo\rvert$					
0-17	6·78/16	1·61/242	1·17/991	0·96/63	1·31/1312
17-34	6·03/16	1·18/379	1·36/511	0·78/3	1·37/909
34-67	4·54/53	1·18/404	1·92/113	0·00/0	1·64/570
67-135	1·95/64	1·32/172	1·12/5	0·00/0	1·49/241
135-269	1·60/30	2·12/17	0·00/0	0·00/0	1·79/47
269 UP	0·17/2	0·00/0	0·00/0	0·00/0	0·17/2
TOTALS	3·42/181	1·30/1214	1·28/1620	0·95/66	1·41/3081

$(\mathrm{MeZnON{:}CMe_2})_4$ TABLE 5.3

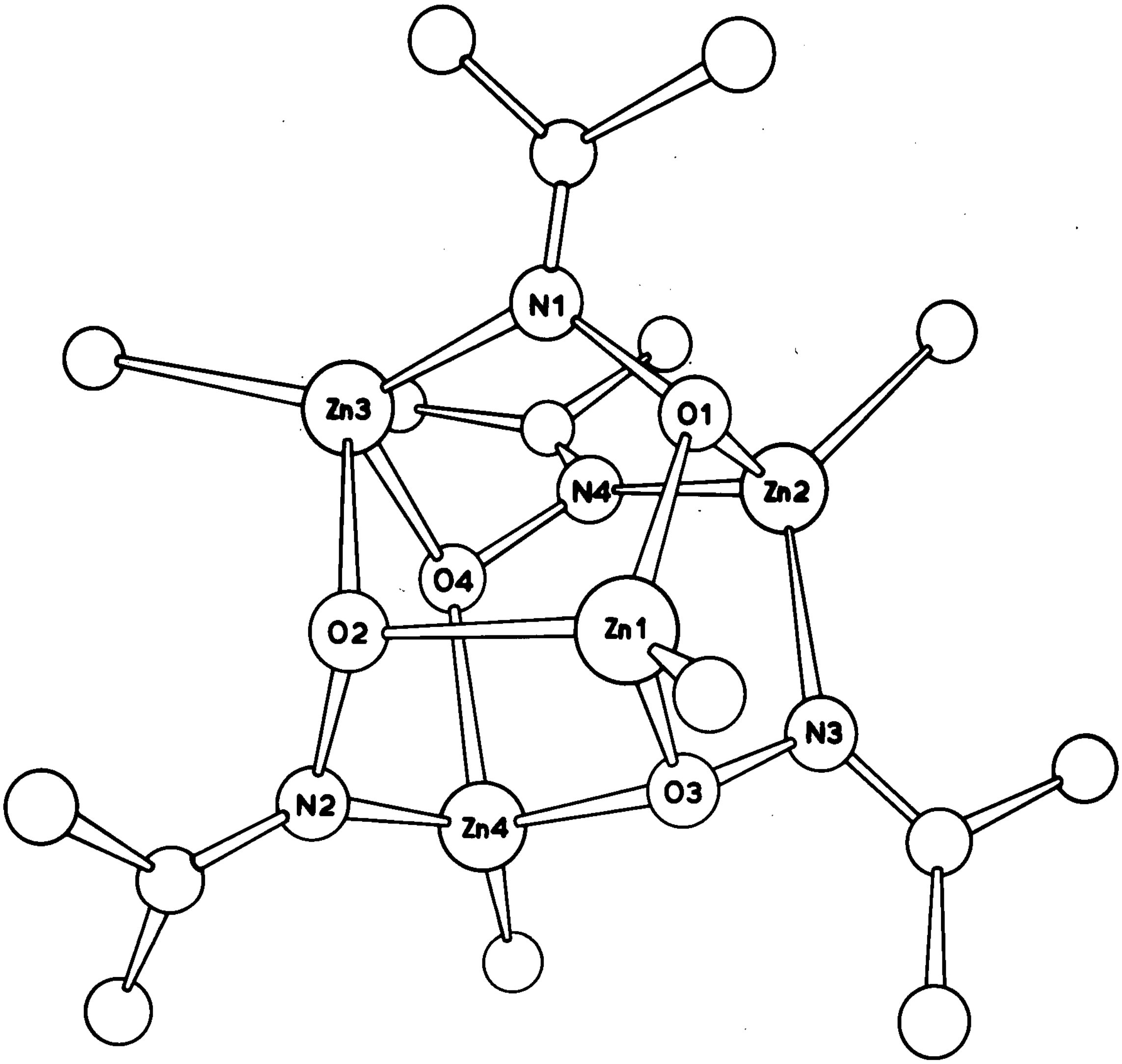
Final Values of Atomic Coordinates and their Standard Deviations

Atom	x/a	y/b	z/c	$\sigma(x/a)$	$\sigma(y/b)$	$\sigma(z/c)$
Zn(1)	0·16388	0·34336	0·13470	0·00018	0·00012	0·00006
Zn(2)	0·42237	0·21008	0·23351	0·00018	0·00013	0·00006
Zn(3)	0·35437	0·19924	0·06745	0·00019	0·00012	0·00006
Zn(4)	0·09492	0·10054	0·12901	0·00019	0·00012	0·00007
O(1)	0·38755	0·31798	0·17072	0·00089	0·00059	0·00031
O(2)	0·14938	0·26499	0·06108	0·00095	0·00058	0·00029
O(3)	0·10479	0·22585	0·17755	0·00089	0·00062	0·00029
O(4)	0·31045	0·09968	0·12491	0·00089	0·00057	0·00029
N(1)	0·46917	0·29371	0·12990	0·00110	0·00079	0·00038
N(2)	0·04535	0·18785	0·05532	0·00116	0·00074	0·00037
N(3)	0·19646	0·21350	0·23297	0·00113	0·00066	0·00035
N(4)	0·42381	0·09175	0·17772	0·00113	0·00072	0·00035
C(1)	0·06383	0·46967	0·13436	0·00180	0·00106	0·00071
C(2)	0·58761	0·23453	0·30204	0·00187	0·00157	0·00064
C(3)	0·39203	0·15242	-0·00404	0·00208	0·00112	0·00056
C(4)	0·00596	-0·01893	0·14930	0·00230	0·00119	0·00079
C(5)	0·59606	0·33772	0·13846	0·00140	0·00099	0·00048
C(6)	0·69354	0·31207	0·09963	0·00201	0·00143	0·00071
C(7)	0·65006	0·41339	0·18505	0·00194	0·00122	0·00071
C(8)	-0·05054	0·18152	0·00776	0·00158	0·00112	0·00052
C(9)	-0·05091	0·25608	-0·04268	0·00255	0·00160	0·00066
C(10)	-0·16126	0·09761	-0·00218	0·00206	0·00158	0·00078
C(11)	0·13048	0·21135	0·27230	0·00147	0·00092	0·00053
C(12)	-0·03635	0·21873	0·26073	0·00188	0·00138	0·00072
C(13)	0·22117	0·19972	0·33404	0·00194	0·00128	0·00063
C(14)	0·52040	0·02595	0·17806	0·00151	0·00094	0·00045
C(15)	0·52385	-0·03466	0·12579	0·00204	0·00120	0·00063
C(16)	0·64097	0·00860	0·23243	0·00181	0·00130	0·00064

$(MeZnON{:}CMe_2)_4$ TABLE 5.4

Final Values of Anisotropic Temperature Parameters (Å^2) and their Standard Deviations ($\text{Å}^2 \times 10^4$)

