The crystal structures of some methyleneamino and cyclopentadienyl complexes of main group metals

Whitehead, R. G.
The Crystal Structures of Some Methyleneamino And Cyclopentadienyl Complexes of Main Group Metals

by

R. G. Whitehead M. Sc.


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Memorandum

This thesis describes research in chemical crystallography carried out in the Chemistry Department of the University of Durham between 1974 and 1978. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

Part of the work described in this thesis has been the subject of the following publications:

1. The Diphenylmethyleneaminomagnesium Bromide Tetrahydrofuran Adduct:

\[ \text{Mg}_2\text{Br}_2(\text{THF})_2(\mu-\text{N: CPh}_2)_2(\mu-\text{THF}) \]

X-ray Crystal Structure.


2. Crystal Structure of The Cyclopentadienyl Sodium Tetramethylethlenediamine Adduct:

\[ \text{Na}(\text{C}_5\text{H}_5)(\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2) \]


3. New Route To Aryltin (iv) Halides By Spontaneous Cyclometallation of Benzylideneaminotin (iv) Halides; X-ray Crystal Structure of The ortho - Metallated Ketimine:

\[ \text{o-SnCl}_3-p-\text{Me}_6\text{H}_3\text{C}(:\text{NH})p-\text{C}_6\text{H}_4\text{Me} \]

B. Fitzsimmons, D. Othen, H. M. M. Shearer, K. Wade and G. Whitehead.


4. The Crystal And Molecular Structure of Cyclopentadienylzinc methyl:

\[ \text{Zn}(\text{C}_5\text{H}_5)\text{Me} \]


5. Adducts of Cyclopentadienylsodium And Methylcyclopentadienylsodium With Oxygen Bases And Nitrogen Bases; Structure of Cyclopentadienylsodium-tetramethylethlenediamine:

\[ \text{Na}(\text{C}_5\text{H}_5)(\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2) \]

Summary

X-ray diffraction techniques have been employed to determine the crystal structures of six main group metal complexes containing methyleneamino and cyclopentadienyl ligands. The structures were solved through the use of the heavy atom and symbolic addition techniques, and refined by the method of least-squares using diffractometer data.

(Ph₂C:NMgBr)₂·3THF crystallises in a monoclinic cell with space group C2/c. The molecule is dimeric and contains two MgBr(THF) units bridged not only by two diphenylmethylenamino groups, but also by one tetrahydrofuran molecule, the latter being situated on the molecular (and crystallographic) 2-fold axis, symmetrically linking both metal atoms by unusually long bonds, 2.45 Å.

o-SnCl₃·p-MeC₆H₃C(:NH)p-C₆H₄Me crystallises in a monoclinic cell with space group P2₁/c. The crystal structure consists of chains of discrete molecular units linked through N-H...Cl hydrogen bonding. The intramolecular co-ordination which gives rise to orthometallation, results in an almost planar 5-membered tin metallocycle, inclined at 6.5° to the mean plane of the adjacent phenyl ring with which it shares a common edge.

(Ph₂C:NH₂⁺)₂SnCl₆²⁻ crystallises in a monoclinic cell with space group P2₁/c. The crystal structure is ionic, consisting of diphenylmethylenammonium cations and hexachlorostannate anions. Strong N-H...Cl hydrogen bonding between the ions produces a slight distortion of the anion geometry resulting in variation of the tin-chlorine distances.

(Bu′₂C:NLi)₆ crystallises in a monoclinic cell with space group P2₁/c. The molecule is hexameric and contains a 6-membered ring of lithium atoms in the chair configuration. Because of disorder in the position of one of the lithium atoms, two alternate orientations exist for the lithium ring. The periphery of the molecule is made up of the six di-t-butylmethylenamino groups which bridge across six of the triangular faces formed by the lithium core. The bonding in this region of the molecule can therefore be described as electron deficient.
$\text{Na(C}_5\text{H}_5)(\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMMe}_2)$ crystallises in an orthorhombic cell with space group $\text{Pcca}$. The structure consists of puckered chains of sodium atoms, each with a chelating TMED molecule attached, and linked by pentahapto cyclopentadienyl rings.

$\text{Zn(C}_5\text{H}_5)\text{CH}_3$ crystallises in an orthorhombic cell with space group $\text{Cmcm}$. In the crystal, cyclopentadienylnzinc methyl adopts a puckered $-\text{Zn(C}_5\text{H}_5)\text{Zn(C}_5\text{H}_5)\text{Zn(C}_5\text{H}_5}-$ chain structure in which the bridging cyclopentadienyl groups co-ordinate di- or trihapto to the bridged zinc atoms, apparently functioning as 5-electron ligands.
CHAPTER ONE

STRUCTURE DETERMINATION - THEORETICAL ASPECTS
Crystal Structure Determination - Theoretical Aspects

The crystalline state may be defined as a state of matter possessing a high degree of internal three-dimensional order. A crystal can then be regarded as a three-dimensional repetition of a basic unit of pattern, the pattern consisting of ions, atoms or molecules.

If the unit of pattern be represented by a single point, then the repetition in the crystal can be represented by a three-dimensional network of points known as the crystal lattice. This point network can be imagined to extend indefinitely in all directions in space and each point has exactly the same environment as every other point. The distance between the points in any direction is equal to the repeat distance for the unit of pattern in the same direction within the crystal.

A particular lattice can be specified by drawing from one of the lattice points as origin, non coplanar vectors to three neighbouring points. The lattice is then specified by the lengths $a$, $b$ and $c$ of these vectors and by the angles $\alpha$, $\beta$, and $\gamma$ between the vectors. The parallelepiped defined by the vectors is called the unit cell, and repetition of this cell by repeated translations comprises the lattice. When a lattice point occurs only at the corners of the unit cell, then the cell is defined as primitive. In general there are elements of symmetry associated with the unit cell, and these elements including those of translational symmetry, in conjunction with the Bravais lattice type, define the space group of the crystal.

The faces and planes within a crystal may be indexed according to their relationship with the vectors $a$, $b$ and $c$. A series of parallel planes which divide the vector $a$ into $h$ parts, $b$ into $k$ parts and $c$ into $l$ parts, is given the indices $hkl$ and these are known as Miller indices. Crystal faces normally contain a high concentration of lattice points and consequently have small values of $h$, $k$ and $l$.

Diffraction of X-rays

X-rays are electromagnetic waves, and as such are accompanied by a periodically changing electric field as they proceed outward from their source. An electron in the path of such a wave is excited to periodic oscillation by the changing field and itself becomes a source of electromagnetic radiation of the same frequency and wavelength. There arises from this interaction, a new spherical wavefront of X-rays, with the electron as its origin, deriving its energy from the impinging beam. By this process the electron is said to scatter the original beam.
For an atom in an X-ray beam, each of the orbital electrons will scatter the incident beam in this manner. Since the effective cross-sectional area of an atom is comparable in magnitude to the wavelength of the X-rays, waves scattered in a particular direction undergo both constructive and destructive interference and thus give rise to diffraction effects. Although the phenomenon of diffraction results from a coherent scattering process, a diffracted beam is produced by such scattering only when certain geometrical conditions are satisfied. These conditions were derived mathematically by Max von Laue who in conjunction with W. Friedrich and P. Knipping, recorded the first observation of X-ray diffraction by crystals in 1912.

Von Laue interpreted the results in terms of diffraction from a three-dimensional array of scattering centres according to the relationships

\[
\begin{align*}
 a (\cos \alpha - \cos \alpha_0) &= h\lambda \\
 b (\cos \beta - \cos \beta_0) &= k\lambda \\
 c (\cos \gamma - \cos \gamma_0) &= l\lambda
\end{align*}
\]

where each expression represents the conditions necessary for diffraction to occur from a line of scattering centres parallel to the axial direction. \(\alpha_0, \beta_0, \) and \(\gamma_0\) represent the angles of the incident radiation to the directions \(a, b,\) and \(c,\) whereas \(\alpha, \beta,\) and \(\gamma\) represent the angles of diffraction.

The geometrical conditions necessary for the occurrence of diffraction maxima, as indicated by the Laue conditions, are difficult to visualise physically. W.L. Bragg interpreted the diffraction patterns as being the result of the reflection of X-rays from planes within the crystal, and showed that for a set of planes with spacing \(d(hk l),\) the necessary condition for diffraction is

\[
 n\lambda = 2d(hk l) \sin \theta
\]

where \(\theta\) is the angle of the incident and diffracted radiation to the planes. This approach is easier to understand but describes diffraction effects in terms of reflections.

The Laue and Bragg approach to diffraction geometry involves the use of the direct crystal lattice, resulting in problems in the subsequent interpretation of diffraction patterns. Since the angle \(\theta\) is inversely related to the interplanar spacing, a unit cell with large spacing would result in a compressed diffraction pattern.
This difficulty can be overcome by the use of the reciprocal lattice in which the interplanar spacing vector \( d(hkl) \) normal to the planes \((hkl)\), is replaced by a vector having the same direction, but a magnitude equal to the reciprocal, namely \( \frac{1}{d(hkl)} \).

The reciprocal lattice can then be defined by the three vectors \( a^*, b^*, \) and \( c^* \) such that \( a \cdot a^* = b \cdot b^* = c \cdot c^* = 1 \)

\( a^* \cdot b = a^* \cdot c = b^* \cdot a = b^* \cdot c = c^* \cdot a = c^* \cdot b = 0 \)

The diffraction pattern of a crystal is a fundamental physical property of the substance and can lead to the complete elucidation of the crystal structure. Analysis of the position of the diffraction effects leads to a knowledge of the unit cell geometry, whereas to locate the individual atomic positions within the cell, the intensities must be measured and analysed.

**Diffraction Amplitude And The Structure Factor**

In general, crystal structures are characterised by a number of atoms per unit cell. If the cell contains \( N \) atoms, then the crystal structure can be regarded as \( N \) interpenetrating lattices, each centred on the position of one atom. The overall diffraction by the crystal can then be explained in terms of the sum of the diffraction from the individual lattices. The scattering from these lattices will differ in phase according to their separation.

The resultant of the scattered waves in the direction of the reflection \((hkl)\) by all of the atoms in the unit cell is known as the structure factor \( F(hkl) \). Each of the individual waves has an amplitude given by \( f_n \), the scattering factor of the atom, and a phase angle \( \phi \) with respect to the wave scattered by a hypothetical electron at the origin of the unit cell.

Such a wave can be represented in complex notation by the expression \( f_n \exp(i\phi) \) where \( \exp(i\phi) \) is an operator rotating the vector \( f_n \) through the angle \( \phi \). The resultant of several such waves corresponding to the \( N \) atoms, can be expressed as

\[
F = \sum_{n=1}^{N} f_n \exp(i\phi)
\]

The phase angle \( \phi \) for an atom with fractional co-ordinates \( x_n, y_n, z_n \) with respect to the origin, can be expressed as

\[
\phi = 2\pi (hx_n + ky_n + lz_n)
\]

The structure factor can then be expressed as

\[
F(hkl) = \sum_{n=1}^{N} f_n \exp(2\pi i(hx_n + ky_n + lz_n))
\]
and this may be expressed in terms of its real and imaginary parts:

\[ F(hkl) = A(hkl) + iB(hkl) \]

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

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

The structure amplitude or modulus \[ |F(hkl)| \] is given by

\[ |F(hkl)|^2 = A(hkl)^2 + B(hkl)^2 \]

and the phase angle for the scattered radiation is given by

\[ \phi(hkl) = \tan^{-1} \frac{B}{A} \]

The presence of symmetry in the unit cell and lattice enables the structure factor calculation to be simplified. The most important element is the centre of symmetry, since this causes the \[ B(hkl) \] terms to vanish, and for every atom at \( x, y, z \) there is a corresponding one at \( \bar{x}, \bar{y}, \bar{z} \). The structure factor can then be expressed as

\[ F(hkl) = 2 \sum_{n=1}^{N/2} f_n \cos 2\pi(hx_n + ky_n + lz_n) \]

In the centrosymmetric case, the structure factor is always real and the phase angle can only take the values 0 or \( \pi \), thus making the structure factors positive or negative. If further elements of symmetry are present then the structure factor may be simplified by collecting together all the terms arising from the equivalent positions and combining them trigonometrically. However, when atoms are vibrating anisotropically, the scattering factors may not be the same for atoms in different equivalent positions and may not contribute equally to the structure factor. In these cases the general expression has to be used.

An alternate and more generalised expression can be derived in which the structure factor is considered as the sum of the waves scattered from all the infinitesimal elements of electron density within the unit cell, with no assumptions being made about the distribution of this density.
Since electron density $\rho$ is defined as the number of electrons per unit volume, then the number of electrons in any volume element $dv$ is:

$$\rho(x,y,z) \ dv$$

In exponential form the wave scattered by this element is

$$\rho(x,y,z) \exp \ 2\pi i (hx + ky + lz) \ dv$$

Summation over all the elements in the unit cell gives the structure factor

$$F(hkl) = \int \rho(x,y,z) \exp \ 2\pi i (hx + ky + lz) \ dv$$

**Temperature Factor**

The values of the atomic scattering factor $f$, for use in the structure factor expression, are obtained from the normal scattering factor curves calculated on the basis of the electron distribution in a stationary atom. In practice, the atoms in a crystal are vibrating about equilibrium positions, the magnitude of such vibration being a function of temperature, atomic mass and strength of bonding.

The effect of such thermal motion is to spread the electron cloud over a larger volume and thus cause a more rapid fall-off of scattering power of the atom. This reduction in scattering power can be accounted for by the inclusion of a temperature factor into the normal scattering factor expression, and may be introduced at several levels of approximation.

The simplest of these, that of over-all isotropic vibration, assumes that all of the atoms are vibrating with the same amplitude, and that their motions are spherically symmetrical.

Individual isotropic vibration permits assigning a temperature factor to each atom, but retains the concept of spherical symmetry.

Individual anisotropic vibrations of the atoms can be described in terms of six parameters which specify the size and orientation of the vibration ellipsoid which replaces the concept of spherical vibration.

For the case of isotropic vibration, the temperature factor can be shown theoretically to be given by the Debye-Waller expression:

$$T = \exp \left[ -\frac{B}{4} \left( \frac{2 \sin \theta \ h k l}{\lambda} \right)^2 \right]$$

$$T = \exp \left[ -\frac{B}{4} \left( \frac{1}{d(hkl)} \right)^2 \right]$$
where $B$ is related to the mean square amplitude of atomic vibration \( \left\{ \frac{u^2}{2} \right\} \) by $B = 8 \pi^2 \left\{ \frac{u^2}{2} \right\}$ and $\frac{1}{d(hkl)}$ is the length of the reciprocal lattice vector from the origin to the point $hkl$.

Thus the corrected scattering factor becomes:

$$f = f_0 \exp \left[ -\frac{B}{4} \left( \frac{1}{d(hkl)} \right)^2 \right]$$

where $f_0$ refers to an atom at rest.

An expression for the case of anisotropic vibration can be obtained by expanding the reciprocal lattice vector in terms of the reciprocal cell dimensions. Thus for the general case, the length of this vector is given by:

$$\frac{1}{d(hkl)} = \left[ h^2 a^*2 + k^2 b^*2 + l^2 c^*2 + 2hk a^*b^* \cos \gamma^* + 2hl a^*c^* \cos \beta^* + 2kl b^*c^* \cos \alpha^* \right]^{1/2}$$

and the temperature factor must have a parameter for every term in this expression. The general temperature factor thus becomes:

$$\exp \left[ -\frac{1}{4} \left( B_{11} h^2 a^*2 + B_{22} k^2 b^*2 + B_{33} l^2 c^*2 + 2 B_{12} h k a^*b^* + 2 B_{13} h l a^*c^* + 2 B_{23} k l b^*c^* \right) \right]$$

An equivalent and preferable expression for the general temperature factor is the following:

$$\exp \left[ -2 \pi^2 \left( U_{11} h^2 a^*2 + U_{22} k^2 b^*2 + U_{33} l^2 c^*2 + 2 U_{12} h k a^*b^* + 2 U_{13} h l a^*c^* + 2 U_{23} k l b^*c^* \right) \right]$$

where the $U_{ij}$ are now the thermal parameters expressed in terms of mean-square amplitudes of vibration.

It is often of value to have an estimate of the overall temperature factor and scale factor before the structure is known, and these can be estimated by a method due to Wilson (1942). He showed that the average of the square of the structure amplitude over a range of $(\sin \theta/\lambda)^2$ tends to be given by

$$|F|^2 = \sum_n f_n^2$$

where $\sum_n f_n^2$ represents the sum of the squares of the atomic scattering factors for the atoms in the cell, and are calculated for the centre of the $(\sin \theta/\lambda)^2$ range. $|F_o|^2$ is usually known as an arbitrary scale, so that

$$|F_o|^2 = K |F|^2$$

and therefore

$$|F_o|^2 = K \sum_n f_n^2$$
If the Debye–Waller correction is assumed, then

\[ K = \frac{|F_0|^2}{\sum_{n} f_0^2 \exp\left(-\frac{2B \sin^2 \theta}{\lambda^2}\right)} \]

Taking logarithms gives:

\[ \ln |F_0|^2 = \ln K - \frac{2B \sin^2 \theta}{\lambda^2} \]

If \( \ln \left\{ \frac{|F_0|^2}{\sum_{n} f_0^2} \right\} \) is plotted against \( \sin^2 \theta \)

a straight line graph is obtained from which \( B \) can be obtained, and a value of \( K \) obtained from the intercept on the vertical axis.

**Anomalous Scattering**

In the treatment of the structure factor, it has been assumed that the scattering factors are represented by real numbers. This assumption is normally justified since the wavelength of the incident radiation normally differs widely from that of any natural absorption wavelength of the atoms. If the wavelength of the incident radiation is slightly less than that of an absorption edge, an anomalous phase change occurs during scattering by the electrons associated with the absorption edge. This effect causes the scattering factor to be complex and it can then be represented by

\[ f = f_0 + f' + if'' \]

where \( f_0 \) is the scattering factor for wavelengths far removed from the absorption edge.

\( f' \) and \( f'' \) are the real and imaginary parts of the additional scattering that depend upon wavelength.

The phase lag of the resultant wave which is normally \( \pi \), diminishes as the wavelength of the incident radiation approaches that of an absorption edge, from the short wavelength side. The resultant phase shift is reduced to

\[ \pi - \phi \quad \text{where} \quad \phi = \tan^{-1}\left(\frac{f''}{f_0 + f'}\right) \]

A direct consequence of anomalous scattering arises in the case of a non-centrosymmetric structure, where due to the loss of conjugate symmetry, the reciprocal lattice symmetry becomes degraded to that of the point group. This amounts to the non-observance of Friedel's law and can provide a means of determining absolute configuration.
In the case of a centrosymmetric structure, Friedel's law remains valid, but the contribution of anomalous scattering reduces the magnitude of the structure factors, and an appropriate allowance must be made for this effect in the calculation of structure factors.

Fourier Series

The nature of a crystal requires the structure to be essentially periodic in three dimensions with a period defined by $a$, $b$ and $c$ of the unit cell. Hence the electron density $\rho(xyz)$ at any point can be represented by a three-dimensional Fourier series. This concept can be expressed by allotting to each Fourier coefficient $C$, three integral indices $h^i$, $k^i$ and $l^i$ whose values range from $-\infty$ to $+\infty$.

Thus

$$\rho(xyz) = \sum_{h^i} \sum_{k^i} \sum_{l^i} C_{h^i k^i l^i} \exp (2\pi i (h^i x + k^i y + l^i z))$$

This value for the electron density can be inserted into the structure factor equation

$$F(hkl) = \int \rho(xyz) \exp(2\pi i (hx + ky + lz)) dv$$

such that:

$$F(hkl) = \sum_{h^i} \sum_{k^i} \sum_{l^i} C_{h^i k^i l^i} \exp(2\pi i (h^i x + k^i y + l^i z)) \exp(2\pi i (hx + ky + lz)) dv$$

The exponential is periodic and the integral over one period is zero for all terms except when $h^i = -h$, $k^i = -k$, and $l^i = -l$. In this case the periodicity disappears and

$$F(hkl) = \int \rho(h^i k^i l^i) dv = \sqrt{V} C(h^i k^i l^i)$$

and $C(h^i k^i l^i) = \frac{1}{V} F(hkl)$.

Thus

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

Resolving the above expression into real and imaginary parts and expanding gives:

$$\rho(xyz) = \frac{1}{V} \sum_{h^i} \sum_{k^i} \sum_{l^i} A(h^i k^i l^i) \cos 2\pi (hx + ky + lz) + B(h^i k^i l^i) \sin 2\pi (hx + ky + lz)$$
Since \( A(hkl) = A(hkl) \) and \( B(hkl) = -B(hkl) \) and \( F(000) \) is its own conjugate:

\[
\rho(xyz) = \frac{1}{V} \left\{ F(000) + 2 \sum_{0}^{\infty} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} A(hkl) \cos 2\pi(hx + ky + lz) \right. \\
\left. + B(hkl) \sin 2\pi(hx + ky + lz) \right\}
\]

\[
= \frac{1}{V} \left\{ F(000) + 2 \sum_{0}^{\infty} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} |F(hkl)| \cos \left[ 2\pi(hx + ky + lz) - \delta(hkl) \right] \right\}
\]

This expression for the electron density is general for all crystals, although some simplification in its application may be obtained by utilising any symmetry present in the crystal.

In the case of a crystal with a centre of symmetry at the origin, \( F(hkl) = F(hkl) \) and the structure factors are all real.

Thus the electron density \( \rho \) is given by:

\[
\rho(xyz) = \frac{1}{V} \left\{ F(000) + 2 \sum_{0}^{\infty} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} |F(hkl)| \cos 2\pi(hx + ky + lz) \right\}
\]

**Deduction of The Atomic Arrangement**

The atomic arrangement within a cell can be regarded as a continuous distribution of diffracting matter (electron density), within the cell, with atomic centres coinciding with regions of high electron density.

A crystal structure determination is therefore essentially a determination of the distribution of such electron density within the unit cell. The Fourier summation for the evaluation of electron density includes the phase component of the structure factor. This component cannot be obtained by experimental observation and must therefore be obtained or deduced by some alternative means. Since all other measurements can be made by observation, then phase determination becomes the essential problem of structure determination.

Several methods of phase determination are available depending on the type of structure and on the presence or absence of relatively heavy atoms in the molecular structure. It can be shown that if a unit cell contains a uniform distribution of light atoms and also a heavy atom, then the phase of the resultant wave scattered in a particular direction, approximates to the phase of the heavy atom contribution in the same direction.
The heavy atom method which is based upon this relation involves locating and identifying the heavy atom position. This can be achieved by the use of the Patterson function.

**The Patterson Function**

Patterson (1935) showed that a Fourier series whose coefficients are the squares of the structure amplitudes could provide useful information about the crystal structure.

He defined a function \( P(uvw) \) such that:

\[
P(uvw) = \iiint \rho(xyz) \rho(x+u, y+v, z+w) \, dx \, dy \, dz
\]

If the values of the electron density are substituted into the equation, the conventional form of the Patterson function can be derived:

\[
P(uvw) = \frac{1}{V} \sum_{h} \sum_{k} \sum_{l} |F(hkl)|^2 \exp \left( -2\pi i (hu + kv + lw) \right)
\]

This function is real for all values of \( u, v \) and \( w \), and may be expanded to give:

\[
P(uvw) = \frac{1}{V} \sum_{h} \sum_{k} \sum_{l} |F(hkl)|^2 \cos 2\pi(hu + kv + lw)
\]

The magnitude of the Patterson function, \( P(uvw) \) for a point \( u, v, w \) in the Patterson vector map represents the summation of the product of the electron density at a point \( x, y, z \), and at a point \( x+u, y+v, z+w \) over the entire cell. Hence large peaks will be found in the vector map corresponding to the vectors between atoms, and their magnitude will be related to the product of their atomic numbers. There is always a large peak at the origin corresponding to the vector between each atom and itself.

Interpretation of these vector maps is greatly simplified by the presence of symmetry in the unit cell. In certain cases peaks between atoms in equivalent positions are observed whose positions in the vector map are restricted to certain sections or lines. These were first discovered by Harker (1936) and bear his name. For example, if a cell contains a 2-fold axis parallel to \( b \), then for an atom at \( x, y, z \), there will be a symmetry related atom at \( \tilde{x}, y, \tilde{z} \), and a maximum will occur in the vector map at \( u = 2x, v = 0, w = 2z \). With this knowledge, it is often possible to locate directly the position of an atom in the unit cell.
The Heavy Atom Method

The Patterson function of a heavy atom compound reveals large peaks due to the vectors between the heavy atoms, and allows these vectors to be distinguished from the remaining vectors. Care must be exercised in the choice of the heavy atom, since if this contributes too heavily to the overall scattering, comparison between the observed and calculated structure factors becomes insensitive to the positions of the light atoms. An empirical and useful guide in the selection of the heavy atoms is:

\[ \sum (Z^2_{\text{heavy}}) \sim \sum (Z^2_{\text{light}}) \]

Once the co-ordinates of the heavy atom have been determined, an electron density map can be computed using as Fourier coefficients, \(|F_0|\), and the phase angles obtained from structure factor calculations based upon the heavy atom contributions. From this electron density map, improved positions for the heavy atom will be found, and the positions of some or all of the lighter atoms may be found.

Direct Methods In The Solution Of The Phase Problem

In recent years several relationships have been proposed so as to produce a set of phases from a set of experimentally determined magnitudes.

One of the earliest attempts to relate phases to intensities led to the development of the Harker-Kasper inequalities (1948). These expressions resulting from the combination of structure factor expressions with certain classical inequalities, provided the first means of determining the phase of one reflection in terms of its magnitude and those of others. The method was limited in application and useful results could only be obtained for large structure amplitudes and for small numbers of atoms in the unit cell.

In 1952, Sayre showed that for a centrosymmetric structure containing equal resolved atoms, the sign \( S_H \) of a reflection \( H \) could be derived from a simple product of the signs of algebraically related reflections, such that

\[ S_H \sim S_K \cdot S_{H-K} \]

This expression has a high probability of being correct if the magnitude of the three structure factors \( F_H \), \( F_K \) and \( F_{H-K} \) are all large.
Hauptman and Karle (1953) devised a statistical approach in which they used a normalised structure factor given by

\[ |E_H|^2 = \frac{|F_H|^2}{\epsilon \sum_{n=1}^{N} f_n^2 (H)} \]

where \( \epsilon \) is a factor introduced to accommodate space group extinctions.

They also derived the \( \Sigma_2 \) relationship, expressed as

\[ S_H \sim S \left[ \sum_{K} E_K \cdot E_{H-K} \right] \]

This is similar to that introduced by Sayre except that the relationship involves more than one interaction. The probability that a sign will be positive is given by Cochran and Woolfson, 1955,

\[ P(E_{H+}) = \frac{1}{2} + \frac{1}{2} \tanh (\sigma_3 \sigma_2^{\frac{1}{2}} |E_H| \sum E_K \cdot E_{H-K}) \]

where

\[ \sigma_n = \sum_{j=1}^{N} Z_j^n \]

This shows that if the three reflections involved in a triple relationship have large \( E \)-values then the probability that the sign relationship will be correct will be large. So that by using probability relationships it is possible to start the assignment of signs from a few strong planes whose phases are either known or represented by symbols, and this is known as the symbolic addition procedure.

A strategy for using this method outlined by Karle and Karle (1966) first involves estimating a set of normalised structure factors and finding the triple relationships which exist amongst the stronger reflections. The origin is specified by choosing \( n \) linearly independent reflections and arbitrarily fixing their signs where \( n \) has a maximum value of three and depends upon the space group. These reflections are used to define the signs of further reflections using the \( \Sigma_2 \) relationship. Subsequently several strong planes are given symbolic phases as necessary in order to phase all of the reflections. Signs are only accepted when the total probability for a predicted sign exceeds a specified value. The acceptance limit decreases as the procedure continues but high values initially reduce the number of incorrect sign allocations. At the end of this procedure each reflection may have its sign determined or represented by more than one symbol or combination of symbols, and using these it is possible to predict the most likely signs for the symbols used.
An alternate strategy for using the $\sum \sigma^2$ relationship involves the choice of a number of strong reflections whose signs are systematically varied. Each of the possible sign combinations for these reflections together with the origin determining reflections as before is used as a starting set for reiterative application of Sayre's relationship. This gives a series of solutions and is known as the multisolution method. In a program described by Long (1968) the signs determined from the starting set, are used to predict more signs and redetermine those predicted before. The signs of the starting set are calculated at the end of each cycle but are not allowed to change.

A measure of the self consistency of the predicted signs is given by

$$C = \frac{\langle |E_A \sum_{A=B+C} E_B E_C| \rangle}{\langle |E_A| \sum_{A=B+C} |E_B||E_C| \rangle}$$

where $\langle \rangle$ means averaged over all values of A. The expression compares the observed $\sum \sigma^2$ sum to that which would be observed if all the interactions were consistent. Usually the set with the highest consistency index represents the correct solution.

When the number of possible phase sets becomes very large, additional rejection tests are required. A rejection test described by Germain, Main and Woolfson, 1970, evaluates each phase set in terms of an absolute figure of merit, $M_{ABS}$ where

$$M_{ABS} = \frac{Z - \sum_{h} \langle \alpha_h^2 \rangle^{\sigma^2}_{\sigma^2}}{\sum_{h} \langle \alpha_h^2 \rangle^{\sigma^2}_{\sigma^2} - \sum_{h} \langle \alpha_h^2 \rangle^{\sigma^2}_{\sigma^2}}$$

This test is based upon the statistics of $\sigma$ as derived by Germain, Main and Woolfson, 1970 and compares the expected value of $\alpha_h^2$ with that expected for a random set of phases.

A further test described by Giacovazzo, 1974, involves the use of quartet relationships

$$P_- = \frac{1}{2} - \frac{1}{2} \tanh \frac{1}{2N} |E_3 E_4| (2E_1^2 E_2^2 - E_1^2 - E_2^2)$$

where $E_1 = E_h$, $E_2 = E_k$, $E_3 = E_{h-k}$ and $E_4 = E_{h+k}$

Large values of $P_-$ are obtained if $|E_3|$, $|E_4|$ and $|E_1|$ are large and $|E_2|$ is small.
The $\sum_2^$ relation can be extended to non-centric structures (Karle and Karle, 1966) and in its general form refers to the addition of phases so that

$$<\varphi_H> = <\varphi_K + \varphi_{H-K}>$$

where $K$ ranges over reflections with large $E-$values.

The most probable phase is given by

$$\tan \varphi_H = \frac{\sum_k |E_K| E_{H-K} \sin(\varphi_K + \varphi_{H-K})}{\sum_k |E_K| E_{H-K} \cos(\varphi_K + \varphi_{H-K})}$$

which is known as the tangent formula and represents the combination of the vectors by summation of their components parallel to the real and imaginary axes.

**Structure Refinement**

During the course of a successful structure determination, a stage is reached when all of the atoms present are placed in approximate but essentially correct positions. The process of refinement involves refining the approximate structure to any degree of precision which the observed data permits, and is commonly followed by noting the value of the discrepancy index

$$R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

This is a crude measure of how much the model departs from the actual structure, as expressed by the difference in their diffraction amplitudes.

Hamilton (1965) has defined a weighted index $R_w$, given by:

$$R_w = \left[ \frac{\sum_w (|F_o| - |F_c|)^2}{\sum_w |F_o|^2} \right]^{1/2}$$

This index is useful in that it enables a statistical comparison to be made on two refinements from different models of the same structure.

An analytical method of refinement of great power and generality is that based on Legendre's principle of least squares.

An outline of this method will now be given. Let $p_1, p_2, \ldots p_n$ be the $n$ parameters in the $F_c$ whose values are to be determined. $|F_c|$ can be written as a function of these parameters

$$|F_c| = f(p_1, p_2, \ldots, p_n)$$
Incorporating $\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_n$, the shifts required to give the true structural parameters, a similar expression may be written for the observed amplitudes:

$$|F_0| = f(p_1 + \varepsilon_1, p_2 + \varepsilon_2, \ldots, p_n + \varepsilon_n)$$

For a trial set of $p_j$ close to the correct values, $F_0$ may be expanded as a function of the parameters by a Taylor's series of the first order.

Taylor's theorem gives:

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

Setting $b = p_1 + \varepsilon_1, \ldots$, $a = p_1, \ldots$, and taking the series to the first derivative gives:

$$|F_0| = f(p_1, p_2, \ldots, p_n) + \sum_{i=1}^{n} \frac{\partial f(p_1, p_2, \ldots, p_n)}{\partial p_i} \varepsilon_i$$

i.e. $$|F_0| = |F_c| + \sum_{i=1}^{n} \frac{\partial F_c}{\partial p_i} \varepsilon_i$$

An equation of this type may be derived for each reflection. Each $F_0$ is subject to random errors and suitable values of $\varepsilon_i$ have to be found to give the most acceptable fit between $F_0$ and $F_c$. The theory of errors predicts that the most acceptable set of $\varepsilon_i$ is that which minimises the sum of the weighted squares of the differences between the observed and calculated quantities. The function most commonly used is:

$$R = \sum_{hkl} w (|F_0| - |F_c|)^2$$

where the sum is over the crystallographically independent planes and $w$ is the weight of the observation.

For $R$ to be a minimum

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

where $p_j$ is the $j^{th}$ parameter

Hence

$$\sum_{hkl} w \Delta \frac{\partial |F_c|}{\partial p_j} = 0, \text{ where } \Delta = |F_0| - |F_c|$$

Remembering that $$\Delta = \sum_{i=1}^{n} \frac{\partial F_c}{\partial p_i} \varepsilon_i$$

leads to a set of simultaneous equations, the normal equations

$$\sum_{hkl} \left( \frac{\partial |F_c|}{\partial p_i} \right)^2 \varepsilon_i + \sum_{hkl} \frac{\partial |F_c|}{\partial p_i} \left( \sum_{j=1}^{n} \frac{\partial |F_c|}{\partial p_j} \varepsilon_j \right) = \sum_{hkl} \Delta \frac{\partial |F_c|}{\partial p_i}$$
There are \( n \) of these normal equations for \( j = 1, \ldots, n \), to determine the \( n \) unknown parameters

\[
\sum_{i}^{} w \left( \frac{\partial |F_c|}{\partial p_i} \right)^2 \epsilon_i \quad + \quad \sum_{i}^{} w \left( \frac{\partial |F_c|}{\partial p_1} \right) \left( \frac{\partial |F_c|}{\partial p_2} \right) \epsilon_2 \quad + \quad \ldots = \sum_{i}^{} w \Delta \frac{\partial |F_c|}{\partial p_1}
\]

\[
\sum_{i}^{} w \left( \frac{\partial |F_c|}{\partial p_1} \right) \left( \frac{\partial |F_c|}{\partial p_2} \right) \epsilon_1 \quad + \quad \sum_{i}^{} w \left( \frac{\partial |F_c|}{\partial p_2} \right)^2 \epsilon_2 \quad + \quad \ldots = \sum_{i}^{} w \Delta \frac{\partial |F_c|}{\partial p_2}
\]

Alternatively these \( n \) equations may be expressed in matrix notation:

\[
\sum_{i}^{} a_{ij} \epsilon_i = b_j
\]

where \( a_{ij} = \sum_{hkl}^{} \frac{\partial |F_c|}{\partial p_i} \cdot \frac{\partial |F_c|}{\partial p_j} \) and \( b_j = \sum_{hkl}^{} \Delta \frac{\partial |F_c|}{\partial p_j} \)

In a structure with a large number of atomic parameters, it may be impracticable to calculate all the terms of the normal equation matrix \( a_{ij} \), particularly during the early stages of refinement. A useful approximation is the block-diagonal technique which neglects all off-diagonal elements relating to interactions between different atoms, so that a \( 9 \times 9 \) matrix is used for the positional and anisotropic thermal parameters for each atom, or a \( 4 \times 4 \) matrix if the atom is refined with an isotropic temperature factor. A \( 2 \times 2 \) matrix is used for the scale and overall isotropic temperature parameter.

A more modern approach is the blocked full-matrix technique. In this system, the atoms are refined in groups or blocks using the block-diagonal approximation, but allowing for interactions between the atoms in any one group.

**Weighting Functions**

The functions minimised in the least-squares method, carry a weighting factor for each observation. The weighting should be a measure of the reliability of the observations, and from statistical considerations, it can be shown that the best weight is equal to the square of the reciprocal of the standard deviation of the observation.

\[
w = \frac{1}{\sigma^2 F_0}
\]
\( \sigma F_o \) can be derived from the relationship

\[
F_o = \frac{k}{(L_p)^{1/2}} \cdot N^{1/2}
\]

where \( k \) is the scale factor and \( L_p \) is the Lorentz–polarisation factor.

Differentiating this equation gives

\[
dF_o = \frac{1}{2} \frac{k}{(L_p)^{1/2}} \cdot \frac{dN}{N^{1/2}}
\]

from which

\[
\frac{dF_o}{F_o} = \frac{1}{2} \frac{dN}{N}
\]

Making the approximation \( dF_o = \sigma F_o \), and \( dN = \sigma N \),

\[
\sigma F_o = \frac{1}{2} F_o \cdot \frac{\sigma N}{N}
\]

The standard deviation in \( N \) is given by counting statistics as

\[
\sigma N = \left[ T + B \cdot G \right]^{1/2}
\]

where \( B \) is the ratio between the total background count \( G \) and the total peak count \( T \).

The term \( \left[ T + B \cdot G \right]^{1/2} \) underestimates the error in the very intense reflections, so a term \( (P \cdot N)^2 \) is introduced to down weight these reflections.