Atom	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Zn(1)	0·0887(10)	0·0678(9)	0·0601(7)	-0·0126(13)	0·0192(12)	0·0050(15)
Zn(2)	0·0862(10)	0·0858(10)	0·0508(7)	-0·0086(13)	0·0223(12)	0·0031(15)
Zn(3)	0·0935(10)	0·0713(9)	0·0527(7)	-0·0065(12)	0·0303(12)	-0·0020(15)
Zn(4)	0·0912(10)	0·0741(9)	0·0649(8)	-0·0105(14)	0·0262(13)	-0·0246(16)
O(1)	0·0818(47)	0·0695(47)	0·0612(39)	-0·0190(65)	0·0269(63)	0·0035(70)
O(2)	0·0978(53)	0·0684(46)	0·0491(35)	-0·0146(63)	0·0143(63)	-0·0271(76)
O(3)	0·0807(47)	0·0862(53)	0·0492(34)	-0·0187(67)	0·0213(60)	-0·0095(75)
O(4)	0·0894(49)	0·0619(42)	0·0514(36)	0·0003(59)	0·0199(61)	-0·0097(71)
N(1)	0·0764(57)	0·0901(67)	0·0562(46)	0·0057(89)	0·0234(75)	-0·0132(100)
N(2)	0·0931(65)	0·0718(59)	0·0528(45)	-0·0019(78)	0·0187(79)	0·0080(94)
N(3)	0·0949(62)	0·0602(51)	0·0466(39)	-0·0111(71)	0·0238(74)	-0·0067(86)
N(4)	0·0916(62)	0·0712(57)	0·0476(43)	0·0096(75)	0·0213(75)	0·0100(92)
C(1)	0·1128(105)	0·0664(77)	0·1094(103)	-0·0119(140)	0·097(154)	0·0230(140)
C(2)	0·1016(100)	0·1480(149)	0·0754(81)	-0·0531(173)	-0·0217(134)	-0·0079(188)
C(3)	0·1542(131)	0·0831(86)	0·0657(69)	-0·0459(126)	0·0784(147)	0·0017(169)
C(4)	0·1477(140)	0·0756(89)	0·1135(114)	0·0147(160)	0·0684(195)	-0·0367(176)
C(5)	0·0833(73)	0·0829(77)	0·0641(61)	0·0109(108)	0·0053(96)	-0·0103(120)
C(6)	0·1146(114)	0·1242(125)	0·0921(94)	0·0258(173)	0·0840(160)	-0·0209(184)
C(7)	0·1172(109)	0·0928(98)	0·0987(97)	-0·0556(158)	0·0255(154)	-0·0659(166)
C(8)	0·0948(87)	0·0966(94)	0·0628(63)	-0·0124(116)	-0·0050(107)	0·0103(135)
C(9)	0·1705(164)	0·1340(139)	0·0643(77)	0·0202(168)	-0·0661(170)	0·0693(256)
C(10)	0·1116(115)	0·1372(144)	0·1013(107)	-0·0704(201)	0·0103(163)	-0·0603(205)
C(11)	0·0870(78)	0·0735(72)	0·0761(67)	0·0055(110)	0·0506(109)	-0·0036(116)
C(12)	0·0992(100)	0·1236(130)	0·0978(98)	-0·0218(178)	0·0592(151)	-0·0082(172)
C(13)	0·1218(113)	0·1099(109)	0·0727(73)	0·0238(148)	0·0482(139)	-0·0189(177)
C(14)	0·1043(83)	0·0739(71)	0·0535(55)	0·0097(97)	0·0162(99)	0·0130(122)
C(15)	0·1351(121)	0·0894(95)	0·0807(81)	-0·0243(144)	0·0186(150)	0·0580(175)
C(16)	0·1025(97)	0·1103(112)	0·0823(81)	0·0157(149)	0·0173(131)	0·0231(160)



(MeZnON:CMe$_2$)$_4$

Figure 5·1

5.7 Description and Discussion of Structure

The structure is as shown in Figure 5.1. The four zinc atoms are at the corners of a slightly distorted tetrahedron, and above each face of the tetrahedron is an acetoximate group in which the oxygen atom is attached to two zincs and the nitrogen to the third. Thus between each pair of zinc atoms can be traced a Zn-O-N-Zn linkage. Tracing the counter-clockwise spirals from Zn(1) we have for example:

Zn(1)-O(3)-N(3)-Zn(2)
Zn(1)-O(1)-N(1)-Zn(3)
Zn(1)-O(2)-N(2)-Zn(4)

and similar linkages connect Zn(4) to Zn(2), Zn(3) to Zn(4) and Zn(3)-Zn(2). Since each oxygen atom is bonded directly to two zinc, four pairs of zinc atoms:

Zn(1)-Zn(2); Zn(1)-Zn(3); Zn(3)-Zn(4); Zn(4)-Zn(1);

are connected by a Zn-O-Zn link.

This pattern of bonding results in a "cage" structure which has four puckered five-membered rings and two adjacent six-membered rings in which Zn(2), N(4) and O(4) are common to both. Each five-membered ring is composed of two zinc, two oxygen and one nitrogen atom. Although both of the six-membered rings contain two zinc, two oxygen and two nitrogen atoms they are however intrinsically different. In the first, both oxygen atoms are bonded to a common zinc and similarly the nitrogens. In the other, each zinc is bonded to one nitrogen and one oxygen atom. The six-membered ring formed by Zn(2),N(3),O(3),Zn(4),O(4),N(4) is analogous in shape to a cyclohexane ring in the chair conformation. The atoms Zn(2), N(3),Zn(4),O(4) are approximately coplanar (all atoms lie within 0·03 Å of the mean plane), and N(4) is situated 0·7 Å to one side of the plane, O(3) is 0·8 Å to the other side. The atoms Zn(3),N(1),O(1),Zn(2),N(4), O(4) in the other six-membered ring are approximately related by a two-fold axis.

The outcome of this arrangement is that no four-membered rings are found but the four zinc atoms are in three different kinds of environment. In addition to the methyl carbons:

Zn(1) is bonded to three oxygen atoms O(1), O(2),and O(3);
Zn(2) is bonded to two nitrogens N(3) and N(4) and one oxygen O(1);
Zn(3) and Zn(4) are each bonded to one nitrogen and two oxygens;
Zn(3) to N(1), O(2) and O(4) and Zn(4) to N(2), O(3) and O(4).

Thus the coordination number at zinc is four and at oxygen is three.

Bond lengths and bond angles with their standard deviations are given in Tables 5.5 and 5.6. Some bond lengths are also shown on Figure 5.2.

The mean Zn-C length is 1·95 Å, none of the individual values differing significantly from each other. The mean values of the Zn-C lengths found in the three structures presented are:

in $(MeZnOMe)_4$ - 1·948 Å,
in $(MeZnNPh_2)_2$ - 1·949 Å,
in $(MeZnON{:}CMe_2)_4$ - 1·950 Å.

Comment has already been made on the difference between these observed values and the sum of the Pauling radii.

In methylzinc acetoximate the Zn-O lengths vary from 2·024 to 2·069 Å and with e.s.d.'s of 0·008 Å, for these extreme cases this represents a value for Student's t function of 4·0 and the difference is significant. In spite of the differences in environment of the zinc atoms however, the Zn-O distances agree fairly closely with one another, and with the exception of Zn(4)-O(4), the shortest, the variation is only from 2·043 to 2·069 Å. These seven Zn-O lengths may be taken to be the same within experimental error, with a mean value of 2·055 Å. This distance is significantly shorter than the mean value of 2·08 Å observed in methylzinc methoxide. In methylzinc acetoximate, because of the absence of four-membered rings, the angles at oxygen do not depart appreciably from tetrahedral. The strained environment in the methoxide is thus relaxed and atomic orbitals with greater 's' character will be used in bond formation, with a resultant shortening of the Zn-O bond. There is no evident reason for the value of Zn(4)-O(4).

For the extreme Zn-N distances of 2·047 Å and 2·098 Å, t_0 is 3·6 and the difference must be regarded as significant. Again however, it is one distance which is appreciably shorter than the rest, the other three values agree very closely and have a mean of 2·090 Å. This mean value is the same as the distance observed in mono-thiosemicarbazide zinc chloride, $Zn(SC(NH_2)NHNH_2)Cl_2$, where zinc is both tetrahedrally coordinated and together with nitrogen is part of a five-membered ring system. The mean Zn-N distance in $(MeZnNPh_2)_2$ is 2·073 Å. Arguing by analogy with the Zn-O distances one would expect the Zn-N in the acetoximate to be shorter than 2·073 Å. However, in this case the comparison is complicated by the differing hybrid states of both zinc and nitrogen in the two compounds.

The four O-N distances may be taken to be the same within experimental error, as may the four N=C lengths. None of the individual values differ significantly from each other or from the mean values of 1·41 Å and 1·26 Å respectively. The results of various X-ray and neutron diffraction studies which have been made of oxime molecules have been summarized by Hamilton (1961). The observed lengths of C=N bonds vary from 1·25 to 1·29 Å, and of N-O bonds from 1·32 to 1·39 Å. However, a recent microwave study of formaldoxime, CH_2=NOH (Levine,1963), revealed C=N and N-O bonds of 1·276 and 1·408 Å respectively. Because of resonance the N-O bond is expected to be shorter than a pure single bond and the C=N bond longer than a pure double bond, and when these distances in formaldoxime were corrected for resonance by a simple Huckel treatment, the lengths were in excellent agreement with the predictions of the Schomaker-Stevenson relation (C=N, pure double bond, 1·26$_5$ Å; N-O, pure single bond, 1·44 Å). The values in methylzinc acetoximate are in good agreement with the distances observed in formaldoxime.