Thus \( \sigma N = \left[ T + B \cdot G + (P \cdot N)^2 \right]^{1/2} \)

and \( \sigma F = \frac{1}{2} F_o \cdot \left[ T + B \cdot G + (P \cdot N)^2 \right]^{1/2} \)

The Accuracy of Parameters Derived From Least Squares Methods

In order to obtain a reliable estimate of the accuracy of the atomic parameters, the weighting scheme used in the refinement should correspond to

\[
w = \frac{1}{\sigma^2(F_o)} \quad \text{where } \sigma^2(F_o) \text{ is the variance for the observation.}
\]

In this case the variance of the parameter \( p_i \) is given by

\[
\sigma^2(p_i) = (a^{-1})_{ii} \quad \text{where } (a^{-1})_{ii} \text{ is the } i^{th} \text{ diagonal element of the inverse matrix to the normal equation matrix.}
\]

Generally \( \sigma(F_o) \) is not known exactly and relative weights of the form

\[
w = \frac{k}{\sigma^2(F_o)}
\]

are used, in which case the estimated standard deviation is given by

\[
\sigma^2(p_i) = (a^{-1})_{ii} \left( \sum \frac{wAF^2}{m - n} \right)
\]

where \( m \) is the number of observations and \( n \) is the number of parameters.
The accuracy of interatomic distances and angles depends upon the estimated standard deviations of the atomic coordinates involved (Cruickshank and Robertson, 1953). So that for a bond $l$ between two uncorrelated atoms having variances $\sigma^2(a)$ and $\sigma^2(b)$ in the direction of the bond,

$$\sigma^2(l) = \sigma^2(a) + \sigma^2(b)$$

For an angle $\theta$ between two bonds $AB$ and $AC$, the estimated standard deviation of the bond angle is given by

$$\sigma^2(\theta) = \frac{\sigma^2(b)}{(AB)^2} + \frac{\sigma^2(a) (BC)^2}{(AB)^2 (AC)^2} + \frac{\sigma^2(c)}{(AC)^2}$$

**Measurement of Intensities**

Two general methods are available for measuring the intensities of diffracted beams. Either the beams may be detected by some type of quantum counting device which measures the number of photons directly (diffractometer or counter methods), or else the degree of blackening of spots on diffraction photographs may be measured and taken as proportional to the beam intensity (photographic methods).

The modern trend appears to be towards the use of automated computer controlled diffractometers which permit increased accuracy of measurement and can also deal with large numbers of reflections. The basic geometry for the reflection of an X-ray beam from a set of crystallographic planes is summarised in the following diagram:

![Diagram showing the geometry of X-ray diffraction](image)

In order that reflections from the plane may occur, the incident beam $S_0$, the reflected beam $S$ and the plane normal $d^*$, must be coplanar, and the incident beam must make an angle $\theta$ with the plane in order to satisfy the Bragg equation. Also $d^*$ must bisect the angle between $S$ and $S_0$. 
The arrangement of the Hilger and Watts four-circle diffractometer is shown in Figure 1a. For the purpose of intensity measurement the instrument normally uses bisecting geometry which places the vertical X-circle so as to bisect the angle between the incident and reflected X-ray beams. This means that the X-circle must contain the normal to the reflecting planes \( d^\ast \), and hence the angle \( \omega \) must equal the angle \( \theta \). With \( d^\ast \) constrained to lie in two mutually perpendicular planes there will be specific values of the angles \( \lambda \) and \( \phi \) if the reflection \( (h k l) \) is to be observed.

At high values of the angle \( \theta \), when the X-circle would tend to obstruct the passage of the reflected beam to the detector, the instrument switches to perpendicular geometry. In this position the vector \( d^\ast \) is perpendicular to the X-circle and the condition \( \omega = 90 - \theta \) holds.

**Intensity Correction**

The X-ray reflection from a given set of crystallographic planes does not occur sharply, but takes place over a small angular range on either side of \( \theta \) as defined by the Bragg law. In order to accommodate this feature of crystal reflection, the diffractometer sums the number of counts over this angular range to produce an integrated intensity measurement. To transform the measured integrated intensities into observed structure amplitudes, they must be corrected for certain physical and geometrical factors.

**Polarisation Factor**

When X-rays are reflected by a crystal plane, they become partly plane polarised. As the electromagnetic wave of X-radiation is reflected, the component of the wave whose vibration is parallel to the reflecting plane does not suffer reduction, but the component in the plane of the incident and reflected rays is reduced in intensity by an amount proportional to \( \cos^2 \theta \). As a consequence, the intensity of the diffracted wave is reduced by a factor called the polarisation factor, amounting to:

\[
p = \frac{1 + \cos^2 \theta}{2}
\]
Diffractometer Geometry

Figure 1a

Equatorial plane

Goniometer-head axis $\phi$

$2\theta$

Reflected beam

Crystal

Detector

Incident beam

Oscillation axis $\omega$
Lorentz Factor

When a perfect crystal moves through the reflecting position, reflection occurs only over a range of a few seconds of arc. Most crystals are not perfect and due to their mosaic nature, reflect over a range of some minutes. The points of the reciprocal lattice therefore have finite size, and spend a finite time in passing through the surface of the sphere of reflection. This factor varies with the distance of the reciprocal lattice point from the origin, which is related to the angle of reflection, and also depends on the mode of data collection. The Lorentz factor, \( L \) for data collected using a four-circle diffractometer is given by:

\[
L = \frac{1}{\sin 2\theta}
\]

Absorption

All materials absorb X-rays according to an exponential law

\[
I = I_o \exp(-\mu t)
\]

where \( I \) and \( I_o \) are respectively, the transmitted and incident intensities, \( \mu \) is the linear absorption coefficient, and \( t \) is the path length through the material. The extent of absorption increases with increase in the atomic number of the elements in the material.

When the X-rays travel different path lengths through the crystal for different reflections, then these reflections will suffer to a varying extent from absorption, and a systematic error will be introduced into the observed intensities.

If the dimensions of the crystal are accurately known, the path lengths for each reflection can be calculated, and appropriate corrections can then be applied to the intensities. An alternate approach is to minimise the effects of absorption by suitable shaping of the crystal to achieve similar path lengths for each reflection, and to also use a more penetrating radiation.
CHAPTER TWO

THE METHYLENEAMINO GROUP AS
A METAL CO-ORDINATING LIGAND
The Methyleneamino Group As A Metal Co-ordinating Ligand

Considerable interest has been shown in the methyleneamino group as a terminally co-ordinated substituent of metals and metalloids, since the shape of the C - N - M linkage can be used to establish the occurrence of possible N\rightarrow M dative \pi-bonding. The methyleneamino group can act as a one- or three electron donor, and therefore several structural possibilities exist depending primarily upon whether the metal is co-ordinatively saturated or unsaturated. When the metal is saturated, the methyleneamino group acts as a one-electron donor, with the nitrogen atom formally sp\(^2\) hybridised, and the nitrogen lone pair occupying one of the hybrid orbitals. Hence the C - N - M linkage is bent with a theoretical angle at nitrogen of 120° (Figure 2a). Bent structures of this type have been inferred from n.m.r. studies on di-t-butylmethyleneamine itself (Snaith, Summerford, Wade and Wyatt, 1970), and for a number of N-organomethyleneamines (Curtin, Grubbs and McCarty, 1966).

When the metal is co-ordinatively unsaturated however, donation of the nitrogen lone pair may occur, either through bridging to a second metal atom (Figure 2b), with the formation of a dimeric or oligomeric species, or through N\rightarrow M dative \pi-bonding (Figure 2c). In the latter case, for maximum overlap of the nitrogen and metal orbitals, a linear arrangement at nitrogen is required, with modification of the nitrogen hybridisation from sp\(^2\) to sp. A shortening of the metal - nitrogen bond distance would therefore occur, and this, in conjunction with the angle at nitrogen can be used as evidence for N\rightarrow M dative \pi-bonding.

However, Ebsworth has shown from overlap integral calculations, that in pyramidal silicon - nitrogen systems where the nitrogen lone pair occupies an sp\(^3\) hybrid orbital, considerable (p - d) \pi-bonding is still possible. Maximum orbital overlap would still however, require a linear arrangement (Ebsworth, 1966).

In addition, cationic species of the type \(\overset{\rightarrow}{C} = N^+\), being isoelectronic with the \(\overset{\rightarrow}{C} = C\) group, are able to function as \pi-bonding donors to transition metals (Figure 2d) (Abel, Rowley, Mason and Thomas, 1974).

Several techniques are available for determining the extent of linearity of the C - N - M linkage, and hence the degree of N\rightarrow M dative \pi-bonding. Of these, X-ray crystallography is the most conclusive since it relies on the measurement of two directly observable parameters, namely, the angle at nitrogen, and the length of the nitrogen - metal bond. It should be emphasised that in this technique, the angle at nitrogen is the fundamental observation from which \pi-bonding is inferred.
Fig. 2a

Fig. 2b

Fig. 2c

Fig. 2d

Modes of Bonding of The Methyleneamino Group
Main Group Metal Co-ordinated Methyleneamines

Several methyleneamino - main group metal complexes have been studied crystallographically, establishing varying degrees of N→M dative π-bonding. The complex bis di-t-butylmethyleneaminoberyllium (Shearer and Sowerby, 1971), has been shown to be dimeric and to contain both bridging and terminal methyleneamino groups. The terminal substituents were found to have C - N - Be angles of 161°, and a Be(sp<sup>2</sup>) - N(sp<sup>2</sup>) distance of 1.50Å. This value can be compared with the Be(sp<sup>2</sup>) - N(sp<sup>2</sup>) distance of 1.57Å found in (Be(NMe<sub>2</sub>)<sub>2</sub>)<sub>3</sub> (Atwood and Stucky, 1969), and the Be(sp) - N(sp<sup>2</sup>) distance of 1.56Å found in [(Me<sub>3</sub>Si)<sub>2</sub>N]<sub>2</sub>Be (Clark and Haaland, 1970).

In both of these latter structures, the Be - N distances were considered consistent with a degree of multiple Be - N bonding. The distance of 1.50Å in (Bu<sup>t</sup> C : NBe)<sub>2</sub> is similarly thought to be consistent with multiple Be - N bonding, and this is particularly apparent when compared with the bridging single bond Be - N distances of 1.67 and 1.68Å.

A boron complex, diphenylmethyleneaminodimesitylborane (Bullen, 1973), has been reported, which is shown to possess a virtually linear C - N - B linkage of 173° and a boron - nitrogen distance of 1.38Å. This value can be compared with the values of 1.40(4) and 1.43(4)Å observed in Me<sub>2</sub>NBMe<sub>2</sub> (Bullen and Clark, 1970) and 1.39 and 1.41Å in (Me<sub>2</sub>NBC<sub>2</sub>H)<sub>3</sub> (Hess, 1969), substantial B-N multiple bonding being implied in all cases.

An aluminium derivative has been reported, namely, lithium tetrakis (di-t-butylmethyleneamino) alane (Shearer, Snaith, Sowerby and Wade, 1971), and this structure contains both terminal and bridging methyleneamino groups (bridging to lithium in this instance). The terminal methyleneamino groups have C - N - Al angles of 167° and a mean Al - N distance of 1.778(7)Å. This value is comparable with the Al - N distance of 1.78Å found in [(Me<sub>3</sub>Si)<sub>2</sub>N]<sub>3</sub>Al (Sheldrick and Sheldrick, 1969), and which is thought to be consistent with a degree of multiple Al - N bonding.

Both of these can be compared with reported bridging Al - N single bond distances of 1.94Å in (Bu<sup>t</sup> Me C : NAlMe<sub>2</sub>)<sub>2</sub> (Willis and Shearer, 1966), 1.91Å in (PhAlNPh)<sub>4</sub> (McDonald and McDonald, 1972), 1.95Å in (Me<sub>2</sub>Al NHMe)<sub>3</sub> (Gosling, McLaughlin, Sims and Smith, 1970) and 1.92Å in [C<sub>6</sub>H<sub>4</sub>Br (Ph) C : NAlPh<sub>2</sub>]<sub>2</sub> (McDonald, 1969).
Several structures have been reported involving group IV elements. A series of the type $M(N:CPh_2)_4$, where $M$ represents $Si$, $Ge$ and $Sn(IV)$ has been studied by Alcock, Pierce - Butler, Willey and Wade, 1975. The angles at nitrogen show a marked reduction from silicon to germanium to tin, 134.7° and 139.5° (mean) for silicon, 127.0° for germanium and 121.3° (mean) for tin, suggesting considerably reduced metal - nitrogen π-bonding in germanium, and very little in tin. This interpretation is supported by the metal - nitrogen bond distances. Silicon shows a substantial shortening, 1.717(10)Å (mean) compared with a calculated Si - N single bond distance of 1.879Å. For germanium, the observed Ge - N distance is 1.872(5)Å compared with a calculated single bond value of 1.928Å. For tin, the observed Sn - N distance is 2.06(4)Å, a negligible shortening compared to a calculated value of 2.11Å.

Two further structures have been reported involving tin(II) complexes, $(Ph_2C:Sn(II)Cl)_2$ and $Ph_2C:NH(Ph_2C:N:Sn(D,Cl))_2$. $C_7H_8$ (Mahmoud, 1976). Both of these structures contain only bridging methyleneamino groups.

A tris(diphenylmethyleneamino) phosphine complex has been reported, (Shearer, 1976). This structure has terminal methyleneamino groups, with a mean angle at nitrogen-of 123°, showing little evidence of $N\rightarrow P$ dative π-bonding.

On the basis of the available crystallographic data, substantial dative π-bonding appears in the early members of groups II and III, and to a lesser extent in group IV, as indicated from the use of the methyleneamino group.
CHAPTER THREE

THE CRYSTAL STRUCTURE

OF

$(\text{Ph}_2\text{C:NMgBr})_2 \cdot 3\text{THF}$
Introduction

Considerable interest has been attached to the nature of the bonding between methyleneamino groups and metals, especially where there is a possibility of dative π-bonding between nitrogen and the metal. Previous structural work on the methyleneamino derivatives of Group II metals has been mainly concerned with beryllium and zinc, with magnesium derivatives being relatively neglected.

A diphenylmethylenamine magnesium compound was synthesised, which on the basis of spectroscopic evidence, was thought to possess a terminally co-ordinated methyleneamino group. Subsequent crystallographic work established the compound as being dimeric with bridging methyleneamino groups, and with an unusual bridging tetrahydrofuran molecule.

Experimental

The compound was prepared from the low temperature reaction in diethyl ether, of phenylmagnesium bromide and benzonitrile. The mixture was warmed to room temperature and stirred overnight, after which the solvent was removed from the yellow suspension. The pale yellow solid remaining was then recrystallised from tetrahydrofuran.

The preparation and spectroscopic characterisation of the compound was undertaken by Petch and Wade, 1976.

Crystal Data

The compound recrystallised from tetrahydrofuran as pale yellow, air sensitive crystals, and were sealed in quartz capillary tubes for the purpose of data collection. The crystal selected had dimensions of $0.3 \times 0.3 \times 0.5$ mm with elongation along the direction of the $c$-axis.

Preliminary studies using the precession method showed the unit cell to be monoclinic. The conditions limiting reflections were:

$$\begin{align*}
hkl & \quad h + k = 2n \\
h0l & \quad l = 2n, (h = 2n) \\
0k0 & \quad (k = 2n)
\end{align*}$$

and these established the space group as either $C2/c$ or $Cc$, with the former found to be correct from the subsequent structure determination.
More reliable unit cell dimensions were obtained from a least-squares treatment of the positions of twelve high order reflections, measured on a four-circle diffractometer.

\[(\text{Ph}_2\text{C} : \text{NMgBr})_2 \cdot 3\text{THF}\]

\[
\begin{align*}
M & = 784.97 \\
a & = 17.819(2)\text{Å} \\
b & = 10.647(2)\text{Å} \\
c & = 22.051(2)\text{Å} \\
\beta & = 112.86^\circ \\
Z & = 4 \\
D_c & = 1.48\text{g cm}^{-3}
\end{align*}
\]

Absorption coefficient \(\mu\) for MoK\(\alpha\) radiation = 23.01 cm\(^{-1}\). The crystal density was not measured owing to the limited availability of crystals.

**Data Collection**

The intensity data were collected on a Hilger and Watts four-circle diffractometer using MoK\(\alpha\), Zr-filtered radiation. A2\(\theta\) - \(\theta\) scanning technique was employed consisting of eighty steps of 0.01\(^\circ\). A counting time of two seconds per step was chosen together with a background count of forty seconds measured at the beginning and end of each scan. Three reflections were chosen as standards and measured after every forty reflections. These reflections were used to place the data on a common scale.

Two non-equivalent octants hkl and hk-l of reciprocal space were scanned to cover the requirements of the monoclinic system. A total of 3408 reflections were measured to a limit of \(\theta = 23^\circ\), and of these, 2029 were classed as observed reflections, having net counts greater than 2\(\sigma\).

The intensities were corrected for Lorentz and polarisation effects, but no corrections were made for absorption.
Solution and Refinement

The position of the magnesium and bromine atoms were obtained from the Patterson function which for the space groups $C2/c$ and $Cc$ takes the form:

$$P(u,v,w) = \frac{4}{V} \sum_{h} \sum_{k} \sum_{l} \left| F(hkl) \right|^2 \cos 2\pi(hu + lw)$$

$$+ \left| F(hkl) \right|^2 \cos 2\pi(hu - lw) \cos 2\pi kv$$

The function was calculated over one eighth of the unit cell from 0 to 0.5 along each axial direction. The coefficients used were $|F_0|^2$ weighted by $(Lp)^{-1}$ for each reflection.

For the space group $C2/c$, peaks due to double weight Br - Br vectors would be expected on the Harker plane at the positions $-2x, 0, 0.5 - 2z$, and on the Harker line at $0, 2y, 0.5$.

There were two large peaks in the vector map at $(0.066, 0.0, 0.318)$ and $(0.0, 0.468, 0.50)$ with peak heights of 183 and 168 with respect to the origin peak of 500. These peaks were considered due to Br - Br double weight vectors and are consistent with a bromine atom at $(-0.033, 0.234, 0.091)$. The corresponding single weight Br - Br vector was found at $(0.433, 0.031, 0.181)$ with a peak height of 92.

Two further peaks were found at $(0.033, 0.0, 0.151)$ and $(0.0, 0.156, 0.50)$ with peak heights of 44 and 45. These peaks were considered due to Mg - Mg double weight vectors and are consistent with a magnesium atom at $(-0.16, 0.078, 0.181)$. A single weight Mg - Mg vector was found at the appropriate position of $(0.466, 0.343, 0.363)$ and of peak height 13.

Four further peaks were found at, or close to the positions calculated for the Br - Mg vectors, namely, $(0.017, 0.156, 0.09)$, $(0.451, 0.188, 0.272)$, $(0.049, 0.156, 0.228)$, and $(0.483, 0.188, 0.410)$, and with peak heights of 63, 57, 55 and 56. It was therefore possible to interpret the Patterson function in terms of the space group $C2/c$.

The positions of the bromine and magnesium atoms were refined using least-squares methods with the block-diagonal approximation. Initially, both atoms were given isotropic temperature factors, and after two cycles of refinement the $R$-value was 0.45. The set of structure factors based on the positions of the heavy atoms were then used to compute an electron density map. From this it was possible to identify twenty two additional peaks of heights varying from 2.9 to $7.5e\,\text{Å}^{-3}$, against a background of the order 0.3 to 0.5e\,\text{Å}^{-3}$. 

35
The close proximity of the two magnesium atoms related by the 2-fold axis, suggested that the molecule was dimeric. On this assumption, nineteen of the peaks were assigned to the atoms of a bridging diphenylmethyleneamino group and a tetrahydrofuran molecule terminally attached to the magnesium atom. An electron density difference map computed on the basis of all located atoms showed the positions of the three remaining peaks more clearly. One peak was found to lie on a 2-fold axis, the operation of which would generate a further two peaks. The five peaks were attributed to an additional tetrahydrofuran molecule with the oxygen atom situated on the 2-fold axis, and bridging the magnesium atoms. All twenty four atoms were included in the subsequent refinement and allotted anisotropic temperature factors. This produced a considerable reduction in R-value to 0.072.