For seven of the C-C bonds the length varies between 1·496 Å and 1·512 Å with a mean value of 1·505 Å. This distance agrees closely with the value of 1·510 ± 0·005 Å obtained by averaging several independent estimates of the Csp^3-Csp^2 bond distance (Interatomic Distances - Supplement, 1965). The eigth C-C distance in methylzinc acetoximate, C(8)-C(9), has a value of 1·58 Å. The electron density peak representing C(9) in the second Fo synthesis was broad and diffuse and its height of 5·6 e.Å^{-3} was the smallest shown by a carbon atom. In addition the temperature parameters of C(9) tend to be larger than those of the other methyl carbon atoms. Neglect of certain off-diagonal elements in the least-squares matrix may lead to underestimate of the e.s.d.'s particularly if there is large overlap of electron density (Hodgson and Rollett, 1963). It is also recalled that the positions of C(9) improved appreciably in the last few cycles of refinement, so in view of these considerations it is not believed that there is a real difference in length between this bond and the others.

One would expect to find the greatest inter-bond angles in the two six-membered rings and this is fully borne out in practice. The largest angles at zinc are in the "cyclohexane-type" ring, N(3)-Zn(2)-N(4) with a value of 101·0° and O(3)-Zn(4)-O(4) with a value of 97·9°. The two angles in the other six-membered ring, O(1)-Zn(2)-N(4) and O(4)-Zn(3)-N(1) with values of 95·7° and 94·3° respectively, are the largest O-Zn-N angles observed. The remaining O-Zn-O angles vary from 89·5° to 96·1° and the O-Zn-N angles from 87·6° to 94·0°. Individual values are given in Table 5.6. The absence of four-membered rings has meant that, in general, the bond angles at zinc are about 10° larger than those observed in methylzinc methoxide.

The angles at oxygen vary from 106·1° to 117·3° and so are not greatly distorted from tetrahedral, although in general they are slightly greater than the tetrahedral value. Since throughout this molecule, the inter-bond angles at oxygen are fairly normal, the relief of valence angle strain on going to a six-membered ring is felt mainly by the zinc atoms and so the angles at oxygen in the six-membered rings are not necessarily the largest.

None of the C-C-C or the N-C-C angles differ significantly from the expected value of 120°.

In each of the four cases the sum of the three angles at nitrogen is 360 ± 1°. This means that there are four individual zinc acetoximate "Me_2C:NOZn" units which are approximately planar. These involve Zn(2), Zn(3) and Zn(4) but not Zn(1). And to a lesser extent the methyl carbon atoms attached to zinc also lie near to these planes. This arrangement brings each isopropylidene group into close proximity with the methyl carbon atom on the adjacent zinc atom (contacts designated by an obelus† in Table 5.7) and results in the distortion of the four Zn-N=C angles to values greater than 130°. The requirements of the five-membered rings necessitate a Zn-N-O angle of around 110°, leaving the third angle at nitrogen, the O-N=C angle, with a value of about 115°. The mean values of the four Zn-N=C, Zn-N-O and O-N=C angles, are respectively 132·7°, 111·8° and 115·1°. None of the individual values differ significantly from the appropriate mean. Thus, the mean O-N=C angle of 115·1° does not differ greatly from the values of 109·7° to 112° observed in free oxime molecules where lone-pair repulsions are responsible for the distortion from 120°.

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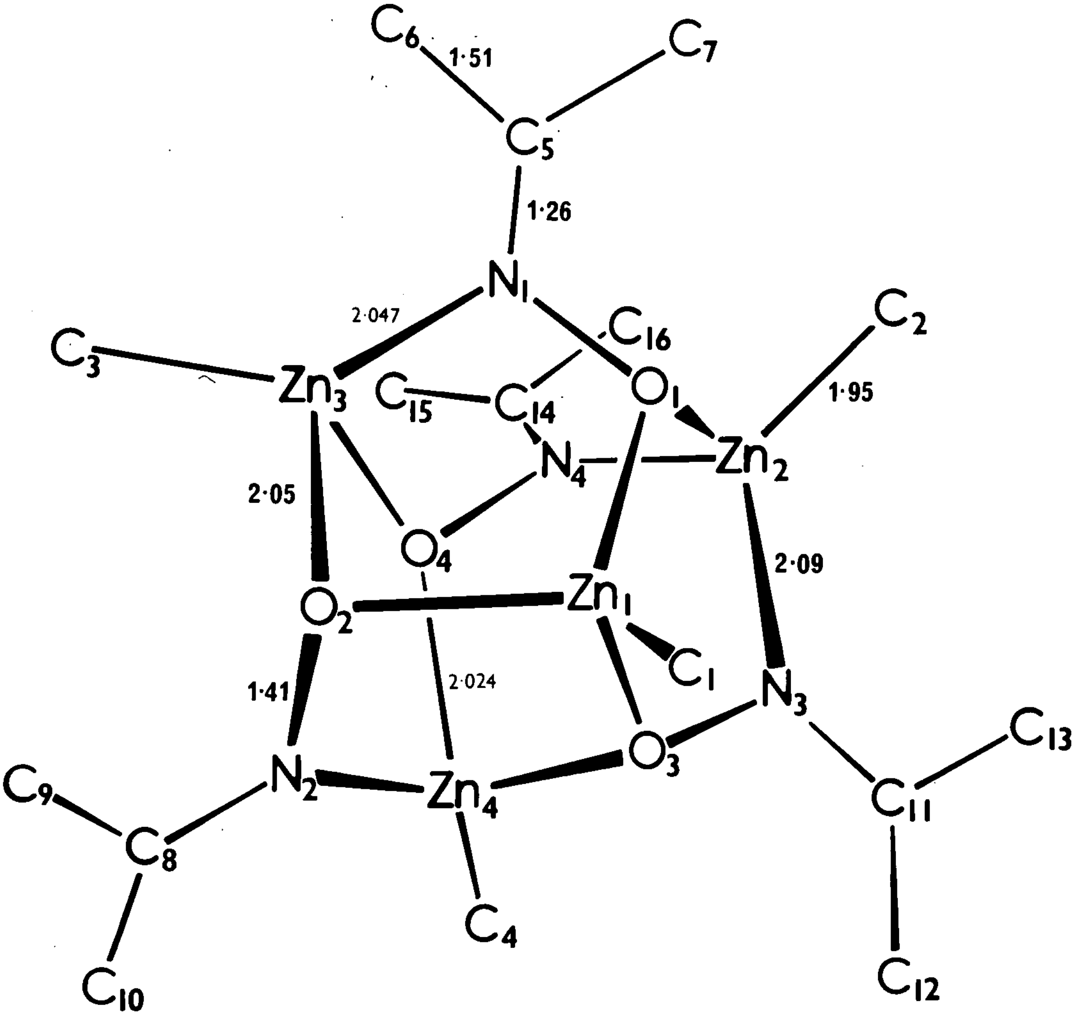


$(MeZnON{:}CMe_2)_4$

Mean Bond Lengths in Bold Type

Figure 5·2

(MeZnON:CMe$_2$)$_4$ TABLE 5.5

Bond Lengths (A) and their Standard Deviations (Å x 10^3)

Zn(1)-Zn(2)	3·411(2)
Zn(1)-Zn(3)	3·330(2)
Zn(2)-Zn(3)	3·885(1)
Zn(2)-Zn(4)	3·698(2)
Zn(3)-Zn(4)	3·416(2)
Zn(4)-Zn(1)	3·355(2)
Zn(1)-C(1)	1·948(15)
Zn(2)-C(2)	1·958(17)
Zn(3)-C(3)	1·953(15)
Zn(4)-C(4)	1·940(18)
Zn(1)-O(1)	2·050(8)
Zn(1)-O(2)	2·043(8)
Zn(1)-O(3)	2·053(8)
Zn(2)-O(1)	2·069(8)
Zn(3)-O(2)	2·066(9)
Zn(3)-O(4)	2·052(8)
Zn(4)-O(3)	2·053(8)
Zn(4)-O(4)	2·024(8)
Zn(2)-N(3)	2·089(10)
Zn(2)-N(4)	2·098(10)
Zn(3)-N(1)	2·047(10)
Zn(4)-N(2)	2·082(10)
O(1)-N(1)	1·430(13)
O(2)-N(2)	1·405(13)
O(3)-N(3)	1·389(12)
O(4)-N(4)	1·422(12)
N(1)-C(5)	1·285(16)
N(2)-C(8)	1·252(17)
N(3)-C(11)	1·257(16)
N(4)-C(14)	1·263(16)
C(5)-C(6)	1·504(22)
C(5)-C(7)	1·506(21)
C(8)-C(9)	1·581(24)
C(8)-C(10)	1·509(25)
C(11)-C(12)	1·498(21)
C(11)-C(13)	1·509(21)
C(14)-C(15)	1·512(20)
C(14)-C(16)	1·496(21)