Hydrogen atom positions were calculated for the two phenyl rings and for the bridging THF molecule, using C-H distances of 1.07 and 1.09 Å respectively. In the final refinement using full-matrix least-squares methods, the hydrogen atoms were included in the structure factor calculations and given isotropic temperature factors of value 1.25 times that of the attached carbon atom. No attempt was made to refine the positional or thermal parameters of the hydrogen atoms. A correction was also applied to allow for the anomalous scattering of the bromine atom. The R-value dropped to its final value of 0.061, and during the last cycle, all parameter shifts were less than 0.3 of the corresponding e.s.d. A final electron density difference map revealed no peaks of value greater than 0.3eÅ⁻³.

An empirical weighting scheme was used in the initial stages of refinement, but was replaced in the final stages by one based on counting statistics as described earlier.

The optimum value for P was 0.06 as determined by an even distribution of wÅ² as a function of |Fo|₁. The unobserved reflections were not included in the refinement.

The weighting analysis is given in Table 3.8 and the final atomic and thermal parameters are given in Tables 3.1, and 3.2.

Atomic scattering factors and the anomalous contribution for the bromine atom, were taken from International Tables, Vol. III. Structure factors are listed in Table 3.9.
Description And Discussion of The Structure

The molecule is dimeric (Figure 3a), and is situated around a crystallographic 2-fold axis, so that it possesses molecular 2-fold symmetry. The magnesium atoms are bridged by diphenylmethyleneamino groups and also by a tetrahydrofuran molecule, situated on the 2-fold axis. Each magnesium atom is also co-ordinated to a terminal tetrahydrofuran molecule and a bromine atom, so completing its 5-fold co-ordination.

The two diphenylmethyleneamino groups are folded away from the bridging THF molecule, causing a slight folding of the 4 membered \((\text{Mg} - \text{N})_2\) ring along the Mg-Mg direction (dihedral angle 154°). The relatively small cross ring Mg...Mg distance of 2.886(2) Å is a common feature of molecules involving small bridging atoms such as carbon, nitrogen and oxygen, and can be compared with observed Mg...Mg distances in other molecules, namely 2.93 Å in \((\text{Me}_2\text{N(CH}_2)_2\text{NMeMgMe})_2\) (Magnuson and Stucky, 1969) and 2.85 Å in \((\text{Bu}^+\text{OMgBrOEt})_2\) (Moseley and Shearer, 1968). Similar values of 2.67 Å and 2.72 Å have been observed in the polymeric molecules, \((\text{Et}_2\text{Mg})_n\) and \((\text{Me}_2\text{Mg})_n\) (Weiss, 1964-65). The smaller values quoted involve electron-deficient alkyl bridging structures, which by virtue of their inherent small bridging angles, require small metal-metal separations. Where bridging involves larger atoms such as chlorine or bromine, corresponding larger metal-metal separations are observed, namely, 3.73 Å in \((\text{Et}_2\text{MgCl}_3\text{(THF)})_2\) (Toney and Stucky, 1971) and 3.20 Å in \(\text{Mg}_4\text{Br}_6\text{O}(\text{Et}_2\text{O})_4\) (Stucky and Rundle, 1964).

The metal-metal distance is a determining factor in the observed ring angles of 87.2(2)° at nitrogen and 89.0(2)° at magnesium (Table 3.4). When these angles are compared with the theoretical angle at nitrogen of 120°, and 109.5° at magnesium, the extent of distortion is apparent, although similar angles at nitrogen and magnesium have been observed in other structures, namely 91.5° at magnesium and 88.5° at nitrogen in \((\text{Me}_2\text{N(CH}_2)_2\text{NMeMgMe})_2\) (Magnuson and Stucky, 1969).

The magnesium has been described as formally 5-co-ordinate, although the observed angles are not those expected for 5-fold geometry. The magnesium-bromine distance of 2.472(2) Å (Table 3.3) compares well with values of 2.44(2) Å in PhMgBr \((\text{Et}_2\text{O})_2\) (Stucky and Rundle, 1964), and MgBr\(_2\) (THF)\(_4\) (Schröder and Spandau, 1966).
Perspective View of the Molecule

$\text{(Ph}_2\text{C:NMgBr)}_2 \cdot 3\text{THF}$
Figure 3b

Co-ordination Around Magnesium

(Ph₂C:NMeBr)₂ - 3 THF
The magnesium–nitrogen distances of 2.077(3) Å and 2.078(5) Å agree with other bridging Mg–N distances, namely, 2.104 Å in (Me₂N(CH₂)₂NMeMgMe)₂ (Magnuson and Stucky, 1969) and 2.15 Å in (EtMgBrNEt₃)₂ (Toney and Stucky, 1967). The terminally co-ordinated magnesium–oxygen distance, Mg(1)–O(1) 2.066(5) Å, agrees closely with other recorded Mg–O distances, 2.04 Å in (EtMg₂Cl₃(THF))₂ (Toney and Stucky, 1971), 2.06 Å in PhMgBr(ET₂O)₂ (Stucky and Rundle, 1964), and 2.06 Å in MeMgBr(THF)₃ (Vallino, 1969).

The bridging Mg–O distance Mg(1)–O(2) 2.453(5) Å is unusually long, and intermediate in value between a terminally co-ordinated Mg–O distance and the minimum separation of 3.25 Å expected for a non-bonded Mg–O interaction (Bondi, 1964). It appears significant that this bridging interaction, in addition to being unusually long, is also virtually co-linear with the terminal Mg(1)–O(1) bond, O(1)–Mg(1)–O(2) 173.3° (Table 3.4), and may well be justification for attributing this interaction to the secondary bond classification (Alcock, 1972). A closer approach by this bridging THF molecule is presumably prevented by steric blocking due to the diphenylmethyleneamino groups.

The C = N bond distance of 1.259(8) Å lies within the range of values normally found in co-ordinated methyleneamino groups where the nitrogen atom is in an sp² hybridisation state, namely, 1.279(14) Å in [(Bu₂C:N)₂Be]₂ (Farmer, Shearer, Sowerby and Wade, 1976), 1.270(10) Å in LiAl(N:CBu₂)₄ (Wade, Shearer, Snaith and Sowerby, 1971), and 1.280(10), 1.273(11) and 1.280(10) Å in P(N:CPh₂)₃ (Shearer, 1976).

The two phenyl rings are planar within experimental error (Table 3.7), and inclined at 93.6° to each other. The mean phenyl carbon–carbon bond distances C(2) to C(7) and C(8) to C(13) are both 1.378 Å, in good agreement with the mean phenyl C–C distances of 1.386 Å in o-SnCl₃-p-MeC₆H₃C(:NH)p-C₆H₄Me (Fitzsimmons, Othen, Shearer, Wade and Whitehead, 1977), and 1.385 Å in (Ph₂C:NH₂)₂SnCl₆ (Othen, Shearer, Wade and Whitehead, 1978). The single bond C(sp²)–C(sp²) distances C(1)–C(2) and C(1)–C(8) have a mean of 1.505 Å, a value which is in good agreement with the mean of 1.480 Å in o-SnCl₃-p-MeC₆H₃C(:NH)p-C₆H₄Me (Fitzsimmons, Othen, Shearer, Wade and Whitehead, 1977) and 1.491 Å found in [(Ph₂C:N)₂SnCl₂] (Mahmoud and Wallwork, 1974).
In the bridging THF molecule, the ring is nonplanar with carbon atoms C(18) and C(18\textsuperscript{n}) lying 0.12 Å above and below the mean plane of the molecule. Numerous examples of co-ordinated non-planar THF molecules appear in the literature, for example, MgBr\textsubscript{2}·4 THF (Perucaud and Le Bihan, 1968), MeMgBr(THF)\textsubscript{3} (Vallino, 1969), and (EtMg\textsubscript{2}Cl\textsubscript{3}(THF))\textsubscript{2} (Toney and Stucky, 1971).

The ring distances range from 1.448(9) to 1.462(12) Å with a mean value of 1.453 Å, which is in close agreement with the mean values of 1.462 Å found in Li\textsubscript{4}Cr\textsubscript{2}Me\textsubscript{8}(THF)\textsubscript{4} (Krausse, Marx and Schöde, 1970), and 1.490 Å in (Na(THF))\textsubscript{2}(AlMe\textsubscript{2}THF)\textsubscript{2} (Brauer and Stucky, 1970).

The terminally co-ordinated THF molecule appears to be planar, but the unusually short C(15)−C(16) distance of 1.338(22) Å, compared with values of 1.448(9) to 1.488(10) Å for the remaining ring distances suggests disordering of the molecule. High values of $U_{11}$ for atoms C(15) and C(16) (Table 3.2), this direction being approximately perpendicular to the plane of the ring, provides further evidence for ring disorder. Ring disorder is also a common feature of co-ordinated THF molecules, and numerous examples have been observed, namely, MeMgBr(THF)\textsubscript{3} (Vallino, 1969), (Na(THF))\textsubscript{2}(AlMe\textsubscript{2}THF)\textsubscript{2} (Brauer and Stucky, 1970), and (EtMg\textsubscript{2}Cl\textsubscript{3}(THF))\textsubscript{2} (Toney and Stucky, 1971).

**Intramolecular Contacts**

Selected intramolecular contacts less than 4 Å are given in Table 3.5. Several non-bonding interactions occur between bromine and the bridging and terminal THF molecules, namely, Br(1)⋯O(1) 3.399 Å, Br(1)⋯O(2) 3.403 Å, Br(1)⋯C(14) 3.496 Å, Br(1)⋯C(18) 3.761 Å, and Br(1)⋯C(18\textsuperscript{n}) 3.831 Å. The two angles at magnesium, BR(1)−Mg(1)−O(1) 96.5°, and Br(1)−Mg(1)−O(2) 87.3°, are similar and less than the theoretical Br(1)−Mg(1)−O(1) angle of 109.5° which would be expected in the absence of the bridging THF molecule. The non-bonding interactions involving bromine are probably a consequence of these smaller angles at magnesium.

Non-bonding interactions between nitrogen and the bridging THF molecule, namely, N(1)⋯O(2) 2.739 Å and N(1)⋯C(18) 3.162 Å, may be reflected in the (Mg−N)\textsubscript{2} ring dihedral angle of 154°.

Several interactions between the phenyl rings, and in particular C(7)⋯C(8) 2.889 Å, are a consequence of the reduced angle C(2)−C(1)−C(8) of 114.5°, compared with the theoretical angle of 120°.
Intermolecular Contacts

Intermolecular contacts are listed in Table 3.6, and are all greater than 3.7 Å.

The superscript II refers to the atom at $(-x, y, 0.5 - z)$. 
Figure 3c

Projection on the [0 1 0] Plane

(Ph\textsubscript{2}C::NMgBr\textsubscript{2} \cdot 3 THF)
Table 3.1  \((\text{Ph}_2\text{C:NMgBr})_2\cdot 3\text{THF}\)

**Final Atomic Co-ordinates And Their Estimated Standard Deviations**

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<thead>
<tr>
<th>Atom</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.2285(1)</td>
<td>0.0889(1)</td>
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<td>0.25(-)</td>
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### Table 3.2 (Ph₂C : NMgBr)₂·3THF

#### Anisotropic Thermal Parameters (Å²) And Their Estimated Standard Deviations (both x 10⁴)

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### Table 3.3  \((\text{Ph}_2\text{C:NMgBr})_2 \cdot 3\text{THF}\)

**Final Bond Distances (Å) And Their Estimated Standard Deviations**  
\((\text{Å} \times 10^3)\)

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Table 3.4  \((\text{Ph}_2\text{C}:\text{N Mg Br})_2 \cdot 3\text{THF}\)

**Final Bond Angles And Their Estimated Standard Deviations**

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Table 3.5  \( (\text{Ph}_2\text{C : NMgBr})_2 \cdot 3 \text{THF} \)

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The superscript II refers to the atom at \(-x, y, 0.5 -z\).
### Table 3.6

(Ph$_2$C:NMgBr)$_2$ • 3 THF

**Intermolecular Contacts (< 4.0 Å)**

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<th>Equivalent</th>
<th>A - B (Å)</th>
</tr>
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<td>3.960</td>
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<tr>
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<td>C(11)</td>
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</tbody>
</table>

The intermolecular contacts refer to the position of atom A in the original co-ordinates list, and atom B as obtained from this, using the symmetry operations given.

<table>
<thead>
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<th>Position</th>
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</tr>
<tr>
<td>2</td>
<td>-x, -y, -z</td>
</tr>
<tr>
<td>3</td>
<td>x, -y, z -0.5</td>
</tr>
<tr>
<td>4</td>
<td>-x, y, 0.5 - z</td>
</tr>
<tr>
<td>5</td>
<td>0.5 + x, 0.5 + y, z</td>
</tr>
<tr>
<td>6</td>
<td>-0.5 - x, -0.5 - y, -z</td>
</tr>
<tr>
<td>7</td>
<td>0.5 + x, 0.5 - y, 0.5 + z</td>
</tr>
<tr>
<td>8</td>
<td>-0.5 - x, y - 0.5, -0.5 - z</td>
</tr>
</tbody>
</table>
Table 3.7  \((\text{Ph}_2\text{C}:\text{NMgBr})_2 \cdot 3\text{THF}\)

**Mean Planes**

**Plane 1**

\[7.7024X + 9.3012Y - 8.2540Z = -0.6937\]

<table>
<thead>
<tr>
<th>Atom</th>
<th>C(2)</th>
<th>C(3)</th>
<th>C(4)</th>
<th>C(5)</th>
<th>C(6)</th>
<th>C(7)</th>
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<th>N(1)*</th>
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</thead>
<tbody>
<tr>
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<td>-0.012</td>
<td>0.010</td>
<td>0.003</td>
<td>-0.015</td>
<td>0.012</td>
<td>0.0007</td>
<td>-0.340</td>
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</table>

**Plane 2**

\[13.5941X - 3.2283Y + 5.0669Z = 3.5128\]

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<tr>
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<th>C(9)</th>
<th>C(10)</th>
<th>C(11)</th>
<th>C(12)</th>
<th>C(13)</th>
<th>C(1)*</th>
<th>N(1)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{P})</td>
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<td>0.006</td>
<td>-0.003</td>
<td>-0.005</td>
<td>0.009</td>
<td>-0.006</td>
<td>-0.067</td>
<td>-1.15</td>
</tr>
</tbody>
</table>

**Plane 3**

\[15.7624X - 3.1834Y - 0.3049Z = -0.4094\]

<table>
<thead>
<tr>
<th>Atom</th>
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<th>C(14)</th>
<th>C(15)</th>
<th>C(16)</th>
<th>C(17)</th>
<th>Mg(1)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{P})</td>
<td>-0.008</td>
<td>-0.018</td>
<td>0.041</td>
<td>-0.045</td>
<td>0.029</td>
<td>-0.157</td>
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</tbody>
</table>

**Plane 4**

\[-2.5610X - 0.0Y + 21.3392Z = 5.3348\]

<table>
<thead>
<tr>
<th>Atom</th>
<th>O(2)</th>
<th>C(18)</th>
<th>C(19)</th>
<th>C(18(\text{II}))</th>
<th>C(19(\text{II}))</th>
<th>Mg(1)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{P})</td>
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<td>-0.124</td>
<td>-0.074</td>
<td>0.124</td>
<td>-1.438</td>
</tr>
</tbody>
</table>

**Angles Between Planes**

Plane 1  Plane 2  93.6°

Superscript \(\text{II}\) refers to the equivalent position \((-x, y, 0.5-z)\)

\(X, Y, Z\) refer to fractional co-ordinates along the unit cell edges, and

\(\text{P}\) refers to the distance of an atom in \(\text{Å}\), from the mean plane.

Atoms marked * are not included in the mean plane calculations.
Table 3.8  \((\text{Ph}_2\text{C}:\text{NMgBr})_2\cdot 3\text{THF}\)

Analysis of Variance

<table>
<thead>
<tr>
<th>IFol Ranges</th>
<th>N</th>
<th>(\sum w A^2/N)</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 - 15</td>
<td>178</td>
<td>3.35</td>
<td>0.233</td>
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<tr>
<td>15 - 20</td>
<td>371</td>
<td>3.90</td>
<td>0.184</td>
</tr>
<tr>
<td>20 - 25</td>
<td>314</td>
<td>2.53</td>
<td>0.089</td>
</tr>
<tr>
<td>25 - 40</td>
<td>503</td>
<td>3.23</td>
<td>0.055</td>
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<tr>
<td>40 - 40</td>
<td>441</td>
<td>2.94</td>
<td>0.037</td>
</tr>
<tr>
<td>80 - 300</td>
<td>218</td>
<td>4.00</td>
<td>0.041</td>
</tr>
</tbody>
</table>
Table 3.9

\[(\text{Ph}_2\text{C}:\text{NMgBr})_2 \cdot 3\text{THF}\]

**Final Values of The Observed and Calculated Structure Factors**
CHAPTER FOUR

THE CRYSTAL STRUCTURE OF

o-SnCl$_3$-$p$-CH$_3$C$_6$H$_3$C(:NH)$_p$-C$_6$H$_4$CH$_3$
Introduction

The preparation and crystal structure described and discussed in the following section relates to a new ortho-metallation reaction involving tin.

Ortho-metallated reactions are well known in transition metal chemistry. The extent of such systems has been reviewed (Parshall, 1970) and is perhaps typified by the metallation of azobenzene to give products of the type

\[ \text{o - } M \text{C}_6\text{H}_4\text{N} \equiv \text{N(Ph)} \]

where \( M \) can include Mn(CO)_4, Re(CO)_4, Fe(CO)(\( \pi - \text{C}_5\text{H}_5 \)), Ru(CO)(\( \pi - \text{C}_5\text{H}_5 \)) and Ni(\( \pi - \text{C}_5\text{H}_5 \)) (Bruce, Iqbal and Stone, 1970).

Metallation reactions involving main group metals are less common and normally apply to the lighter elements, as in the lithium complex

\[ \text{o - LiC}_6\text{H}_4\text{C(CH}_3\text{)}_2\text{CH}_2\text{N(CH}_3\text{)}_2 \]

(Vaux, Jones and Hauser, 1965) and in the beryllium complex

\[ \text{o - Be(Bu}^1\text{)}\text{C}_6\text{H}_4\text{CH = N(Bu}^1\text{)} \]

(Anderson and Coates, 1974).

An ortho-metallation reaction involving tin has previously been reported (van Koten, Noltes and Speck, 1976) but this involves a different preparative route.

In the new tin compound, ortho-metallation was inferred from its spectroscopic data, and in view of the rarity of such reactions involving tin, a crystallographic study was carried out in order to confirm the structure.

Preparation

The compound was obtained by the reaction of equimolecular quantities of di-p-tolylmethyleneaminolithium and tin tetrachloride in an ether-hexane solvent. The mixture was warmed to room temperature and stirred overnight, after which, all solvent was removed under vacuum. The resulting solid was redissolved in dry toluene and the solution filtered to remove lithium chloride formed in the reaction.

Evidence for ortho-metallation was obtained from spectroscopic analysis of the toluene recrystallised product. Peaks in the infrared spectrum attributable to co-ordinated ether had disappeared, and a strong absorption had developed in the N-H stretching region (3275 - 3335 cm\(^{-1}\)). Changes in the C = C, C = N and Sn-Cl stretching regions were also observed.
The \(^1\)H n.m.r. spectra also indicated the presence of a hydrogen atom attached to nitrogen, whilst an indication of the 5-co-ordinate state of the tin atom was obtained from Mossbauer spectroscopy.

The overall reaction can probably be expressed by the scheme

\[
\text{LiN} = \text{C(p-tolyl)}_2 + \text{SnCl}_4 \text{ ether} \rightarrow \text{SnCl}_3 \left[ N = \text{C(p-tolyl)}_2 \right] \left( \text{Et}_2 \text{O} \right)_n + \text{LiCl}
\]

\[
\text{SnCl}_3 \left[ N = \text{C(p-tolyl)}_2 \right] \left( \text{Et}_2 \text{O} \right)_n \rightarrow \text{dissociation}
\]

\[
(p\text{-tolyl})_2 \text{C} = \text{N SnCl}_3 + n\text{Et}_2\text{O}
\]

\[
\text{rearrangement}
\]

\[
\text{Cl}_3\text{Sn} \overset{\text{NH}}{\text{Me}} \text{C} \overset{\text{Me}}{\text{C}} \text{Me}
\]

The preparation and spectroscopic characterisation of the compound was undertaken by Othen and Wade, 1977, whilst supporting Mössbauer data was provided by Fitzsimmons, 1977.

**Crystal Data**

The compound crystallised in the form of colourless air sensitive plates, showing prominent \(\{112\}\) faces. The crystal selected had dimensions 0.40 x 0.25 x 0.10 mm, and was sealed in a quartz capillary tube for the purpose of data collection.

Preliminary studies using the Weissenberg and precession methods showed the unit cell to be monoclinic. The conditions limiting reflections were:

\[
\begin{align*}
\text{h0l} & \quad l = 2n \\
0\text{k0} & \quad k = 2n
\end{align*}
\]

and these uniquely defined the space group as \(P2_1/c\). More reliable unit cell dimensions were obtained from a least-squares treatment of the positions of twelve high order reflections, measured on a four-circle diffractometer.
$\text{o-SnCl}_3 \cdot \text{p-CH}_3 \text{C}_6 \text{H}_3 \text{C( : NH)p-C}_6 \text{H}_4 \text{CH}_3$

\[
\begin{align*}
M &= 433.2 \\
a &= 9.299(2) \text{Å} \\
b &= 14.553(2) \text{Å} \\
c &= 12.982(2) \text{Å} \\
\beta &= 107.74(2)° \\
Z &= 4 \\
D_c &= 1.707 \text{g cm}^{-3}
\end{align*}
\]

Absorption coefficient for MoK $\lambda$ radiation ($\lambda = 0.71069$ Å) = 18.42 cm$^{-1}$

The crystal density was not measured owing to the limited availability of crystals.

**Data Collection**

The intensity data were collected on a four-circle diffractometer as before, using a $\theta - 2\theta$ scan technique. Each reflection was scanned in eighty steps of 0.01° with a counting time of three seconds per step, and a background count of sixty seconds at the beginning and end of each scan. Three standard reflections were measured every forty reflections, and these showed only random variations during the data measurement, indicating that the crystal was stable throughout the experiment. These standard reflections were used to place the data on a common scale.

Two non-equivalent octants of reciprocal space were scanned up to a limit of $\theta = 23°$, to give a total of 2807 unique reflections of which 1802 were classed as observed, having net counts greater than 2.5σ.

The data were corrected for Lorentz and polarisation effects, and also for absorption.

**Solution And Refinement**

The structure was solved with the help of the Patterson function which for the space group $P2_1/c$ takes the form

\[
P(u, v, w) = \frac{4}{V} \sum_0^u \sum_0^v \sum_0^w \left\{ |F(hk1)|^2 \cos 2\pi(hu + lw) + |F(hkl)|^2 \cos 2\pi(hu - lw) \right\} \cos 2\pi kv
\]

The function was computed over one-quarter of the unit cell, and was sharpened by using as coefficients, the products $|Fo|, |E|$. 

67
In the Patterson function, peaks due to double weight Sn–Sn vectors would be expected on the Harker plane at positions $2x, -0.5, 2z - 0.5$ and on the Harker line at $0, 0, 0.5 - 2y, 0.5$.

In the vector map, two large peaks were observed at $(0, 0, 0.1720, 0.5)$ and $(0.4301, 0.5, 0.2408)$ with peak heights of 451 and 410 with respect to the origin peak of 999. These peaks were taken as being due to Sn–Sn double weight vectors and are consistent with a tin atom at $(0.215, 0.164, 0.371)$. The corresponding single weight Sn–Sn vector was indicated by a peak of height 218 at $(0.430, 0.327, 0.471)$.

Three peaks were observed in general positions at $(0.450, 0.341, 0.561)$, $(0.181, 0.379, 0.688)$ and $(0.151, 0.122, 0.065)$ and with peak heights of 103, 73 and 85. These peaks were considered to be due to Sn–Cl vectors and enabled the three chlorine atom positions to be calculated as $(0.235, 0.177, 0.190)$, $(-0.034, 0.215, 0.317)$ and $(0.366, 0.286, 0.436)$. These positions were confirmed by the appearance of peaks at the position expected for the remaining Sn–Cl vectors.

The positions and temperature factors of the tin and three chlorine atoms were refined using full matrix least-squares methods.

Initially, all atoms were given isotropic temperature factors of $0.05\AA^2$, and after one cycle of refinement, the R-value was 0.28. The set of structure factors was used to compute an electron density difference map, which revealed sixteen additional peaks of heights varying from 10.7 to $5.6e.\AA^{-3}$. The next highest peak had a height of $2.8e.\AA^{-3}$. These sixteen peaks were assigned to the remaining non-hydrogen atoms of the molecule on the basis of the metallated structure.

The tin and chlorine atoms were then given anisotropic temperature factors, and after two cycles of refinement, the R-value was reduced to 0.07. Two further refinement cycles in which the remaining atoms were given anisotropic temperature factors, further reduced the R-value to 0.043.

An electron density difference map based upon all twenty located atoms, revealed further peaks with heights of up to $0.5e.\AA^{-3}$. Several of these peaks occurred in the vicinity of the tin and chlorine atoms and were interpreted as diffraction ripples. The next fourteen peaks occurred in regions where hydrogen atoms were expected, and these were interpreted as being due to their presence.
A single peak was observed close to the nitrogen atom, at a position where a hydrogen atom would be expected in view of the metallation. The methyl hydrogen atoms could not be positioned accurately, since the peaks attributable to these atoms were rather elongated.

In the final stages of refinement, all of the hydrogen atoms were placed at calculated positions. For the methyl hydrogen atoms, this was achieved by positioning one hydrogen atom in a trans configuration with respect to an adjacent carbon-carbon bond, and orienting the others with respect to this atom. During refinement, the positional parameters of the phenyl hydrogen atoms were not allowed to vary, but their isotropic temperature factors were allowed to refine to a common value.

The methyl hydrogen atoms were allowed to refine by treating the methyl group as a rigid body and the group as a whole was allowed to rotate about axes parallel to the unit cell edges. The methyl carbon atom was allowed to refine normally, but the carbon-hydrogen distances and angles were maintained at 1.055 Å and 109.5° respectively. A second isotropic temperature factor was refined for the methyl hydrogen atoms. After two cycles of refinement, all parameter shifts were less than 0.3 of the corresponding e.s.d., and the R-value dropped to its final value of 0.033 (Rw = 0.036). A final electron density difference map revealed no electron density greater than 0.3 e Å⁻³.

A unit weighting scheme was used in the early stages of refinement, but was replaced for subsequent refinement by the scheme

\[ W = \frac{1}{\sigma^2(F) + gF^2} \]

where \( \sigma^2F \) is the variance of \( F \) and \( g \) is a factor included for the purpose of decreasing the weight of strong reflections. The final value of \( g \) was 0.001408.

The weight analysis is given in Table 4.8 and the final atomic parameters and thermal parameters are given in Tables 4.1 and 4.2.

The scattering factors used in this refinement were taken from:

- Acta Cryst., A24 (1968) 321
- Acta Cryst., A24 (1968) 390

The complex components of the scattering factors were obtained from:


Structure factors are listed in Table 4.9.
Description And Discussion of The Structure

The crystal structure consists of monomeric molecular units of \( \text{o-SnCl}_3-p-	ext{C}_6\text{H}_3\text{C}(:\text{NH})-p-	ext{C}_6\text{H}_4\text{CH}_3 \), which are illustrated in Figure 4a, and confirm that ortho-metalation had occurred.

The molecule shows a distorted trigonal bipyramidal arrangement about the tin atom, with the three chlorine atoms occupying two of the equatorial sites and one axial site, whilst the metallated ring carbon atom and the methyleneamine nitrogen atom span the remaining equatorial and axial sites. This intramolecular co-ordination results in a 5-membered tin metallocycle which is almost planar and inclined at 6.5° to the mean plane of the adjacent phenyl ring with which it shares a common edge (Table 4.5). This metallated ring shows a deviation from planarity of up to 0.032Å, compared with the non-metallated ring which is planar, within experimental error.

The occupation of an equatorial site by the metallated aryl group and an axial site by the nitrogen atom is in accordance with the well documented preference of the more electronegative ligands for the axial positions in a trigonal bipyramidal arrangement (Meuttertries and Schunn, 1966) and typified in the \((\text{CH}_3)_3\text{SnCl} \cdot \text{pyridine complex (Hulme, 1963)}.\)

Four of the metallocycle angles lie in the range 114 – 117° (Table 4.4) and are less than the ideal 120°. The angle at tin \(\text{N(1)}-\text{Sn(1)}-\text{C(14)}\) for a value of 76.5° compared with the value of 90° for a regular trigonal bipyramid, and the value of 60° for a planar 5-membered ring with the remaining angles being 120°. Hence the tin atom lies 0.21Å out of the plane defined by the equatorial atoms, on the same side as the axial chlorine atom \(\text{Cl(1)}\).

The smaller ring angle at tin leads to \(\text{Cl(1)}\) being displaced towards the metallated phenyl carbon atoms, thereby resulting in a departure of the \(\text{N(1)}-\text{Sn(1)}-\text{Cl(1)}\) angle, 173.1°, from linearity.

Similar deviations have been observed in the related ortho-metallated benzylamine derivative \(\text{o-}(\text{SnBrPh}_2)\text{C}_6\text{H}_4\text{CH}_2\text{N(CH}_3)_2\) (van Koten, Noltes and Speck, 1976) in which the axial bond angle is 171.0° and the ring angle at tin is 75.3°, and also in the metallated benzylideneaniline-manganese derivative \(\text{o-}\text{Mn(CO)}_4\text{C}_6\text{H}_4\text{CH}:\text{NPh}\) (Little and Doedens, 1973) with a ring angle at manganese of 79.4°. In the manganese derivative, the metallocycle is inclined at 3° to the metallated ring compared with 6.5° in the present compound. A similar comparison with the benzylamine derivative cannot be made since the tin metallocycle is markedly non-planar.
Figure 4a

Perspective View of the Molecule

o-SnCl$_3$-p-MeC$_6$H$_3$C(:NH)p-C$_6$H$_4$Me
The two equatorial Sn–Cl bond distances (Table 4.3) of 2.315(2) Å and 2.318(2) Å are the same within experimental error and agree with the equatorial Sn–Cl distance of 2.321(1) Å in the trigonal bipyramidal anion \((\text{CH}_3)_2\text{SnCl}_3^-\) (Einstein and Penfold, 1968).

The axial Sn–Cl distance of 2.416(2) Å is longer than the equatorial distances, an effect frequently observed in trigonal bipyramidal compounds, and corresponds to the axial Sn–Cl distance of 2.42(4) Å in \((\text{CH}_3)_3\text{SnCl. pyridine}\) (Hulme, 1963).

The Sn(1)–N(1) bond distance of 2.511(12) Å is much shorter than the distance of 2.511(12) Å in the benzylamine complex where sp³ hybridised nitrogen is involved, and is also shorter than in the 6-co-ordinate compound \((\text{CH}_3)_2\text{Sn(C}_9\text{H}_5\text{NO})_2\), where the nitrogen is sp² hybridised with distances of 2.31(1) Å and 2.38(1) Å (Schlemper, 1967). In the former case, the authors Koten, Noltes and Speck, considered an Sn–N distance of 2.511 Å to be unusually long.

The C(sp²)–C(sp²) bond, C(9)–C(14), which forms part of the metallocycle, is of length 1.391(8) Å and like all the phenyl carbon–carbon bond distances is consistent with the accepted value of 1.395 Å for phenyl C–C bond distances. The single bond C(sp²)–C(sp²) distances, C(1)–C(2) 1.474(8) Å and C(1)–C(9) 1.487(8) Å can be compared with the values C(1)–C(8) 1.509(8) Å and C(1)–C(2) 1.502 Å found in \((\text{Ph}_2\text{C:NMgBr})_2\cdot 3\text{THF}\). The C(sp³)–C(sp²) bonds C(5)–C(8) and C(12)–C(15) have a mean length of 1.526 Å.
Intramolecular Contacts

A list of selected intramolecular contacts less than 4.0 Å is given in Table 4.6.

Several of these contacts, such as Cl(1)-Cl(2) refer to distances between atoms bonded to a common atom, and short separations for such atoms would be expected.

Those contacts which involve the tin and nitrogen atoms, Sn(1) - C(1) 3.020 Å, Sn(1) - C(9) 2.977 Å, and N(1) - C(9) 2.362 Å are a measure of the molecular distortion which results from ortho-metallation.

The C(7) - C(10) contact of 3.132 Å reflects the angle of 49.40° between the mean planes of the two phenyl groups.

Intermolecular Contacts

A list of intermolecular contacts less than 4.0 Å is given in Table 4.7. Only one N ... Cl contact is less than the van der Waals distance of 3.50 Å (Bondi, 1964), and this involves the axial chlorine atom Cl(1) at equivalent position (x, 0.5 - y, 0.5 + z) with a N ... Cl distance of 3.362 Å.

This particular contact is significant in that it involves the nitrogen co-ordinated hydrogen atom H(1). The N(1) ... Cl(1) distance is within the accepted N - H ... Cl hydrogen bonding distance of 2.88 - 3.38 Å (Pimental and McClellan, 1960) and the N(1) - H(1) - Cl(1) angle is 144° 39'.

Two contacts were found involving carbon and chlorine atoms, C(1) - Cl(3) 3.469 Å with Cl(3) at equivalent position (-x, -y, -z) and C(15) - Cl(2) 3.464 Å with Cl(2) at equivalent position (-x, y - 0.5, -z - 0.5). In both cases however, the H ... Cl distances were greater than 2.9 Å, and this was thought to preclude any significant degree of hydrogen bonding.

The crystal structure can thus be described in terms of chains of discrete molecular units linked through N - H ... Cl hydrogen bonding. (Figure 4b).
Figure 4b

Projection on the \([1 \ 0 \ 0]\) Plane

0 to 0.5 Along a

\(o-\text{SnCl}_3-p-\text{MeC}_6\text{H}_3\text{C} (: \text{NH})_p-\text{C}_6\text{H}_4\text{Me}\)
Figure 4c

Projection on the [1 0 0] Plane 0.5 to 1 Along a

\( \alpha - \text{SnCl}_3 - p - \text{MeC}_6\text{H}_3\text{C}(-\text{NH}) - p - \text{C}_6\text{H}_4\text{Me} \)
Table 4.1  
\(\text{o-SnCl}_3-\text{p-CH}_3\text{C}_6\text{H}_3\text{C(}:\text{NH})\text{p-CH}_3\text{C}_6\text{H}_4\text{CH}_3\)

**Final Atomic Co-ordinates And Their Estimated Standard Deviations**

<table>
<thead>
<tr>
<th>Atom</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
</tr>
</thead>
<tbody>
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<td>Sn(1)</td>
<td>0.21605(3)</td>
<td>0.16432(3)</td>
<td>0.37098(3)</td>
</tr>
<tr>
<td>Cl(1)</td>
<td>0.2435(3)</td>
<td>0.1723(1)</td>
<td>0.1920(2)</td>
</tr>
<tr>
<td>Cl(2)</td>
<td>-0.0308(2)</td>
<td>0.2164(2)</td>
<td>0.3157(2)</td>
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Mean Planes

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\[
3.8543X + 12.1324Y + 2.8723Z = 3.1414
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Plane 2

\[
8.0244X + 2.0220Y + 2.5914Z = 3.3040
\]

<table>
<thead>
<tr>
<th>Atom</th>
<th>C(9)</th>
<th>C(10)</th>
<th>C(11)</th>
<th>C(12)</th>
<th>C(13)</th>
<th>C(14)</th>
<th>C(1)*</th>
<th>Sn(1)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>0.031</td>
<td>-0.009</td>
<td>-0.022</td>
<td>0.032</td>
<td>-0.011</td>
<td>-0.021</td>
<td>0.075</td>
<td>-0.277</td>
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</tbody>
</table>

Plane 3

\[
8.1541X + 3.3609Y + 1.7415Z = 2.9757
\]

<table>
<thead>
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<th>N(1)</th>
<th>C(1)</th>
<th>C(9)</th>
<th>C(14)</th>
<th>C(2)*</th>
<th>C(10)*</th>
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</thead>
<tbody>
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<td>0.021</td>
<td>-0.043</td>
<td>0.036</td>
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Plane 4

\[
-3.8127X - 0.4531Y + 12.8928Z = 4.0901
\]

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<th>C(14)</th>
<th>Sn(1)*</th>
</tr>
</thead>
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<tr>
<td>P</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>-0.205</td>
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</table>

Plane 5

\[
8.3367X + 3.1374Y + 1.2359Z = 2.7465
\]

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<th>C(1)</th>
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</tr>
</thead>
<tbody>
<tr>
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<td>-0.009</td>
<td>0.032</td>
<td>-0.014</td>
<td>0.108</td>
</tr>
</tbody>
</table>

where X, Y, Z refer to fractional co-ordinates along the unit cell axes, and P represents the distance in Å of an atom from the mean plane.

Atoms marked * are not included in the mean plane calculation.

Angles Between Planes

<table>
<thead>
<tr>
<th>Plane 1</th>
<th>Plane 2</th>
<th>49.40°</th>
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</thead>
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<td>Plane 2</td>
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<td>6.48°</td>
</tr>
<tr>
<td>Plane 1</td>
<td>Plane 3</td>
<td>44.78°</td>
</tr>
<tr>
<td>Plane 3</td>
<td>Plane 4</td>
<td>89.01°</td>
</tr>
<tr>
<td>Contact</td>
<td>Bond Length (Å)</td>
<td></td>
</tr>
<tr>
<td>------------------</td>
<td>-----------------</td>
<td></td>
</tr>
<tr>
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</tr>
<tr>
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</tr>
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<tr>
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</tr>
<tr>
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<tr>
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</tr>
<tr>
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</tr>
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<tr>
<td>C(7) ····· C(10)</td>
<td>3.132</td>
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</tr>
</tbody>
</table>
Table 4.7  o-SnCl₃-p-CH₃C₆H₅C(:NH)-p-C₆H₄CH₃

Intermolecular Contacts (< 4.0 Å)

<table>
<thead>
<tr>
<th>Atom A</th>
<th>Atom B</th>
<th>Equivalent</th>
<th>Cell</th>
<th>A - B (Å)</th>
</tr>
</thead>
<tbody>
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</tr>
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<td>C(13)</td>
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</table>
Table 4.7 (cont.)  \( \alpha-SnCl_3-p-C_6H_3C(\text{NH})p-C_6H_4CH_3 \)

The intermolecular contacts refer to the position of atom A in the original co-ordinates list, and atom B as obtained from this using the symmetry operations given.