$(MeZnON{:}CMe_2)_4$ TABLE 5.6

Bond Angles with their Standard Deviations

	Angle	e.s.d.
N(3)-Zn(2)-N(4)	101·0°	0·4
O(1)-Zn(1)-O(2)	96·1	0·3
O(1)-Zn(1)-O(3)	91·8	0·3
O(2)-Zn(1)-O(3)	93·9	0·3
O(2)-Zn(3)-O(4)	89·5	0·3
O(3)-Zn(4)-O(4)	97·9	0·3
O(1)-Zn(2)-N(3)	91·1	0·3
O(1)-Zn(2)-N(4)	95·7	0·3
O(2)-Zn(3)-N(1)	94·0	0·4
O(4)-Zn(3)-N(1)	94·3	0·4
O(3)-Zn(4)-N(2)	88·9	0·4
O(4)-Zn(4)-N(2)	87·6	0·4
Zn(1)-O(1)-N(1)	114·0	0·6
Zn(1)-O(1)-Zn(2)	111·8	0·4
Zn(2)-O(1)-N(1)	109·4	0·6
Zn(1)-O(2)-N(2)	111·1	0·6
Zn(1)-O(2)-Zn(3)	108·3	0·4
Zn(3)-O(2)-N(2)	106·1	0·6
Zn(1)-O(3)-N(3)	113·7	0·6
Zn(1)-O(3)-Zn(4)	109·6	0·3
Zn(4)-O(3)-N(3)	111·8	0·6
Zn(3)-O(4)-N(4)	115·0	0·6
Zn(3)-O(4)-Zn(4)	113·9	0·4
Zn(4)-O(4)-N(4)	117·3	0·6
O(1)-N(1)-C(5)	114·2	1·0
Zn(3)-N(1)-C(5)	133·1	0·9
Zn(3)-N(1)-O(1)	112·6	0·7
O(2)-N(2)-C(8)	116·2	1·0
Zn(4)-N(2)-C(8)	133·1	1·0
Zn(4)-N(2)-O(2)	110·5	0·6
O(3)-N(3)-C(11)	115·6	1·0
Zn(2)-N(3)-C(11)	133·0	0·9
Zn(2)-N(3)-O(3)	111·3	0·6
O(4)-N(4)-C(14)	114·3	0·9
Zn(2)-N(4)-C(14)	131·6	0·9
Zn(2)-N(4)-O(4)	112·7	0·6

$(MeZnON{:}CMe_2)_4$ TABLE 5.6 (continued)

	Angle	e.s.d.
C(1)-Zn(1)-O(1)	125·1°	0·5°
C(1)-Zn(1)-O(3)	119·8	0·6
C(1)-Zn(1)-O(2)	122·3	0·6
C(2)-Zn(2)-O(1)	115·6	0·6
C(2)-Zn(2)-N(4)	122·3	0·6
C(2)-Zn(2)-N(3)	123·9	0·6
C(3)-Zn(3)-O(2)	116·8	0·6
C(3)-Zn(3)-O(4)	119·7	0·5
C(3)-Zn(3)-N(1)	132·3	0·6
C(4)-Zn(4)-O(3)	120·5	0·6
C(4)-Zn(4)-O(4)	119·9	0·6
C(4)-Zn(4)-N(2)	132·8	0·7
C(6)-C(5)-C(7)	119·1	1·3
C(9)-C(8)-C(10)	120·0	1·4
C(12)-C(11)-C(13)	117·8	1·3
C(15)-C(14)-C(16)	117·9	1·3
C(6)-C(5)-N(1)	117·8	1·2
C(7)-C(5)-N(1)	123·0	1·2
C(9)-C(8)-N(2)	121·0	1·4
C(10)-C(8)-N(2)	118·9	1·4
C(12)-C(11)-N(3)	122·8	1·3
C(13)-C(11)-N(3)	119·4	1·2
C(15)-C(14)-N(4)	123·5	1·2
C(16)-C(14)-N(4)	118·6	1·2

The carbon and nitrogen atoms of the individual isopropylideneamine units "$Me_2C:N$" are strictly coplanar,the greatest value of χ^2 for one such unit being 1·8. The equations of the mean planes (referred to orthogonal axes parallel to a^*, b and c) are given below. The out-of-planes deviations indicate the extent to which the zinc and oxygen atoms are displaced.

Equation of Plane for atoms N(1),C(5),C(6),C(7):

$$-0{\cdot}3023x' + 0{\cdot}7936y - 0{\cdot}5280z' = 0{\cdot}0058$$

Deviations (Å): N(1) 0·001; C(5) -0·002; C(6) 0·001; C(7) 0·001;
Zn(3) 0·194; O(1) -0·089.

Equation of Plane for atoms N(2),C(8),C(9),C(10):

$$0{\cdot}6214x' - 0{\cdot}4879y - 0{\cdot}6131z' = -1{\cdot}5571$$

Deviations (Å): N(2) 0·006; C(8) -0·016; C(9) 0·005; C(10) 0·005;
Zn(4) 0·114; O(2) 0·034.

Equation of Plane for atoms N(3),C(11),C(12),C(13):

$$0{\cdot}0549x' + 0{\cdot}9967y + 0{\cdot}0590z' = 3{\cdot}3929$$

Deviations (Å): N(3) -0·001; C(11) 0·004; C(12) -0·001; C(13) -0·001;
Zn(2) -0·068; O(3) 0·024.

Equation of Plane for atoms N(4),C(14),C(15),C(16):

$$0{\cdot}5825x' + 0{\cdot}5925y - 0{\cdot}5565z' = 1{\cdot}3876$$

Deviations (Å): N(4) 0·003; C(14) -0·008; C(15) 0·003; C(16) 0·003;
Zn(2) 0·435; O(4) -0·059.

In addition to the end-on methyl-methyl repulsions which distort the Zn-N=C angles to 132·7°, various side-on repulsions, between zinc-methyl carbon atoms and the isopropylidene groups, (contacts marked by a double-obelus‡ in Table 5.7) may be seen to influence the deviations from the planes of the isopropylideneamine groups.

In particular the approximate twofold symmetry of the six-membered ring Zn(3),N(1),O(1),Zn(2),N(4),O(4) brings four of the isopropylidene methyl and two of the zinc methyl carbon atoms into close proximity. In addition to contacts† with the isopropylidene group with which they are roughly coplanar, C(2) makes a contact‡ of 3·88 Å across the ring with C(7) in the Me$_2$C: group attached to N(1), and similarly, C(3) makes a contact‡ of 3·96 Å across the ring with C(15). Twisting of the isopropylidene groups attached to N(1) and N(4) about their C=N axes, increases these short contacts and is evident in the deviations of the appropriate zinc and oxygen atoms from the planes in question.

TABLE 5.7

Intramolecular Contacts between Peripheral Carbon Atoms (Å)

	C(1)..... C(7)	5·29	‡	C(2)..... C(7)	3·88
	C(1)..... C(9)	5·03	†	C(2)..... C(13)	3·70
	C(1)..... C(12)	4·82	†	C(2)..... C(16)	3·59
†	C(3)..... C(6)	3·88	†	C(4)..... C(10)	3·90
	C(3)..... C(9)	4·20		C(4)..... C(12)	4·28
‡	C(3)..... C(15)	3·96		C(4)..... C(15)	4·98

As with methylzinc methoxide there is wide variation in the bond angles subtended at zinc by the methyl carbons and adjacent "cage" atoms. In addition to the distortion from 120° at nitrogen, this variation also, is consistent with a consideration of the intramolecular contacts between peripheral carbon atoms given in Table 5.7.

Zn(1) is bonded directly only to oxygen in the cage structure with the result that there are no short intramolecular contacts between C(1) and any of the isopropylidene carbon atoms. Zn(2) is bonded directly to two nitrogen atoms and so C(2) has three contacts of less than 4 Å with neighbouring isopropylidene groups. C(3) and C(4) have an environment which is intermediate between these two extremes.

Displacement of C(2) away from C(16) and C(13) is in such a direction as to make O(1)-Zn(2)-C(2) the smallest of the three angles at Zn(2).

Movement of C(3) to make N(1)-Zn(3)-C(3) the largest of the three angles at Zn(3) increases the short contact between C(3) and C(6) to a value of 3·88 A. The short contact C(3).....C(15) of 3·96 Å is also consistent with the observed order of:

$$N(1)\text{-}Zn(3)\text{-}C(3) > O(4)\text{-}Zn(3)\text{-}C(3) > O(2)\text{-}Zn(3)\text{-}C(3)$$

However, it is noted that C(3) also makes a contact of 3·60 Å with C(15) in the molecule at x,-y,-z. Movement of C(3) in a direction away from this atom would appear to favour O(4)-Zn(3)-C(3) as the largest angle at Zn(3).