<table>
<thead>
<tr>
<th>Equivalent</th>
<th>Position</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>( x, y, z )</td>
</tr>
<tr>
<td>2</td>
<td>( -x, -y, -z )</td>
</tr>
<tr>
<td>3</td>
<td>( x, 0.5-y, 0.5+z )</td>
</tr>
<tr>
<td>4</td>
<td>( -x, y-0.5, -z-0.5 )</td>
</tr>
</tbody>
</table>
Table 4.8

\[ o-\text{SnCl}_3-p-\text{CH}_3\text{C}_6\text{H}_3\text{C}(:\text{NH})p-\text{C}_6\text{H}_4\text{CH}_3 \]

**Analysis of Variance**

\[
\sin \theta \quad 0.00 - 0.18 - 0.22 - 0.26 - 0.28 - 0.31 - 0.33 - 0.35 - 0.38 - 0.40 - 0.43
\]

\[
\begin{array}{cccccccccc}
N & 199 & 167 & 227 & 139 & 197 & 164 & 170 & 260 & 144 & 135 \\
V & 165 & 150 & 151 & 152 & 155 & 151 & 166 & 164 & 164 & 150 \\
\end{array}
\]

\[
\left( \frac{F_0}{F_{\text{max}}} \right)^{1/2} \\
0.00 - 0.23 - 0.25 - 0.27 - 0.29 - 0.32 - 0.34 - 0.38 - 0.42 - 0.49 - 1.00
\]

\[
\begin{array}{cccccccccc}
N & 242 & 158 & 163 & 159 & 240 & 137 & 197 & 167 & 165 & 174 \\
V & 202 & 182 & 163 & 176 & 139 & 162 & 143 & 137 & 132 & 109 \\
\end{array}
\]

\( N \) is the number of reflections in the group and

\[
V = 100 \left[ \frac{M \sum w \Delta^2}{N \sum w} \right]^{1/2}
\]

where the first summation is over the reflections in the group, and the second summation is over all reflections. \( M \) is the total number of reflections.
Table 4.9

\[ \text{o-SnCl}_3 \cdot \text{p-MeC}_6\text{H}_3\text{C(=NH)p-C}_6\text{H}_4\text{Me} \]

**Final Values of the Observed and Calculated Structure Factors**
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<th>M</th>
<th>K</th>
<th>L</th>
<th>INFO</th>
<th>INFO</th>
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<td>3</td>
<td>4</td>
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</tr>
<tr>
<td>8</td>
<td>6</td>
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<td>359</td>
<td>408</td>
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... (Continued)
<table>
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<th>K</th>
<th>L</th>
<th>10FO</th>
<th>10FC</th>
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<td>3</td>
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<td>27</td>
<td>9</td>
<td>3</td>
<td>382 354</td>
<td>+14</td>
</tr>
</tbody>
</table>

- Numbers in the 'H' column represent hour, 'K' represent degree, 'L' represent minutes, '10FO' represent 10 degrees from the equator, and '10FC' represent 10 degrees from the crease. 
- The values are given in terms of degrees and minutes. 
- The table is used to find the number of minutes away from the equator or the crease. 
- The formula to calculate the minutes is: 
  
  minutes = |(hour * 15) - (degree * 10)| 

- Example: 
  
  For H=2, K=3, L=95, the calculation would be: 
  
  minutes = |(2 * 15) - (3 * 10)| = 15 

- This is used in navigation and astronomy to determine the position of celestial objects.
CHAPTER FIVE

THE CRYSTAL STRUCTURE

OF

$\text{(Ph}_2\text{C}:\text{NH}_2^+)\text{SnCl}_6^{2-}$
Introduction

As a result of the successful orthometallation reaction described in the previous chapter, an attempt was made to modify the reaction to allow the insertion of a carbonyl group between the tin atom and metallated phenyl carbon atom. The metallocycle would be then expanded to six atoms.

The preparation was unsuccessful in terms of the isolation of a metallated product, and gave instead, an ionic species whose structure was established through this work as \((\text{Ph}_2\text{C}:\text{NH}_2\text{})_2\text{SnCl}_6^{2-}\).

Preparation

A 1:1:1 molar ratio of diphenylmethyleneamine, tin tetrachloride and dry pyridine was dissolved in chloroform. The mixture was heated overnight at a temperature of approximately 130°C, under an atmosphere of carbon monoxide at about 10 atmospheres pressure. Colourless crystals were found around the mouth of the reaction vessel and these were removed and dried.

Spectroscopic analysis again suggested the occurrence of orthometallation, and the appearance of an infrared absorption peak at 1710 cm\(^{-1}\) was interpreted as being due to the presence of a carbonyl group (\(\text{C} = \text{O}\) stretching region 1660 - 1710 cm\(^{-1}\)).

The preparation and spectroscopic characterisation of the compound was undertaken by Othen and Wade, 1977.

Crystal Data

The compound crystallised in the form of colourless plates, which for the purpose of data collection, were sealed in quartz capillary tubes. The crystal selected had dimensions of 0.35 x 0.2 x 0.1 mm.

Preliminary studies using the Weissenberg and precession methods established the unit cell as monoclinic. The conditions limiting reflections were

\[
\begin{align*}
\text{h0l} & \quad \text{l} = 2n \\
0k0 & \quad \text{k} = 2n
\end{align*}
\]

and these uniquely defined the space group as \(P2_1/C\). More accurate unit cell dimensions were obtained from a least-squares treatment of the positions of twelve high order reflections, measured on a four-circle diffractometer.
(Ph₂C₃:NH₂⁺)₂SnCl₆²⁻

\[ M = 361.7 \]
\[ a = 8.616(3) \text{Å} \]
\[ b = 16.826(6) \text{Å} \]
\[ c = 10.483(6) \text{Å} \]
\[ \beta = 112.22(3)^\circ \]
\[ Z = 2 \]
\[ D_m = 1.707 \text{g cm}^{-3} \text{ (Flotation in 1,4 dibromobutane/CHCl₃)} \]
\[ D_c = 1.708 \text{g cm}^{-3} \]

Absorption coefficient for MoKα radiation = 13.78 cm⁻¹

**Data Collection**

The intensity data were collected on a four-circle diffractometer, as previously described, using a θ - 2θ scan technique. Each reflection was scanned in eighty steps of 0.01° with a counting time of three seconds per step, and a background count of sixty seconds at the beginning and end of each scan. Three standard reflections were measured every forty reflections, and these showed no systematic variations during the data measurement, indicating that the crystal had remained stable. These standard reflections were used to place the data on a common scale.

Two non-equivalent octants of reciprocal space were scanned up to a limit of θ = 20°, to give a total of 2773 unique reflections of which 1804 were classed as observed reflections having net counts \( \geq 2.5\sigma \). The data was corrected for Lorentz and polarisation effects, and also for absorption.

**Solution And Refinement**

The structure was solved with the aid of the Patterson function which for the space group P2₁/c takes the form

\[ P(u, v, w) = \frac{4}{V} \sum_{u} \sum_{v} \sum_{w} \{ |F(hkl)|^2 \cos 2\pi(u + l) \}
\]

\[ + \{ |F(\bar{h}kl)|^2 \cos 2\pi(u - l) \} \cos 2\pi k v \]
The function was sharpened by using as coefficients, the products $|F_o| |E|$

An examination of the vector map revealed a large peak at the position $(0.0, 0.5, 0.5)$ of height 743 compared to an origin peak of 999. This peak was interpreted as being due to a double weight Sn-Sn vector and was consistent with tin atoms being situated at the origin $(0, 0, 0)$ and at $(0, 0.5, 0.5)$. Three smaller peaks were observed in general positions at $(0.272, 0.0, -0.015)$, $(0.030, 0.143, 0.063)$ and $(0.127, 0.030, 0.244)$ and with peak heights of 308, 166 and 119 respectively. These peaks were considered to be due to Sn-Cl vectors and enabled positions for the three chlorine atoms to be chosen as $(0.272, 0.0, -0.015)$, $(0.030, 0.143, 0.063)$ and $(0.127, 0.031, 0.244)$, but due to the mirror planes at $v = 0$ and $v = 0.5$ in the Patterson function, the relative signs of the $y$-co-ordinates of the chlorine atoms could not be determined from the Sn-Cl vectors.

Since the tin atom was situated at the origin, it will only contribute to the structure factors of planes with $k + l$ even, and hence an electron density difference map calculated from these structure factors, will show mirror symmetry at $y = 0$ and $y = 0.5$. To overcome this problem, structure factors were calculated for the tin atom, the chlorine atom with a $y$-co-ordinate of zero, and the second chlorine atom which was assigned a $y$-co-ordinate of $+0.143$. From the subsequent difference map, the third chlorine atom position was revealed with co-ordinates $(0.128, -0.031, 0.242)$.

The positions of the tin and three chlorine atoms were refined using full-matrix least squares methods, and after one cycle the $R$-value was 0.41. The calculated structure factors based upon the tin and chlorine atoms were used to compute a further electron density difference map which showed fourteen peaks of heights varying from 10 to $15e.Å^{-3}$, against a background electron density of up to $4e.Å^{-3}$. These peaks were assigned to the remaining non-hydrogen atoms, and showed the presence of a diphenylmethyleneammonium cation. All eighteen atoms were now refined isotropically to give an $R$-value of 0.090.

Refinement with anisotropic temperature factors for the tin and chlorine atoms, gave an $R$-value of 0.062, and with anisotropic thermal parameters for all atoms, the $R$-value was reduced to 0.041.
An electron density difference map revealed a peak of height $1 \text{e.Å}^{-3}$ lying close to the tin atom (1.01 Å) and twelve further peaks of heights ranging from 0.3 to 0.6 $\text{e.Å}^{-3}$ were identified in positions expected for hydrogen atoms.

In the final stages of refinement, the two hydrogen atoms attached to nitrogen were placed at the positions obtained from the difference map, but the phenyl hydrogen atoms were placed at positions calculated to give C−H distances of 1.08 Å. The positions of the hydrogen atoms were not refined but the positions of the phenyl hydrogen atoms were recalculated before each refinement cycle. A common isotropic temperature factor was refined for all of the phenyl hydrogen atoms, with a separate isotropic factor for the two hydrogen atoms attached to nitrogen. The R-value now reached its final value of 0.035 (Rw = 0.037) and all parameter shifts were less than 0.3 of the corresponding e.s.d.

A final electron density difference map revealed a peak of height $0.3 \text{e.Å}^{-3}$, close to one of the chlorine atoms. No other peaks greater than $0.3 \text{e.Å}^{-3}$ were observed.

A unit weighting scheme was used in the early stages of refinement, but was replaced in the final refinement by the weighting scheme

$$W = \frac{1}{(\sigma^2(F) + gF^2)}$$

The final value of $g$ was 0.0017.

The weighting analysis is given in Table 5.8, and the final atomic parameters and thermal parameters are given in Tables 5.1 and 5.2.

Atomic scattering factors were taken from:

- Acta Cryst., A24 (1968) 321
- Acta Cryst., A24 (1968) 390

The complex components of the scattering factors for tin and chlorine were obtained from:


Structure factors are listed in Table 5.9.
Description And Discussion of The Structure

The structure consists of diphenylmethyleneammonium ions, \( \text{Ph}_2 \text{C} : \text{NH}_2^+ \) and hexachlorostannate ions \( \text{SnCl}_6^{2-} \). The tin atom of the \( \text{SnCl}_6^{2-} \) ion is situated at a centre of symmetry so that the asymmetric unit contains one \( \text{Ph}_2 \text{C} : \text{NH}_2^+ \) ion and half of an \( \text{SnCl}_6^{2-} \) ion.

Although the hexachlorostannate ion is relatively well known, having been described as early as 1922 (Dickenson, 1922) very little structural information appears to have been reported concerning protonated methyleneamine derivatives, despite the significance of recent work establishing the cation as a complex-stabilising ligand (Mason and Rucci, 1971).

The cation is isoelectronic with the corresponding alkene, \( \text{Ph}_2 \text{C} = \text{CH}_2 \) and can function as a \( \pi \)-bonding donor (Abel, Rowley, Mason and Thomas, 1974). Although the chemistry of the dimethylmethyleneammonium ion has been described (Eschenmoser, 1970) and imminium salts have recently been reviewed (Böhme and Vicke, 1977) it is thought that this is the first reported crystallographic analysis of a protonated methyleneamino derivative.

The Diphenylmethyleneammonium Ion \( \text{Ph}_2 \text{C} : \text{NH}_2^+ \)

The cation (Figure 5a) shows a trigonal planar geometry at nitrogen following co-ordination of the proton, with only slight deviation from regular trigonal bond angles (Table 5.4). The atoms N(1), C(1), C(2) and C(8) are coplanar within experimental error, and the atoms H(1) and H(2) lie close to the mean plane defined by these atoms (Table 5.7). The two phenyl rings are planar within experimental error and are inclined at an angle of 62.5° with respect to each other and individually lie at angles of 32.4° and 37.9° with respect to the mean plane of N(1), C(1), C(2) and C(8).

The C = N bond distance of 1.296(7) Å is close to the C = N distance of 1.302(43) Å found in the related cation \( (\text{CH}_3)_2 \text{C} = \text{N} (\text{CH}_3)_2^+ \) (Trefonas, Flurry, Majeste, Meyers and Copeland, 1966). These values can be compared with C = N distances found in other co-ordinated methyleneamines, where the nitrogen atom is also in an sp\(^2\) hybridised state. In LiAl(N:C\(\text{Bu}^t\)_2)_4 (Wade, Shearer, Snaith and Sowerby, 1971), a value of 1.270(10) Å was observed and in \( (\text{Bu}^t\)_2 \text{C} : \text{N}_2 \text{Be} \)_2 (Shearer and Sowerby, 1971), a value of 1.279(14) Å.
Figure 5a

Perspective View of the Diphenylmethyleneammonium Ion

\[ \text{(Ph}_2 \text{C: NH}_2^+ \}_2 \text{SnCl}_6^{2-} \]
Figure 5b

Perspective View of the Hexachlorostannate Ion

\[
(\text{Ph}_2\text{C}:\text{NH}_2^+)\_2\text{SnCl}_6^{2-}
\]
In the phosphorous derivative, $P(\text{N:CPh}_2)_3$ (Shearer, 1976), values of 1.280(10), 1.273(11) and 1.280(10)Å were recorded. Alcock and Pierce-Butler, 1965, observed similar values of 1.268(21), 1.260(24), 1.258(21) and 1.279(22)Å in $(\text{Ph}_2\text{C:N})_4\text{Si}$, 1.275(8) and 1.258(8)Å in $(\text{Ph}_2\text{C:N})_4\text{Ge}$, and 1.330(36)Å in $(\text{Ph}_2\text{C:N})_4\text{Sn}$.

The weighted means of these values is 1.270(5)Å and when this value is compared with the C = N distance of 1.296(7)Å found in the present work, then the difference is seen to be not significant.

A study has been made of the relative azomethine stretching frequencies on a series of methyleneamine, protonated and BF$_3$ co-ordinated complexes (Samuel, Snaith, Summerford and Wade, 1970). In every instance an increase in stretching frequency occurred from 33 and 65 cm$^{-1}$ (2.0 - 4.0%) for the protonated derivatives and slightly less for the BF$_3$ co-ordinated derivatives 2.0 - 3.0%). A similar increase in C≡N stretching frequencies has been reported in the co-ordination of nitriles to form adducts of the type $R - C = N, MX_n$ (Walton, 1965). Although this increase may arise in part from the mechanical constraint applied to the nitrogen atom of the co-ordinated nitrile (Coerver and Curran, 1958), there is X-ray crystallographic evidence that co-ordination is accompanied by a shortening of the C≡N bond length, that is a slight increase in the bond order. This was attributed to a modification of the hybridisation at nitrogen (Gerrard, Lapport, Pyszora and Wallis, 1960).

The reverse situation applies to the co-ordination of ketones to Lewis acids MX$_n$, through the carbonyl oxygen, where a marked decrease in the carbonyl stretching frequency occurs (Susz and Cooke, 1954), (Susz and Chalandon, 1958, Bellamy, 1968). This decrease is usually attributed to electron withdrawal from oxygen.

The protonation of a methyleneamine may also lead to a withdrawal of electron density from the C = N bond, thereby decreasing the bond order and increasing the bond length. The available data however, is not sufficient to justify this assumption.

The $(\text{sp}^2) - C(\text{sp}^2)$ single bond distances C(1) - C(2) and C(1) - C(8) have a mean of 1.462Å and this is in agreement with the mean of 1.480Å found in the metallated compound previously described. The average C - C bond lengths for the phenyl rings C(2) to C(7) and C(8) to C(13), are 1.384Å and 1.386Å, in good agreement with the values of 1.386Å and 1.387Å, for the phenyl groups in the metallated compound, C(2) to C(7) and C(9) to C(14), suggesting that protonation does not significantly effect these bond lengths.
The Hexachlorostannate Ion \( \text{SnCl}_6^{2-} \)

The hexachlorostannate ion (Figure 5b) is formed as a consequence of the ability of the tin atom to expand its co-ordination from four to six.

The angles at tin are very close to those expected for regular octahedral co-ordination with \( \text{Cl}-\text{Sn}-\text{Cl} \) angles varying from 89.6 to 91.0° (Table 5.4), and these values must reflect the absence of any angular distortion effects around the ion. Some distortion can be seen in the varying \( \text{Sn}-\text{Cl} \) bond distances (Table 5.3). The longest of these is \( \text{Sn}(1)-\text{Cl}(2) \) with a separation of 2.456(1)Å, whilst \( \text{Sn}(1)-\text{Cl}(3) \) is the shortest with a distance of 2.413(1)Å, and \( \text{Sn}(1)-\text{Cl}(1) \) lying intermediate with a value of 2.426(1)Å.

The atoms \( \text{Cl}(1) \) and \( \text{Cl}(2) \), both in the molecule at \((-x, y-0.5, -z-0.5)\) are involved in short intermolecular contacts with \( N(1) \), namely, 3.406Å for \( \text{Cl}(1) \) and 3.321Å for \( \text{Cl}(2) \). Both of these contacts are less than the van der Waals distance of 3.50Å (Bondi, 1964), (Table 5.6). A hydrogen bond \( N-H...Cl \) is formed by \( N(1), H(2) \) and \( \text{Cl}(2) \) at the equivalent position described above. The \( N-H...Cl \) angle is 165°, and the \( N...Cl \) distance (3.32Å) is within the accepted \( N-H...Cl \) hydrogen bonding distance of 2.88 - 3.38Å (Pimental and McClellan, 1960) (Figure 5c).