The contact of 3·90 Å with C(10) is the only contact less than 4 Å involving C(4). Movement of C(4) away from C(10) is in a direction which increases N(2)-Zn(4)-C(4) to a value of 132·8°.

Because of the environment of Zn(1), C(1) is more "exposed" than the other three methyl carbon atoms attached to zinc, these being shielded to some extent by the isopropylidene groups bound to adjacent nitrogen atoms. It would be expected that the three O-Zn-C angles at Zn(1) will therefore be much more sensitive to distortion by <u>inter</u>molecular forces than were C(2), C(3) and C(4). The intermolecular contacts less than 4 Å are given in Table 5.8, only three of these being less than 3·8 Å.

A contact of 3·66 Å between C(1) and C(16) in the molecule at x, $\frac{1}{2}$+y, $\frac{1}{2}$-z is indeed in such a direction that displacement of C(1) away from this atom would make O(1)-Zn(1)-C(1) the largest angle at Zn(1). The shortest intermolecular contact involving C(2) is 3·86 Å. C(4) is involved in no intermolecular contacts less than 4 Å.

The packing in the crystal is shown in Figure 5.3 where the structure is projected along the <u>b</u> axis.

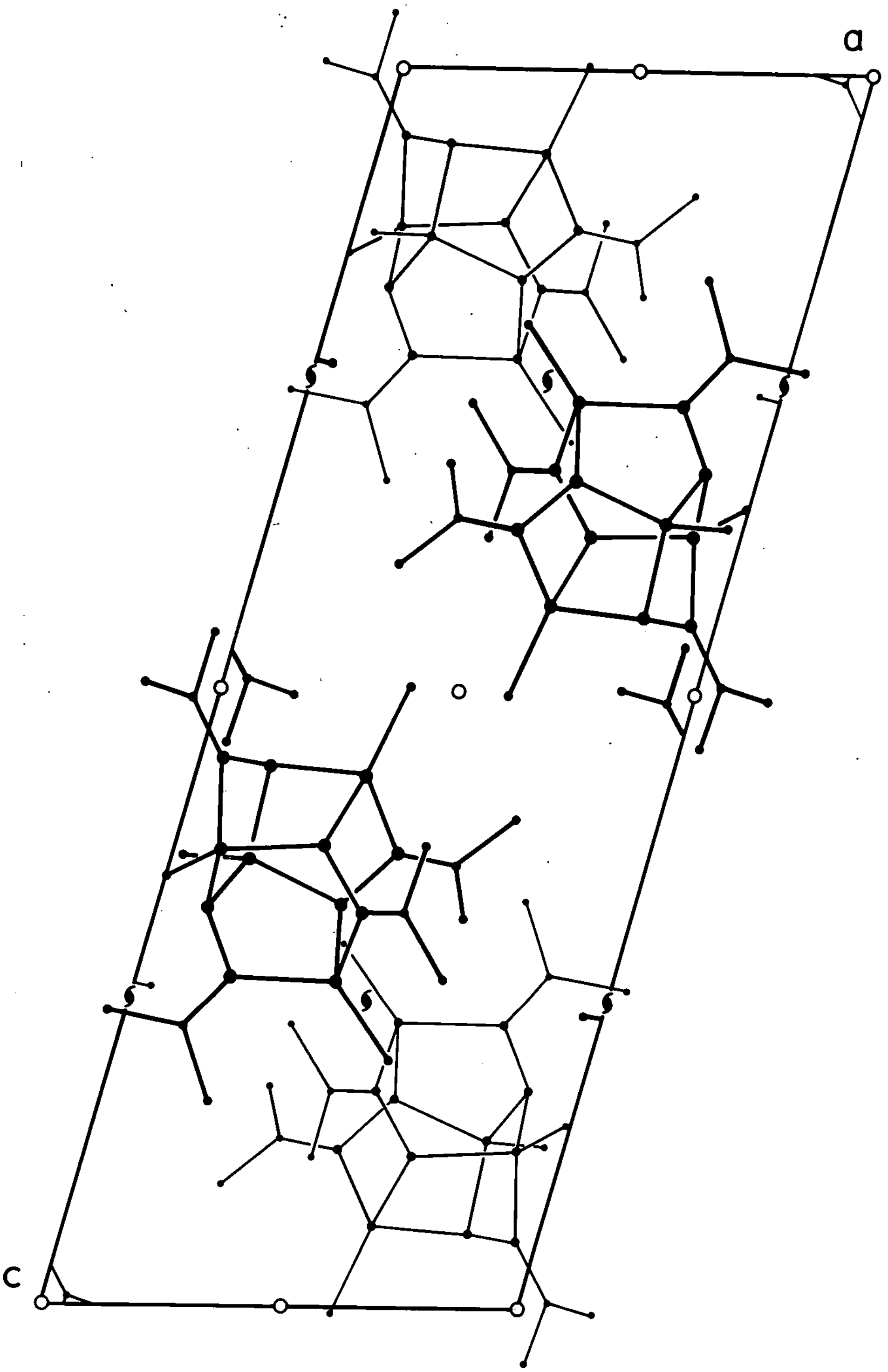
The temperature factors of the zinc, nitrogen and oxygen atoms are very similar and have B values of about 6 Å^2. The largest thermal parameters are found among the methyl carbon atoms in the isopropylidene groups where some of the vibrations are also markedly anisotropic.

$(MeZnON{:}CMe_2)_4$ TABLE 5.8

Intermolecular Contacts less than 4 Å

Equivalent Position Number 1: x, y, z;
Equivalent Position Number 2: -x, -y, -z;
Equivalent Position Number 3: -x, $\frac{1}{2}$+y, $\frac{1}{2}$-z;
Equivalent Position Number 4: x, $\frac{1}{2}$-y, $\frac{1}{2}$+z.

Atom A	Atom B	Equivalent Position	Cell	A-B Angstroms
Zn(1)	C(16)	3	(1, 0, 0)	3·93
O(1)	C(16)	3	(1, 0, 0)	3·54
O(3)	C(6)	1	(-1, 0, 0)	3·95
O(4)	C(10)	2	(0, 0, 0)	3·96
C(1)	C(16)	3	(1, 0, 0)	3·66
C(1)	C(6)	1	(-1, 0, 0)	3·94
C(2)	C(15)	3	(1, 0, 0)	3·86
C(2)	C(12)	1	(1, 0, 0)	3·87
C(3)	C(15)	2	(1, 0, 0)	3·60
C(7)	C(16)	3	(1, 0, 0)	3·97
C(7)	C(12)	1	(1, 0, 0)	3·99
C(10)	C(15)	2	(0, 0, 0)	3·94
C(10)	C(10)	2	(0, 0, 0)	3·97



$(MeZnON{:}CMe_2)_4$ *projection on the [010] plane*

Figure 5·3

5.8 The "Cage" Structure of Methylzinc Acetoximate

In methylzinc acetoximate both nitrogen and oxygen can take part in coordination to the metal and it is quite reasonable that this molecule departs from the cubane arrangement of the methoxide and so avoids the strain of four-membered rings. However, using molecular models with flexible bonds, it is possible to fit together alternative arrangements for $(MeZnON:CMe_2)_4$. All the isomeric structures which have been built up retain the feature of two six-membered rings, but arrangements in which each zinc has a similar environment, being bonded to two oxygens and one nitrogen, do seem feasible. Although the very careful model building, which would be required to obtain reasonable estimates of the inter-bond angle distortions and the peripheral contacts in these alternative structures, has not been possible, superficially then, isomeric forms do seem feasible. Why then does the molecule adopt this arrangement rather than a more symmetrical structure?

The significant features of the structure of methylzinc acetoximate also seem to exist in that of methylberyllium acetoximate. The p.m.r. spectrum of $(MeBeON:CMe_2)_4$ in benzene solution shows three beryllium-methyl resonances with intensities in the ratio 2:1:1 (Coates and Fishwick, 1968). These observations are, of course, consistent with $(MeBeON:CMe_2)_4$ having a structure similar to that found for the zinc analogue. It should be noted that the p.m.r. spectrum of $(MeZnON:CMe_2)_4$ itself, showed only a single, sharp zinc-methyl resonance. However, the work of Bruce and co-workers (1966) on the p.m.r. spectra of the methanolysis products of methyl- and phenylzinc, has shown that, in solution, exchange of alkyl groups attached to zinc is fast, and this may account for the absence of a zinc-methyl triplet in the spectrum of $(MeZnON:CMe_2)_4$.