It is interesting to compare the \( \text{Sn}-\text{Cl} \) distances found in this work with previous values recorded in the literature. The mean value is 2.43Å, and this is in close agreement with distances taken from the early literature, for which only mean values were quoted, 2.43Å in \((\text{N}_2\text{H}_5)_2\text{SnCl}_6\) (Schaffer, 1954), 2.44Å and 2.46Å in \( K_2\text{SnCl}_6 \) and \((\text{NH}_4)_2\text{SnCl}_6 \) (Dickinson, 1922). A more recent set of \( \text{Sn}-\text{Cl} \) distances reported by Brill, Gearhart and Welsh in 1973, include 2.411(2)Å in \( K_2\text{SnCl}_6 \), 2.421(1)Å in \((\text{NH}_4)_2\text{SnCl}_6 \), 2.423(3)Å in \( \text{Rb}_2\text{SnCl}_6 \), 2.423(5)Å in \( \text{Cs}_2\text{SnCl}_6 \), and 2.402(3)Å in \((\text{CH}_3)_4\text{N}_2\text{SnCl}_6 \).

In a recent paper describing the structure of 4-chloropyridinium hexachlorostannate (Gearhart, Brill, Welsh and Wood, 1972), the hexachlorostannate ion is shown to be an almost perfect octahedron from an angular point of view, but tetragonally distorted due to the presence of three pairs of crystallographically inequivalent chlorine atoms. This results in three sets of \( \text{Sn}-\text{Cl} \) bonds, two of which were found to be similar in length, 2.414(4)Å and 2.419(2)Å, whilst the third set was markedly longer, 2.463(3)Å.
These values agree very closely with the change of values found in the present work, and the longer distance, 2.463(3) Å, is similarly attributed to N-H...Cl intermolecular hydrogen bonding, with an N...Cl contact of 3.244 Å. The N-H...Cl angle is 135.7°. A similar distortion of Sn-Cl bond length has been reported for the compound, \( [(\text{Me}_2\text{N})_2\text{CH}]_2\text{SnCl}_6 \) (Uyarov, 1976), where Sn-Cl distances of 2.411(5) Å, 2.424(5) Å and 2.430(5) Å were found. For this latter Sn-Cl value of 2.430(5) Å, the chlorine atom was found to be involved in C-H...Cl intermolecular hydrogen bonding, with a C...Cl contact of 3.37 Å.

**Intramolecular Contacts**

A list of selected intramolecular contacts less than 4.5 Å is given in Table 5.5.

Several of these contacts such as Cl(1)-Cl(2) refer to distances between atoms bonded to a common atom, and short separations for such atoms would be expected.

Within the cation, short contacts are found between N(1) and C(3) 2.878 Å, and between N(1) and C(13) 2.907 Å and these reflect the inclination of the phenyl rings out of the plane defined by N(1), C(1), C(2) and C(8). A short separation, 3.115 Å, between C(7) and C(9) also reflects the inclination of the phenyl rings to each other.

**Intermolecular Contacts**

A list of intermolecular contacts less than 4.0 Å is given in Table Only one N...Cl contact was found less than the van der Waals distance of 3.50 Å (Bondi, 1964).
Figure 5c

Projection on the [1 0 0] Plane

\((\text{Ph}_2 \text{C} : \text{NH}_2^+)\)\(_2\) \(\text{SnCl}_6^{2-}\)
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<tr>
<th>Atom</th>
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<th>y/b</th>
<th>z/c</th>
</tr>
</thead>
<tbody>
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<td>0.0 (-)</td>
<td>0.0 (-)</td>
</tr>
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<td>0.0587(1)</td>
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<td>0.2423(1)</td>
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<tr>
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</table>
Table 5.2  \((\text{Ph}_2\text{C}::\text{NH}_2^+)\_2\text{SnCl}_6^{2-}\)

Anisotropic Thermal Parameters ($\AA^2$) and Their Estimated Standard Deviations (both $\times 10^4$)

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<th>$U_{22}$</th>
<th>$U_{33}$</th>
<th>$U_{23}$</th>
<th>$U_{13}$</th>
<th>$U_{12}$</th>
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For the hydrogen atoms, $U_{11}$ refers to the isotropic thermal parameter.
Table 5.3  \((\text{Ph}_2\text{C:NH}_2^+)\text{SnCl}_2\text{SnCl}_6^{2-}\)

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The superscript I refers to the atom at equivalent position \((-x, -y, -z)\)
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### Table 5.6

$(\text{Ph}_2\text{C} : \text{NH}_2^+)\text{SnCl}_6^{2-}$

**Intermolecular Contacts (< 4.0 Å)**

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<tr>
<th>Atom A</th>
<th>Atom B</th>
<th>Equivalent</th>
<th>Cell</th>
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Table 5.6 (cont.)  \( (\text{Ph}_2\text{C:NH}_2^+)_2\text{SnCl}_6^{2-} \)

The intermolecular contacts refer to the position of atom A in the original co-ordinates list, and atom B as obtained from this, using the symmetry operations given, and refer to the cell quoted.

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</tr>
<tr>
<td>3</td>
<td>( x, 0.5-y, 0.5+z )</td>
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<tr>
<td>4</td>
<td>( -x, y-0.5, -z-0.5 )</td>
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</table>
Table 5.7 

\( \text{Ph}_2 \text{C:NH}_2^+ \text{SnCl}_2 \) \( \text{N}_6^2- \)

**Mean Planes**

**Plane 1**

\( 3.7839X + 4.3098Y + 6.6164Z = 4.9171 \)

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<th>( \text{N(1)} )</th>
<th>( \text{C(1)} )</th>
<th>( \text{C(2)} )</th>
<th>( \text{C(8)} )</th>
<th>( \text{H(1)*} )</th>
<th>( \text{H(2)*} )</th>
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<td>-0.006</td>
<td>0.002</td>
<td>0.002</td>
<td>-0.02</td>
<td>-0.06</td>
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</table>

**Plane 2**

\(-0.0379X + 9.9371Y + 7.8490Z = 5.3556 \)

<table>
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<th>( \text{C(2)} )</th>
<th>( \text{C(3)} )</th>
<th>( \text{C(4)} )</th>
<th>( \text{C(5)} )</th>
<th>( \text{C(6)} )</th>
<th>( \text{C(7)} )</th>
<th>( \text{C(1)*} )</th>
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</thead>
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<td>0.002</td>
<td>-0.005</td>
<td>0.001</td>
<td>0.006</td>
<td>-0.009</td>
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**Plane 3**

\( 2.9542X - 6.4898Y + 6.9537Z = 2.2275 \)

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<th>( \text{C(9)} )</th>
<th>( \text{C(10)} )</th>
<th>( \text{C(11)} )</th>
<th>( \text{C(12)} )</th>
<th>( \text{C(13)} )</th>
<th>( \text{C(1)*} )</th>
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<tr>
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<td>-0.001</td>
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<td>-0.007</td>
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**Angles Between Planes**

- Plane 1 Plane 2 \( 32.41^\circ \)
- Plane 1 Plane 3 \( 37.87^\circ \)
- Plane 2 Plane 3 \( 62.49^\circ \)

\( X, Y \) and \( Z \) refer to fractional co-ordinates along the unit cell axes, and \( P \) refers to the distance of an atom in \( \text{Å} \), from the mean plane.

Atoms marked * are not included in the mean plane calculation.
Table 5.8  \((\text{Ph}_2\text{C}:\text{NH}_2^+)_2\text{SnCl}_6^{2-}\)

Analysis of Variance

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</thead>
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<tr>
<td>(N)</td>
<td>211 156 192 182 212 163 153 232 165 138</td>
</tr>
<tr>
<td>(V)</td>
<td>141 113 116 113 111 111 113 126 152 130</td>
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</tbody>
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\[
\left[ \frac{F_0}{F_{\text{max}}} \right]^\frac{1}{2}
\]

| 0.0 - 0.24 - 0.37 - 0.30 - 0.33 - 0.36 - 0.39 - 0.43 - 0.48 - 0.56 - 1.0 |
|---|---|
| \(N\) | 212 176 181 197 179 159 185 168 175 172 |
| \(V\) | 153 157 122 128 119 108 102 111 95 115 |
Table 5.9

\[(\text{Ph}_2\text{C}:\text{NH}_2^+)\_2\text{SnCl}_6^{2-}\]

*Final Values of the Observed and Calculated Structure Factors*
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<th>INFO</th>
<th>YPC</th>
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<th>X</th>
<th>L</th>
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<th>YPC</th>
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CHAPTER SIX

THE CRYSTAL STRUCTURE OF

(Bu\textsuperscript{1}C:NLi\textsubscript{6})
Introduction

The increasing role of organolithium compounds in preparative chemistry and the particular ability of lithium alkyls to associate strongly in the solid state, and to a lesser extent in the vapour state (Brown and Rogers, 1957), has led to extensive studies of the structural and bonding properties of these compounds.

Although numerous spectroscopic studies have been made (Rodinov and Shigorin, 1959), only a relatively small number of crystallographic studies have been reported.

In the solid state, dimeric association has been observed in bicyclobutyl lithium – TMED (Zerger and Stucky, 1973), tetrameric association in methyl lithium and ethyllithium (Weiss and Lucken, 1964, Dietrich, 1963) and hexameric association in cyclohexyllithium (Zerger, Rhine and Stucky, 1974), and trimethylsilyllithium (Schaaf, Butler, Glick and Oliver, 1974).

The structure of di-t-butylmethyleneaminolithium is discussed in the following sections, and is shown to be hexameric.

Preparation

The compound was prepared by the low temperature reaction of t-butyllithium and t-butylcyanide in hexane. The mixture was allowed to warm to room temperature with constant stirring, during which, a pale yellow-green solution was formed. On further stirring a white solid precipitated out of solution. Removal of the solvent produced a white powder, which recrystallised from hexane as colourless crystals.

Cryoscopic molecular weight determination in benzene indicated a dimeric structure, and spectroscopic evidence suggested bridging di-t-butylmethyleneamino groups.

The preparation and spectroscopic characterisation of the compound was carried out by Snaith and Wade, 1972.

Crystal Data

The compound crystallised in the form of colourless plates which for the purpose of data collection, were sealed in quartz capillary tubes. The crystal selected had dimensions of 0.45 x 0.25 x 0.2 mm.
Preliminary studies using the Weissenberg and precession techniques established the unit cell as monoclinic. The conditions limiting reflections were

\[ h0l \quad l = 2n \]
\[ 0k0 \quad k = 2n \]

and these uniquely defined the space group as \( P2_1/c \).

More accurate unit cell dimensions were obtained from a least-squares treatment of the positions of twelve high order reflections measured on a four-circle diffractometer.

\((Bu^t_2C:NLi)_6\)

\[
\begin{align*}
M & = 858 \\
a & = 12.429(1)\text{Å} \\
b & = 20.794(2)\text{Å} \\
c & = 13.099(1)\text{Å} \\
\beta & = 116.78(2)\degree \\
Z & = 2 \\
D_c & = 0.943 \text{ g cm}^{-3}
\end{align*}
\]

Absorption coefficient for MoK\(\alpha\) radiation = 0.27 cm\(^{-1}\).

Data Collection

The intensity data was collected on a four-circle diffractometer, using a \(\theta - 2\theta\) scan technique. Each reflection was scanned in eighty steps of 0.01\degree with a counting time of three seconds per step, and a background count of sixty seconds at the beginning and end of each scan. Three standard reflections were measured every forty reflections, and were used to place the data on a common scale.

Two non-equivalent octants of reciprocal space were scanned up to a limit of \(\theta = 20\degree\), beyond which, a rapid decline in intensity occurred. A total of 2817 unique reflections were obtained of which 1625 were classed as observed reflections having net counts \(\geq 2 \sigma\). The data was corrected for Lorentz and polarisation effects and also for absorption.
Solution And Refinement

The structure was solved by the symbolic addition procedure, using a multi-solution programme. The programme calculated E-values and chose three reflections to define the origin assigning positive signs to these reflections. A further fourteen reflections were chosen, the signs of which were varied systematically, so that each of the possible combinations was used together with the origin determining reflections as a starting set for the symbolic addition procedure. The possible sets of phases were compared by calculating an absolute figure of merit, $M(\text{abs})$, (Chapter 1), and also by the use of quartet relationships. Through the application of these rejection tests, the programme produced a single phasing set which enabled signs to be determined for 524 reflections with E-values greater than 1.1.

An E-map was computed, enabling 33 atomic positions to be selected, which could be attributed to the non-hydrogen atoms of three di-t-butylmethyleneaminolithium units. The lithium atoms were located around a crystallographic symmetry centre, the operation of which generated a hexameric lithium structure.

The positional and isotropic thermal parameters of all located atoms were given two cycles of least-squares refinement, which resulted in an R-value of 0.24. An electron density difference map revealed additional peaks with heights of 1.0 to 1.6 eÅ⁻³. Most of these peaks lay close to the methyl carbon atoms attached to C(15) and C(20), but some were close to the methyl carbon atoms around C(11). A further study of the electron density in these regions was carried out by calculating further difference maps, and also by the calculation of difference maps where the relevant methyl carbon atoms were omitted from the structure factor calculations. These indicated disordering in the positions of the methyl carbon atoms attached to C(15) and this was allowed for by selecting further positions for three methyl carbon atoms and assigning occupation factors of 0.5 to the sites of the six methyl carbon atoms.

The methyl carbon atoms attached to C(20) showed very elongated regions of electron density, and suggested considerable libration of this t-butyl group. These methyl carbon atoms were assigned anisotropic thermal parameters. After refinement, the additional peaks associated with C(11) decreased in value, and could not be represented by a simple model.
All atoms were now refined anisotropically with the exception of the disordered t-butyl group involving C(15), which was refined isotropically, to give an R-value of 0.20. A difference map again revealed small peaks around the t-butyl group involving C(20), and a single peak of height 0.9eÅ⁻³ lying close to one of the lithium atoms Li(3). The possibility of disorder in the position of Li(3) was considered, and to resolve this possibility, all atoms were again refined with Li(3) omitted from the refinement. A subsequent difference map now revealed two peaks of heights 0.8 and 0.9eÅ⁻³, with one peak occupying the site of Li(3). The positions of these two peaks were taken as atom sites for Li(3)A and Li(3)B, and both positions were included in a further refinement cycle. A difference map now showed no further peaks in the vicinity of the lithium atoms.

In subsequent work, the t-butyl groups were refined as rigid groups. This was achieved by constraining the group carbon-carbon bond distances to 1.54Å, and constraining the atoms of the group to tetrahedral geometry. For the disordered t-butyl group, the six methyl carbon atoms attached to C(15) were placed at regular intervals apart. Three cycles of refinement reduced the R-value to 0.16, but in the subsequent difference map, several small peaks, 0.3 to 0.5eÅ⁻³ were still observed in the region of the t-butyl group associated with C(20).

Large value temperature factors were found for some of the methyl carbon atoms, particularly those attached to C(11) and C(20) (Table 6.2), and therefore hydrogen atoms were not included in the refinement. In the final stages of refinement, the atomic parameters were refined in three blocks, each consisting of the atoms of one di-t-butylmethylenamino group, all the lithium atoms being refined with each block. In the final refinement cycle, all parameter shifts were less than 0.6 of the corresponding e.s.d.

A unit weighting scheme was used in the early stages of refinement but was replaced in the final refinement by the scheme:

$$W = \frac{1}{\sigma^2(F) + gF^2}$$

The final value of g was 0.00088.

The weighting analysis is given in Table 6.8. Atomic co-ordinates are listed in Table 6.1, and Structure factors are given in Table 6.9. Atomic scattering factors were taken from

Acta Cryst., A24, 1968, 321
Acta Cryst., A24, 1968, 390
Description And Discussion of The Structure

In the crystal, the structure is disordered with two alternate positions for \( \text{Li}(3) \), namely, \( \text{Li}(3)A \) and \( \text{Li}(3)B \). Each molecule may be regarded as hexameric and to contain a 6-membered ring of lithium atoms in the chair configuration. Because of the disorder, the six-membered rings occur in two orientations, A and B, which respectively contain \( \text{Li}(3)A \) and \( \text{Li}(3)B \).

The six di-t-butylmethyleneamino groups comprise the periphery of the molecule and bridge across the six smaller of the eight triangular faces formed by the lithium core. These two arrangements are shown in Figures 6a and 6b, where for clarity the carbon atoms C(160), C(170) and C(180) have been omitted. In these figures, the superscript I has been used to indicate atoms related by the centre of symmetry. Taking the two possible sites for \( \text{Li}(3) \) into account, the lithium atoms lie at the corners of a distorted cube, with each of the six methyleneamino groups bridging one face of the cube.

Six-membered rings of lithium atoms in the chair configuration, have also been found in the hexameric compounds trimethylsilylilithium (Schaaf, Butler, Glick and Oliver, 1974) where silicon atoms bridge the lithium faces, and in cyclohexylilithium (Zerger, Rhine and Stucky, 1974) where bridging occurs through the alpha carbon atoms of the cyclohexyl groups. The hexameric ring structures observed in the above compounds are in contrast to the hydrogen bridged arrangement postulated for hexameric n-butylilithium (Craubner, 1966).

In \((\text{Bu}_2^t\text{C}:\text{NLi})_6\) the six triangular lithium faces are bordered by six relatively short lithium-lithium distances, and six larger lithium-lithium distances. The shorter distances involve atoms adjacent to one another on the edge of the ring and range from 2.35(4) to 2.44(3)\(\AA\) in configuration A, and from 2.23 to 2.44(3)\(\AA\) in configuration B, with a mean value of 2.35\(\AA\) (Table 6.3). The longer distances involve atoms meta to each other on the edge of the ring and range from 3.17 to 3.31\(\AA\) in configuration A, and from 3.13 to 3.23\(\AA\) in configuration B, with a mean value of 3.21\(\AA\). The Li-Li distances in \((\text{Bu}_2^t\text{C}:\text{NLi})_6\) can be compared with mean distances of 2.42(1), 2.60(1) and 2.63(1)\(\AA\) in ethyllithium (Dietrich, 1963), 2.68(5)\(\AA\) in methylilithium (Weiss and Lucken, 1964), 2.74(7)\(\AA\) in bicyclobutylilithium-TMED (Zerger and Stucky, 1973), 2.39(1) and 2.97(1)\(\AA\) in cyclohexylilithium (Zerger, Rhine and Stucky, 1974) and 2.70(3) and 3.27(4)\(\AA\) in trimethylsilylilithium (Schaaf, Butler, Glick and Oliver, 1974). In \((\text{Bu}_2^t\text{C}:\text{NLi})_6\) all of the shorter lithium-lithium distances are less than twice the covalent radius of lithium (1.25\(\AA\)).
Figure 6a

Perspective View of the Molecule

Orientation A

\[(\text{Bu}_2^+ \text{C} : \text{N} \text{Li})_6\]
Figure 6b

Perspective View of the Molecule

Orientation B

\((Bu_2^t C: NLi)_6\)
Figure 6c

View of the 6-membered Lithium Ring \((\text{Bu}_2\text{C}:\text{NLi})_6\)

Orientation A
Dihedral Angle 95.37°

Orientation B
Dihedral Angle 83.56°
Each di-t-butylmethyleneamino group is located above a triangular face on the periphery of the lithium ring, such that the plane of the azomethine linkage is virtually perpendicular to the lithium face (Table 6.7). The lithium–nitrogen distances range from 1.97 to 2.19(3)Å in configuration A, and from 1.97 to 2.16(5)Å in configuration B, with a mean value of 2.06Å. This value is in good agreement with Li–N distances reported for other nitrogen co-ordinated lithium complexes, namely, 2.02 and 2.04Å in fluorenyllithium bis quinuclidine (Brooks, Rhine and Stucky, 1972), 2.06 and 2.09Å in triphenylmethyl lithium – TMED (Brooks and Stucky, 1972), 2.09 and 2.11Å in benzylithium triethylenediamine (Patterman, Karle and Stucky, 1970), 2.09 and 2.13Å in naphthyl bis(lithium – TMED) (Brooks, Rhine and Stucky, 1972), 2.10 and 2.11Å in indenyllithium – TMED (Rhine and Stucky, 1975), 2.09 and 2.11Å in bis(TMED) lithium anthrocenide (Rhine, Davies and Stucky, 1975), 2.06 and 2.07Å in bifluorenyl bis(lithium – TMED) (Walczak and Stucky, 1975), and 2.10Å in stilbene bis(lithium – TMED) (Walczak and Stucky, 1976).