A comment on the relative stabilities of the two cage structures of methylzinc methoxide and methylzinc acetoximate is given by the results of attempts to depolymerise them. Although $(MeZnON:CMe_2)_4$ may be recovered unchanged from solutions containing either pyridine, or the more basic 4-dimethylaminopyridine, with the latter, methylzinc methoxide forms a 1:1 adduct, $Me_2N.C_5H_4N.Zn(Me)OMe$, whose infrared spectrum differs markedly from the free tetramer.

I have measured the unit cell dimensions of two of the Group III acetoximate derivatives, the boron and the thallium compounds, and data is also available for dimethylgallium acetoximate (Raper and Shearer, 1967).

Compound:	$Me_2C:NOBMe_2$	$Me_2C:NOGaMe_2$	$Me_2C:NOTlMe_2$
System:	Monoclinic	Monoclinic	Monoclinic
Space-Group:	C2/c or Cc	C2/c or Cc	$P2_1/c$
$\underline{a}$(Å)	11·04	11·74	6·28
$\underline{b}$(Å)	8·84	9·01	12·57
$\underline{c}$(Å)	15·27	16·77	10·50
β	$104^{o}30'$	$111^{o}35'$	$104^{o}05'$
ρ gm.cm.$^{-2}$	1·04	1·38	2·54
Z	8	8	4

If the boron and gallium compounds crystallise with the space-group C2/c, then the observations are consistent with a dimeric structure $(Me_2C{:}NOMMe_2)_2$ (as formulated in § 5.1) having centres or 2-fold axes of symmetry. For the space-group Cc, the dimers would need no special symmetry. The observations on the thallium compound are consistent with dimeric molecules if these have, and utilise, centres of symmetry.

A three-dimensional analysis of dimethylgallium acetoximate (Raper and Shearer, 1967) has now established that the dimer crystallises with the centric space-group and utilises a 2-fold symmetry axis. This GaONGaON ring is very similar in shape to the ring Zn(3), N(1), O(1), Zn(2), N(4), O(4), in methylzinc acetoximate.

$(MeZnON{:}CMe_2)_4$ TABLE 5.9

Final Values of the Observed and
Calculated Structure Factors

h	k	l	|Fo|	Fc
0	2	0	292	-327
0	4	0	60	34
0	6	0	24	28
0	8	0	58	-56
0	10	0	75	79
0	2	1	97	-94
0	3	1	51	-22
0	4	1	50	42
0	5	1	29	-20
0	6	1	104	-94
0	7	1	68	-73
0	8	1	158	165
0	9	1	59	56
0	10	1	41	-41
0	11	1	27	32
0	12	1	21	-23
0	13	1	34	-28
0	0	2	73	-136
0	1	2	356	-391
0	2	2	88	26
0	3	2	61	-69
0	4	2	74	-76
0	5	2	90	76
0	6	2	20	22
0	7	2	7	-7
0	9	2	50	52
0	10	2	13	-15
0	11	2	12	-13
0	12	2	8	9
0	13	2	15	-16
0	1	3	55	-5
0	2	3	9	20
0	3	3	206	-188
0	4	3	122	-99
0	5	3	112	110
0	6	3	80	75
0	7	3	57	50
0	8	3	37	36
0	9	3	82	-83
0	10	3	31	31
0	11	3	8	-3
0	12	3	40	-39
0	13	3	9	8
0	0	4	113	-148
0	1	4	23	-30
0	2	4	94	-126
0	3	4	124	98
0	4	4	163	166
0	6	4	28	-23
0	7	4	31	-31
0	8	4	22	-18
0	9	4	26	26
0	10	4	9	12
0	11	4	19	-20
0	12	4	31	-31
0	13	4	9	10
0	1	5	20	14
0	2	5	158	-138
0	3	5	50	-32
0	4	5	226	258
0	5	5	67	69
0	6	5	167	-157
0	7	5	36	32
0	8	5	42	-41
0	9	5	21	-21
0	10	5	8	2
0	11	5	26	-26
0	12	5	10	9
0	13	5	15	20
0	0	6	50	-5
0	1	6	67	51
0	2	6	147	142
0	3	6	147	141
0	4	6	105	-113
0	5	6	86	-89
0	6	6	11	9
0	7	6	51	-52
0	8	6	32	32
0	9	6	25	27
0	10	6	42	-43
0	11	6	33	-31
0	12	6	41	36
0	13	6	22	24
0	1	7	9	-3
0	2	7	14	31
0	3	7	130	151
0	5	7	224	-196
0	6	7	6	-2
0	8	7	64	-63
0	9	7	36	35
0	10	7	11	9
0	12	7	10	10
0	0	8	160	147
0	1	8	32	11
0	2	8	66	53
0	3	8	54	-70
0	4	8	109	-118
0	5	8	46	41
0	6	8	17	14
0	8	8	30	30
0	9	8	20	-17
0	11	8	20	27
0	12	8	11	11
0	13	8	12	-15
0	1	9	51	40
0	2	9	7	17
0	3	9	16	-10
0	4	9	83	-72
0	5	9	43	-41
0	6	9	13	20
0	7	9	14	-15
0	8	9	91	89
0	9	9	26	26
0	12	9	14	-14
0	0	10	172	-161
0	1	10	49	-57
0	2	10	87	88
0	3	10	59	-71
0	4	10	29	-32
0	5	10	56	52
0	6	10	24	-28
0	7	10	32	33
0	8	10	22	21
0	10	10	11	-13
0	1	11	15	-18
0	2	11	34	35
0	3	11	20	-18
0	4	11	105	-99
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0	6	11	80	81
0	7	11	70	71
0	8	11	10	-11
0	9	11	57	-54
0	11	11	15	-18
0	13	11	20	19
0	0	12	44	-40
0	1	12	160	160
0	2	12	48	-43
0	3	12	68	-70
0	4	12	78	70
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0	7	12	32	31
0	8	12	29	-33
0	9	12	27	-26
0	10	12	9	11
0	11	12	9	13
0	1	13	19	15
0	3	13	52	-56
0	4	13	29	30
0	5	13	91	92
0	6	13	8	-10
0	7	13	39	-38
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0	0	14	87	85
0	1	14	39	38
0	2	14	42	-38
0	3	14	72	73
0	4	14	29	-29
0	5	14	41	-39
0	6	14	36	35
0	7	14	21	-21
0	8	14	14	-14
0	13	14	10	13
0	1	15	20	14
0	2	15	32	35
0	3	15	8	3
0	4	15	7	7
0	5	15	39	-39
0	7	15	25	-23
0	11	15	29	26
0	13	15	21	-20
0	0	16	135	143
0	2	16	29	-30
0	3	16	35	-35
0	4	16	34	-34
0	5	16	38	41
0	10	16	17	19
0	11	16	13	14
0	1	17	54	54
0	3	17	58	-58
0	4	17	20	-20
0	5	17	35	37
0	7	17	27	-29
0	8	17	41	38
0	9	17	16	18
0	12	17	22	-19
0	1	18	117	-122
0	2	18	25	-25
0	3	18	14	17
0	4	18	35	36
0	9	18	26	25
0	10	18	12	13
0	11	18	23	-21
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0	7	19	43	39
0	8	19	17	16
0	9	19	39	-32
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0	3	20	16	18
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0	3	23	38	30
0	5	23	47	-43
0	6	23	15	-15
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0	2	24	28	25
0	3	24	18	-18
0	4	24	26	-24
0	3	25	13	-12
0	4	25	43	-35
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0	3	26	12	-12
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1	5	-14	13	15
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1	9	-14	14	12
1	11	-14	9	-11
1	1	-13	34	-29
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1	8	-13	31	30
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1	2	-12	102	91
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1	6	-11	53	52
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1	11	-11	12	-16
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1	0	-10	28	25
1	1	-10	147	130
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1	3	-10	104	92
1	4	-10	61	-59
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1	13	-10	13	17
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1	3	-9	63	62
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1	5	-9	127	-111
1	7	-9	36	-35
1	8	-9	19	-21
1	9	-9	42	43
1	11	-9	15	17
1	12	-9	17	15
1	13	-9	10	-14
1	0	-8	121	111
1	1	-8	62	58
1	2	-8	100	80
1	3	-8	130	-133
1	4	-8	120	-118
1	5	-8	37	35
1	6	-8	21	13
1	7	-8	39	39
1	8	-8	12	7
1	9	-8	43	-40
1	11	-8	22	24
1	12	-8	18	23
1	13	-8	13	-16
1	1	-7	47	51
1	2	-7	86	77
1	3	-7	44	-42
1	4	-7	232	-221
1	5	-7	51	47
1	6	-7	110	104
1	7	-7	60	-52
1	8	-7	30	27
1	9	-7	37	37
1	10	-7	10	-13
1	12	-7	12	-15
1	0	-6	43	41
1	1	-6	67	-54
1	2	-6	165	-163
1	3	-6	111	-122
1	4	-6	184	160
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1	8	-6	44	-47
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1	12	-6	43	-37
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1	3	-5	126	-128
1	4	-5	63	65
1	5	-5	167	166
1	6	-5	56	-46
1	8	-5	68	57
1	9	-5	49	-55
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1	11	-5	12	-13
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1	0	-4	92	-64
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1	2	-4	71	-52
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1	4	-4	81	75
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1	6	-4	12	7
1	8	-4	40	-40
1	11	-4	13	-14
1	12	-4	10	-13
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1	1	-3	75	43
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1	6	-3	17	-17
1	8	-3	115	-113
1	9	-3	19	-15
1	10	-3	24	22
1	11	-3	17	19
1	12	-3	19	21
1	13	-3	12	-17
1	2	-2	145	-119
1	3	-2	72	70
1	4	-2	27	-24
1	5	-2	21	-14
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1	4	-1	60	46
1	5	-1	74	-54
1	6	-1	98	-84
1	7	-1	140	-112
1	8	-1	43	43
1	9	-1	73	76
1	10	-1	15	-15
1	11	-1	28	29
1	12	-1	14	-16
1	13	-1	16	-19
1	2	0	16	49
1	3	0	57	55
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1	6	0	37	-36
1	7	0	27	-24
1	8	0	71	59
1	9	0	44	41
1	10	0	29	-29
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1	12	0	23	27
1	1	1	8	-43
1	2	1	57	-55
1	3	1	96	64
1	4	1	21	-34
1	5	1	69	-65
1	6	1	27	19
1	7	1	109	100
1	8	1	93	84
1	9	1	55	-46
1	10	1	8	11
1	12	1	34	-32
1	0	2	224	-150
1	1	2	47	55
1	2	2	58	56
1	3	2	125	-100
1	4	2	95	91
1	5	2	12	23
1	6	2	20	-19
1	7	2	45	41
1	9	2	36	-35
1	11	2	16	19
1	12	2	9	-7
1	13	2	16	-17
1	1	3	15	-26
1	3	3	57	21
1	4	3	110	83
1	5	3	56	49
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1	7	3	49	43
1	8	3	42	-39
1	9	3	43	-42
1	11	3	38	-39
1	13	3	18	23
1	0	4	216	-142
1	1	4	76	67
1	2	4	45	8
1	3	4	52	81
1	4	4	11	10
1	5	4	72	-55
1	7	4	30	-26
1	10	4	30	-33
1	11	4	11	-14
1	13	4	12	15
1	1	5	14	-31
1	2	5	128	95
1	3	5	149	116

h	k	l	|Fo|	Fc
1	4	5	20	-39
1	5	5	100	-100
1	6	5	69	56
1	7	5	22	18
1	8	5	119	-109
1	12	5	34	37
1	0	6	106	116
1	1	6	154	154
1	2	6	48	41
1	3	6	23	4
1	4	6	95	-85
1	5	6	28	38
1	6	6	23	25
1	7	6	12	-8
1	9	6	42	-43
1	11	6	44	43
1	1	7	69	60
1	2	7	105	75
1	3	7	83	-86
1	4	7	46	-59
1	5	7	56	43
1	6	7	37	33
1	7	7	113	-104
1	8	7	11	12
1	9	7	76	73
1	11	7	15	18
1	13	7	16	-18
1	0	8	69	71
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1	6	8	25	-18
1	7	8	13	17
1	8	8	17	-14
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1	1	9	28	20
1	2	9	33	-37
1	3	9	29	-32
1	4	9	25	-36
1	6	9	16	14
1	7	9	38	28
1	8	9	51	49
1	9	9	27	-29
1	10	9	9	-6
1	12	9	15	-16
1	0	10	82	-81
1	1	10	84	90
1	2	10	47	-39
1	3	10	149	-132
1	4	10	76	76
1	5	10	18	28
1	6	10	10	20
1	8	10	45	-40
1	9	10	9	-11
1	10	10	21	22
1	12	10	19	-20
1	13	10	13	-16
1	2	11	46	-47
1	3	11	94	-88
1	4	11	47	42
1	5	11	155	146
1	6	11	10	-16
1	7	11	35	-42
1	8	11	21	-24
1	11	11	17	-20
1	0	12	34	32
1	1	12	55	-49
1	2	12	68	-68
1	3	12	151	149
1	4	12	39	42
1	5	12	47	-42
1	6	12	9	15
1	7	12	38	-36
1	8	12	27	-22
1	9	12	32	29
1	11	12	29	-27
1	12	12	10	-7
1	13	12	26	23
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8	1	14	7	7
8	3	14	5	-4
8	5	14	3	5
8	2	15	9	9
8	3	15	4	-5
8	4	15	3	-4
8	0	16	5	5

APPENDICES

APPENDIX I

Computer Programmes

The extensive calculations were carried out using the Elliott 803B computer in Durham and the English Electric KDF9 computer at the University of Newcastle. Thanks are expressed to the staff of the computer units here in Durham and also at Newcastle, for their help in running programmes.

I am indebted to Professor D.J.W. Cruickshank, Dr. J. Sime and their associates, for making available the set of programmes devised by the Glasgow group. All the structure-factor-least-squares calculations were carried out using initially the Mark I and latterly the Mark II (November, 1965) version of the Glasgow S.F.L.S. programme, which has already been mentioned briefly § 1.13. A Fourier programme written by Dr. Sime was available and also programmes for carrying out a Fourier search, and calculations of molecular parameters.

Thanks are also expressed to Mr. (now Dr.) George Adamson for making available his data correction programme (1966). This programme corrects intensity data collected by the equi-inclination Weissenberg technique for anisotropic absorption, Lorentz and polarisation factors, and also, in the case of upper nets, for spot length. The method used for evaluating the absorption correction is essentially that of Busing and Levy (1957).

Other programmes:

I have written a programme in Algol for making rapid calculations (in Durham on the 803B computer) of pre-selected bond lengths and angles at the end of each cycle of least-squares refinement. The programme includes a machine orders input routine which will accept a parameters tape punched in either Elliott 8-hole telecode, or the new parameters tape which is output at the end of each least-squares cycle and which is, of course, punched in KDF9 8-hole telecode. The programme works for all space-groups.

Other short programmes have been written for particular needs. Various machine orders subroutines for rapid condensation (on the Elliott 803B) of the rather large amounts of paper tape output produced by the S.F.L.S. programme, prior to the computation of Fourier syntheses, have been found especially useful.

APPENDIX II

Statistical Treatment of Apparent Centring

We require a function which allows us to assess the statistical significance of an approximate molecular centre of symmetry.

The structure contains 2n atoms and the approximate molecular centre relates the atoms in pairs p_1, p_2,....,p_n. Consider the pair p_1, and let the coordinates of the two atoms be x_1, y_1, z_1 and x_2, y_2, z_2 with associated variances $\sigma_1^2$and σ_2^2 The problem is simplified by considering the centre of gravity of the structure separately along each of the axial directions. Consider the x-direction.

The experimental mean, μ_1, of the pair, p_2, is given by $\frac{1}{2}(x_1 + x_2)$ and this is associated with a variance of $\frac{1}{4}(\sigma_1^2 + \sigma_2^2)$. We wish to test whether $\mu_1 = \mu_2 = \ldots\ldots = \mu$ and to establish the "best" value of μ, $\hat{\mu}$. The best fitting value of μ is obtained by choosing it to minimise the weighted sum of squares of deviations, i.e.

$$\sum \frac{\{\frac{1}{2}(x_1 + x_2) - \mu\}^2}{\frac{1}{4}(\sigma_1^2 + \sigma_2^2)}$$

$$= \qquad \sum\left(\frac{x_1 + x_2}{\sqrt{(\sigma_1^2 + \sigma_2^2)}} - \frac{2\mu}{\sqrt{(\sigma_1^2 + \sigma_2^2)}}\right)^2$$

Differentiating with respect to μ, and equating to zero:

$$\sum \frac{1}{\sqrt{(\sigma_1^2 + \sigma_2^2)}}\left(\frac{x_1 + x_2}{\sqrt{(\sigma_1^2 + \sigma_2^2)}} - \frac{2\mu}{\sqrt{(\sigma_1^2 + \sigma_2^2)}}\right) = 0$$

and the weighted or 'best' mean, $\hat{\mu}$, is

$$\hat{\mu} = \frac{\sum \frac{x_1 + x_2}{\sigma_1^2 + \sigma_2^2}}{2\sum \frac{1}{\sigma_1^2 + \sigma_2^2}}$$

Then, by standard error theory, if $\mu_1 = \mu_2 = \ldots\ldots = \mu$, the function

$$\sum\left(\frac{x_1 + x_2}{\sqrt{(\sigma_1^2 + \sigma_2^2)}} - \frac{2\hat{\mu}}{\sqrt{(\sigma_1^2 + \sigma_2^2)}}\right)^2$$

distributes as χ^2 with (n-1) degrees of freedom. Expanding the numerator this becomes:

$$= \sum\frac{(x_1 + x_2 - 2\hat{\mu})^2}{\sigma_1^2 + \sigma_2^2}$$

$$= \sum\frac{(x_1 + x_2)^2}{\sigma_1^2 + \sigma_2^2} - 4\sum\frac{(x_1 + x_2)\hat{\mu}}{\sigma_1^2 + \sigma_2^2} + 4\hat{\mu}^2\sum\frac{1}{\sigma_1^2 + \sigma_2^2}$$

and since $\displaystyle\sum\frac{x_1 + x_2}{\sigma_1^2 + \sigma_2^2} = 2\hat{\mu}\sum\frac{1}{\sigma_1^2 + \sigma_2^2}$

from the expression defining $\hat{\mu}$:

$$= \sum\frac{(x_1 + x_2)^2}{\sigma_1^2 + \sigma_2^2} - 4\hat{\mu}^2\sum\frac{1}{\sigma_1^2 + \sigma_2^2}$$

$$= \sum\frac{(x_1 + x_2)^2}{\sigma_1^2 + \sigma_2^2} - \frac{\left(\sum\frac{x_1 + x_2}{\sigma_1^2 + \sigma_2^2}\right)^2}{\sum\frac{1}{\sigma_1^2 + \sigma_2^2}}$$

The summation may be carried out independently along the three axial directions, using the appropriate variances associated with x, y and z to give an estimate of the centring in these directions. The sum of the three summations:

$$\sum_{x,y,z} \left(\sum \frac{(x_1 + x_2)^2}{\sigma_1{}^2 + \sigma_2{}^2} - \frac{\left(\sum \frac{x_1 + x_2}{\sigma_1{}^2 + \sigma_2{}^2} \right)^2}{\sum \frac{1}{\sigma_1{}^2 + \sigma_2{}^2}} \right)$$

gives an overall estimate of the centring and has 3(n-1) degress of freedom.

REFERENCES

Adamson, G.W. and Shearer, H.M.M., (1966), "G.W. Adamson - Ph.D. Thesis", see also, Acta Cryst. (1966), Supplement, 7th (Moscow) Congress, Abstract 9.2.

Adamson, G.W. and Shearer, H.M.M., (1967), personal communication.

Allen, G., Bruce, J.M., Farren, D.W. and Hutchinson, F.G., J. Chem. Soc., (1965), 5476;

idem, J. Chem. Soc.(B), (1966), 799;

idem, J. Chem. Soc.(B), (1966), 1020.

Beachley, O.T. and Coates, G.E., (1965), J. Chem. Soc., 3241.

Boersma, J. and Noltes, J.G., (1966), Tetrahedron Letters, 1521.

Bradley, D.C., (1958), Nature, 182, 1211.

Bradley, D.C., (1962), Progress in Stereochemistry, 3, 1.

Bryce-Smith, D. and Graham, I.F., (1966), Chem. Comm., 559.

Burg, A.B. and Wagner, R.I., (1953), J. Amer. Chem. Soc., 75, 3872.

Busing, W.R. and Levy, H.A., (1957), Acta Cryst., 10, 180.

Butlerow, A., (1864), Jahresber., 467.

Cavalca, L., Nardelli, M. and Branchi, G., (1960), Acta Cryst., 13, 688.

Coates, G.E. and Fishwick, A.H., (1967), J. Chem. Soc.(A), 1199.

idem, J. Chem. Soc.(A), paper 7/938.

Coates, G.E. and Fishwick, A.H., (1968), J. Chem. Soc.(A), in press.

Coates, G.E. and Heslop, J.A., (1966), J. Chem. Soc.(A), 26.

Coates, G.E. and Lauder, A., (1966), J. Chem. Soc.(A), 264.

Coates, G.E. and Ridley, D., (1965), J. Chem. Soc., 1870.

Coates, G.E. and Ridley, D., (1966), J. Chem. Soc.(A), 1064; idem, (1966), Chem. Comm., 560.

Coates, G.E. and Ridley, D., (1967), J. Chem. Soc.(A), 56.

Coates, G.E. and Tranah, M., (1967), J. Chem. Soc.(A), 236.

Cruickshank, D.J.W., Pilling, D.E., Bujosa, A., Lovell, F.M. and Truter, M.R., (1961), "Computing Methods and the Phase Problem in X-ray Crystal Analysis", p.32. Oxford, Pergamon.

Dahl, L.F., Davis, G.L., Wampler, D.L. and West, R., (1962), J. Inorg. and Nucl. Chem., 24, 357.

Frankland, E., (1853), Annalen, 85, 347.

Giordano, F., Randaccio, L. and Ripamonti, A., (1967), Chem. Comm., 19.

Hamilton, W.C., (1961), Acta Cryst., 14, 95.

Hodgson, R.I. and Rollett, J.S., (1963), Acta Cryst., 16, 329.

Hoffmann, E.G., (1960), Annalen, 629, 104.

Ibers, J.A., (1963), Nature, 197, 686.

Interatomic Distances, (1958), Chemical Society Special Publication No.11.

Interatomic Distances Supplement, (1965), Chemical Society Special Publication No.18.

Jennings, J.R. and Wade, K., (1967), J. Chem. Soc.(A), 1333.

Koyama, H. and Saito, Y., (1954), Bull. Chem. Soc. Japan, 27, 112.

Levine, I.N., (1963), J. Chem. Phys., 38, 2326.

Lingafelter, E.C., (1966), Acta Cryst., 20, 321.

Lundberg, B.K.S., (1966), Acta Cryst., 21, 901.

MacDonald, T.R.R. and MacDonald, W.S., (1963), Proc. Chem. Soc., 382.

Malone, J.F. and MacDonald, W.S., (1967), Chem. Comm., 444.

Mani, N.V., Ahmed, F.R. and Barnes, W.H., (1965), Acta Cryst., 19, 693,
idem, (1966), Acta Cryst., 21, 375.

Matsui, Y., Kamiya, K., Nishikawa, M. and Tomiie, Y., (1966), Bull. Chem. Soc. Japan, 39, 1828.

Merritt, L., Cady, R.T. and Mundy, B.W., (1954), Acta Cryst., 7, 473.

Moseley, P.T. and Shearer, H.M.M., (1966), Chem. Comm., 876.

Moseley, P.T. and Shearer, H.M.M., (1967), personal communication.

Nardelli, M., Fava, G. and Giraldi, G., (1963), Acta Cryst., 16, 343.

Noltes, J.G. and Boersma, J., (1967), J. Organomet. Chem., 7, P.6

Pauling, L., (1960), "The Nature of the Chemical Bond", 3rd Edition, Cornwell University Press.

Pattison, I. and Wade, K., (1967), J. Chem. Soc.(A), paper 7/469.

Philips, D.C., (1956), Acta Cryst., 12, 610.

Raper, E.S. and Shearer, H.M.M., (1967), personal communication.

Rundle, R.E. (1963), "A Survey of Progress in Chemistry", Ed. A.I. Scott, Academic Press, pp.96-98.

Rundle, R.E., Olson, D.H., Stucky, G.D. and Engebretson, G.R., (1963), Acta Cryst., (1963), Supplement, 6th (Rome) Congress, Abstract 6.20.

Rundle, R.E. and Sturdivant, J.H., (1947), J. Amer. Chem. Soc., 69, 1561.

Schindler, F., Schmidbaur, H. and Kruger, U., (1965), Angew. Chem. Internat. Edn., 4, 876.

Shearer, H.M.M. and Spencer, C.B., (1966), Chem. Comm., 194.

Stone, F.G.A., (1958), Chem. Rev., 58, 101.

Venkateswarlu, P. and Gordy, W., (1955), J. Chem. Phys., 23, 1200.

Watenpaugh, K. and Caughlan, (1967), Chem. Comm., 76.

Wheatley, P.J., (1960), J. Chem. Soc., 4270.

Witters, R.W. and Caughlan, (1965), Nature, 205, 1312.

Woolfson, M.M., (1956), Acta Cryst., 9, 804.

Wright, D.A. and Williams, D.A., (1966), Acta Cryst., Supplement, 7th (Moscow) Congress, Abstract 9.69.