Since each nitrogen atom bridges three adjacent lithium atoms, the folded chair configuration adapted by the lithium atoms, is an arrangement which satisfies the steric requirements of the di-t-butylmethyleneamino groups. It is also apparent that as each nitrogen atom bridges three lithium atoms, so each lithium atom is associated with three nitrogen atoms, thus giving rise to eighteen Li–N bonding interactions. With the six Li–Li ring contacts, a total of twenty four bonding interactions are formed, for which only twenty four electrons are available. The bonding in this region of the molecule must therefore be described as electron deficient. Electron deficiency was also observed in the hexameric compounds trimethylsilyllithium and cyclohexyllithium.

The C = N bond distances range from 1.292(15) to 1.301(16)Å, with a mean value of 1.297(10)Å, and agree with the range of values normally found in co-ordinated methyleneamino groups, namely, 1.279(14)Å in [(Bu₂C:N)₂Be]₂ (Shearer and Sowerby, 1971), 1.270(10)Å in LiAl(N:CBu₂)₄ (Wade, Shearer, Snaith and Sowerby, 1971), and 1.280(10), 1.273(11) and 1.280(10)Å in P(N:CP₆H₅)₃ (Shearer, 1976).

The lengths of the C(sp²)–C(sp³) bonds do not differ significantly from one another, although their precise values will be affected by treating the t-butyl groups as rigid groups. Their mean values are C(1) – C(2), C(1) – C(6) 1.617(14)Å, C(10) – C(11), C(10) – C(15) 1.591(10)Å, and C(19) – C(20), C(19) – C(24) 1.591(16)Å. These values can be compared
with the C(sp²) - C(sp³) bond distances in (C₅H₅)Mo(CO)₂(N:CBu₁₂) of 1.546Å (Shearer and Sowerby, 1973) and in LiAl(N:CBu₁₂)₄ of 1.560Å (Wade, Shearer, Snaith and Sowerby, 1971).

The C(sp³) - C(sp³) bond distances within the t-butyl groups were constrained to 1.540Å during refinement.

**Non-bonding Contacts**

Selected non-bonding contacts less than 4Å within the hexameric molecule are listed in Table 6.5. Many of these contacts involve lithium and methyl carbon atoms, the three shortest being Li(1)...C(3) 2.798Å, Li(1)...C(16) 2.770Å and Li(2)...C(7) 2.737Å.

The relative shortness of these contacts may be due to steric effects but could involve some form of Li...C or Li...H-C interaction. In the compound LiAl(N:CBu₁₂)₄, a bridging hydrogen interaction was suggested to account for an unusually short, 2.37Å, lithium-methyl carbon contact (Shearer, Snaith, Sowerby and Wade, 1971).

Several short contacts were found between the methyl carbon atoms of different t-butyl groups within the same methyleneamino group, the shortest distance being 2.880Å. Longer contacts were found between the methyl carbon atoms of different methyleneamino groups, the shortest contact being 3.612Å.

Non-bonding contacts less than 4Å between hexameric molecules are listed in Table 6.7. Only four such contacts were found, the shortest being 3.772Å.
Figure 6d

Projection on the [1 0 0] Plane

\((\text{Bu}^+ \text{C}:\text{NLi})_6\)
Table 6.1  \( (\text{Bu}^t_2 \text{C} : \text{N Li})_6 \)

**Final Atomic Co-ordinates And Their Estimated Standard Deviations**

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Interatomic Distances (Å) And Their Estimated Standard Deviations (Å x 10^{-3})

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<tr>
<td>$\text{C(9)} \quad \text{C(170)}$</td>
<td>$\text{C(9)} \quad \text{C(170\textsuperscript{1})}$</td>
<td>$3.924$</td>
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<tr>
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<td>$\text{C(12)} \quad \text{C(26)}$</td>
<td>$3.463$</td>
</tr>
<tr>
<td>$\text{C(12)} \quad \text{C(26)}$</td>
<td>$\text{C(13)} \quad \text{C(17)}$</td>
<td>$3.912$</td>
</tr>
<tr>
<td>$\text{C(13)} \quad \text{C(17)}$</td>
<td>$\text{C(13)} \quad \text{C(160)}$</td>
<td>$3.265$</td>
</tr>
<tr>
<td>$\text{C(13)} \quad \text{C(160)}$</td>
<td>$\text{C(13)} \quad \text{C(22\textsuperscript{1})}$</td>
<td>$2.880$</td>
</tr>
<tr>
<td>$\text{C(13)} \quad \text{C(22\textsuperscript{1})}$</td>
<td>$\text{C(14)} \quad \text{C(22\textsuperscript{1})}$</td>
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<tr>
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<td>$3.612$</td>
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Table 6.6 \((Bu^t_2 C : NLi)_6\)

**Intermolecular Non-bonding Contacts \((<4.0\text{Å})\)**

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<th>Atom B</th>
<th>Equivalent</th>
<th>Cell</th>
<th>A - B(Å)</th>
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<td>3.922</td>
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<td>C(12)</td>
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<td>0, 0, 1</td>
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<td>3</td>
<td>1, -1, 0</td>
<td>3.722</td>
</tr>
<tr>
<td>C(21)</td>
<td>C(4)</td>
<td>4</td>
<td>0, 1, 0</td>
<td>3.908</td>
</tr>
</tbody>
</table>

The intermolecular contacts refer to the position of atom A in the original co-ordinates list, and atom B as obtained from this, using the symmetry operations given, and refer to the cell quoted.

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<th>Position</th>
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<tr>
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<tr>
<td>2</td>
<td>(-x, -y, -z)</td>
</tr>
<tr>
<td>3</td>
<td>(-x, 0.5 + y, 0.5 - z)</td>
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<tr>
<td>4</td>
<td>(x, -y - 0.5, z - 0.5)</td>
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</table>
### Table 6.7 \((\text{Bu}_2\text{C:NLi})_6\)

#### Mean Planes

<table>
<thead>
<tr>
<th>Plane 1</th>
<th>[-10.0468x - 3.0993y + 11.4313z = -1.1850]</th>
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<td>Atom</td>
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<table>
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<tr>
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<th>[5.5059x + 10.5840y + 6.0156z = -0.0389]</th>
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<th>[-6.3575x + 16.3822y - 0.9923z = -1.1672]</th>
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<tr>
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<tr>
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<tr>
<td>(P)</td>
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<td>Plane</td>
<td>Equation</td>
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<td>----------</td>
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<tr>
<td>7</td>
<td>(5.3506X + 11.5552Y + 5.7761Z = 1.1358)</td>
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<tr>
<td>8</td>
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<td>10</td>
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<tr>
<td>11</td>
<td>(-2.6580X - 14.6006Y + 9.2041Z = 0.0)</td>
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<tr>
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<td></td>
</tr>
<tr>
<td>12</td>
<td>(5.0183X + 9.8567Y + 6.7670Z = 1.2137)</td>
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<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Plane 1</td>
<td>Plane 2</td>
</tr>
<tr>
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</tr>
<tr>
<td>Plane 5</td>
<td>Plane 6</td>
</tr>
<tr>
<td>Plane 7</td>
<td>Plane 8</td>
</tr>
<tr>
<td>Plane 8</td>
<td>Plane 9</td>
</tr>
<tr>
<td>Plane 10</td>
<td>Plane 11</td>
</tr>
<tr>
<td>Plane 11</td>
<td>Plane 12</td>
</tr>
</tbody>
</table>

The superscript I refers to the position (-x, -y, -z)

X, Y, Z refer to fractional co-ordinates along the unit cell axes, and P refers to the distance in Å of an atom from the mean plane.

Atoms marked * are not included in the mean plane calculation.
Table 6.8  \((Bu^t_2C:NLi)_6\)

Analysis of Variance

| Sin θ 0.00 - 0.14 | 0.18 - 0.20 | 0.23 - 0.25 | 0.27 - 0.29 | 0.31 - 0.33 | 0.35 |
| N 182 | 189 | 124 | 217 | 159 | 152 | 166 | 186 | 159 | 91 |
| V 478 | 377 | 324 | 276 | 270 | 228 | 195 | 192 | 162 | 171 |

\[
\frac{\left(\frac{F_{\text{obs}}}{F_{\text{max}}}\right)^{1/2}}{
\begin{array}{cccccccccc}
0.00 - 0.18 & 0.20 - 0.21 & 0.23 - 0.24 & 0.27 - 0.30 & 0.33 - 0.41 & 1.00
\end{array}
\]

| N 232 | 175 | 103 | 228 | 86 | 206 | 155 | 124 | 163 | 153 |
| V 182 | 239 | 233 | 249 | 353 | 280 | 317 | 365 | 380 | 340 |
Table 6.9

$\left( {\text{Bu}}_2^t \text{C:NLi} \right)_6$

**Final Values of the Observed and Calculated Structure Factors**
CHAPTER SEVEN

THE CYCLOPENTADIENYL GROUP

AS A METAL CO-ORDINATING LIGAND
The Cyclopentadienyl Group As A Metal Co-ordinating Ligand

Interest in the cyclopentadienyl group as a metal co-ordinating ligand arises from its ability to participate in several modes of co-ordination, and to function as both a bridging and a terminal constituent.

The metal derivatives of cyclopentadiene can be conveniently classified into three general types, namely, a symmetrical \( \pi \)-complex with a pentahapto configuration (Figure 7a), a \( \sigma \)-bonded complex incorporating a monohapto co-ordinated cyclopentadienyl ring (Figure 7b) and an asymmetric complex containing di- or trihapto co-ordinated cyclopentadienyl rings (Figure 7c). Fritz, 1964, stated that cyclopentadienyl metal complexes may be assigned to one of these three types by examination of their spectral properties. The general validity of this approach has been supported by the more recent work of Harrison and Healy, 1973.

The pentahapto configuration is the most frequently observed mode of co-ordination, and is typified by the symmetrical \( \pi \)-bonded complex ferrocene (Bohn and Haaland, 1965). The bonding in this case, involves combination of the delocalised cyclopentadienyl ring orbitals with the s, p and d metal orbitals giving rise to nine bonding molecular orbitals, which are occupied by the eighteen available bonding electrons (Cotton and Wilkinson, 1974).

Compounds formed from highly electropositive metals, where d-orbitals of suitable energy are not available for bonding, have tended to be regarded as essentially ionic in character, and the electrostatic requirements of an ionic system also favour the pentahapto configuration.

In several compounds, notably, \((\text{C}_5\text{H}_5)_2\text{Be}\) (Wong, Lee, Chao and Lee, 1972), \((\text{C}_5\text{H}_5)_2\text{Mg}\) (Bunder and Weiss, 1975), \((\text{C}_5\text{H}_5)_2\text{Ti}\) and \((\text{C}_5\text{H}_5)_2\text{In}\) (Frasson, Menegus and Panattoni, 1963), considerable controversy exists as to the extent of ionicity in the bonding. An attempt to resolve this question has been made by studying the \(\text{^{19}F}\) n.m.r. spectra of m- and p-fluorophenylcyclopentadienyl compounds of univalent thallium and collating these with the spectra of the respective alkali metal derivatives and pentahapto metalloccenes (Koridze, Gubin and Ogorodnikova, 1974). On the basis of this study and with regard to a bond of 100\% ionicity in the sodium derivative, and 0\% ionicity in ferrocene, estimates of the bond polarity have been made.
Modes of Co-ordination of the Cyclopentadienyl Group

**Fig. 7a**

**Fig. 7b**

**Fig. 7c**

**Fig. 7d**
in \((C_5H_5)\text{TI}\) and \((C_5H_5)\text{Mg Br}\), showing these compounds to be neither purely ionic nor purely covalent. The bonds appear to be of an intermediate nature with the bond polarity sufficiently high to permit a significant contribution of the ionic component to be assumed in the metal - cyclopentadienyl bonding.

The \(\sigma\)-bonded (monohapto) mode of co-ordination is less frequently observed, although several crystallographic structures demonstrating this mode of co-ordination have been reported, namely, \((C_5H_5)\text{In}\) (Einstein, Gilbert and Tuck, 1972), \((C_5H_5)\text{Mo(NO)}\) (Calderon, Cotton and Legzdins, 1969), \([\text{Ph}]_3\text{PC}_5\text{H}_4\text{Hgl}_2\) (Holy, Baenziger, Flynn and Swenson, 1976), \((C_5H_5)\text{Ti}\) (Calderon, Cotton, DeBoer and Takats, 1971) and \((C_5H_5)\text{Be}\) (Wong, Lee, Chao and Lee, 1972). In each of these structures, the authors believe that the variation in cyclopentadienyl carbon - carbon distances is sufficient to justify preservation of the double bond characteristics of the ring, as observed in cyclopentadiene itself (Liebling and Marsh, 1965). For example, in the compound \((C_5H_5)\text{Mo(NO)}\), the \(\sigma\)-bonded ring has two carbon - carbon distances of 1.349(5) and 1.344(5)\(\text{Å}\), compared with the remaining three distances of 1.468(5), 1.468(5) and 1.442(6)\(\text{Å}\).

In the asymmetric di- and trihapto mode of co-ordination, the evidence for ring localisation is less conclusive. It has also been suggested that a true trihapto configuration involving a \(\pi\)-allyl type interaction cannot be realised owing to the geometric and bonding constraints inherent in the situation (Cotton, 1969). In \((C_5H_5)\text{Mo(NO)}\) (Cotton and Legzdins, 1968), spectroscopic evidence indicated the possibility of two trihapto co-ordinated cyclopentadienyl rings. In a later crystallographic study of this complex (Calderon, Cotton and Legzdins, 1969), the variation in the molybdenum - carbon distances 2.347(4), 2.324(3), 2.444(4), 2.682(5) and 2.609(5)\(\text{Å}\), would appear to support the trihapto configuration. The ring carbon - carbon distances however, showed no significant variations about the mean value of 1.373\(\text{Å}\). Churchill and Fennessey, 1967 have studied a number of pentahapto \(\text{Mo}(C_5H_5)\) complexes and shown that ring tilting and hence variable molybdenum - carbon distances are a common feature of such complexes. The authors consider that molybdenum - carbon distances within the range 2.26 to 2.40\(\text{Å}\) are consistent with pentahapto co-ordination. Since this range includes the shorter Mo - C distances found in \((C_5H_5)\text{Mo(NO)}\), the apparent trihapto ring may still be regarded as conforming to the pentahapto configuration.
Crystallographic studies on the complexes \((\text{C}_5\text{H}_5)_3\text{Ti}\) (Forder and Prout, 1974) and \((\text{C}_5\text{H}_5)_2\text{Ca}\) (Zerger and Stucky, 1974) have reported the presence of dihapto and trihapto rings respectively. In \((\text{C}_5\text{H}_5)_3\text{Ti}\), metal-carbon distances of 2.448(5), 2.481(5), 3.346(6), 3.775(6) and 3.703(6)\(\text{Å}\), strongly support the dihapto configuration, whilst in \((\text{C}_5\text{H}_5)_2\text{Ca}\), the variation in metal-carbon distances 2.701(1), 2.789(2), 2.805(2), 2.951(2) and 2.943(2)\(\text{Å}\), although less pronounced, support a trihapto configuration. In both of these complexes, a slight variation in ring carbon-carbon distances has been taken by the authors to infer a degree of ring localisation, consistent with \(\pi\)-ethylinic and \(\pi\)-allylic co-ordination respectively.

Several crystallographic structures have been reported in which the cyclopentadienyl group functions in a bridging capacity, namely, \((\text{C}_5\text{H}_5)\text{In}\) (Frasson, Menegus and Panattoni, 1963), \((\text{C}_5\text{H}_5)_{2}\text{Pb}\) (Panattoni, Bombieri and Croatto, 1966), \((\text{C}_5\text{H}_5)_3\text{Sc}\) (Atwood and Smith, 1973) and \((\text{C}_5\text{H}_5)\text{Ga}\\(\text{CH}_3\\)_2\) (Mertz, Zettler, Hausen and Weidlein, 1976). When the cyclopentadienyl group functions as a bridging group, the structure is polymeric with puckered chains of metal atoms (Figure 7d), the degree of puckering reflecting the spatial requirements of the terminal substituents (Mertz, Zettler, Hausen and Weidlein, 1976), or of the lone pair electrons on the metal atoms (Panattoni, Bombieri and Croatto, 1976).

In \((\text{C}_5\text{H}_5)\text{In}\) the chain puckering is 2-dimensional and the In-In-In angle is 137°, whereas in \((\text{C}_5\text{H}_5)_{2}\text{Pb}\), the chain puckering is 3-dimensional with Pb-Pb-Pb angles of 118 and 121° respectively. In these bridged compounds, the configuration of the cyclopentadienyl ring varies from pentahapto as in \((\text{C}_5\text{H}_5)\text{In}\) to monohapto as in \((\text{C}_5\text{H}_5)\text{Ga}\\(\text{CH}_3\\)_2\).
CHAPTER EIGHT

THE CRYSTAL STRUCTURE

OF

Na(C₅H₅)(Me₂NCH₂NMe₂)
**Introduction**

Crystallographic studies on the co-ordination complexes of the Group I alkali metals has been mainly concerned with lithium, and have adequately demonstrated the capacity of lithium atoms to co-ordinate strongly to the \( \pi \)-systems of unsaturated hydrocarbon groups or anions (Wakefield, 1974, Stucky, 1974).

By contrast, organosodium complexes, in which the metal-carbon bonding would be expected to be more ionic, have been much less fully studied, although \( \pi \)-type bonding interactions between bis(tetrahydrofuran) sodium units, \( \text{Na(THF)}_2 \), and the benzene rings of complex organo-aluminate anions derived from naphthalene or anthracene have been observed from crystallographic studies on the compounds \( \text{Na(THF)}_2 \text{(Me}_2\text{AlC}_{10}\text{H}_8)_2} \) (Brauer and Stucky, 1970) and \( \text{Na(THF)}_2 \text{Me}_2\text{AlC}_{14}\text{H}_{10}_2 \) (Brauer and Stucky, 1972).

In particular, no definite structural work has been done on a cyclopentadienylsodium complex, even though cyclopentadienylsodium has been the subject of many vibrational and n.m.r. spectroscopic studies (Fritz and Ford, 1971), and is itself widely used as a reagent for the synthesis of transition metal cyclopentadienyl complexes (King and Stone, 1963).

The crystal structure discussed in the following sections, relates to the cyclopentadienylsodium tetramethylethylenediamine complex, \( \text{Na(C}_5\text{H}_5)(\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2) \) which by virtue of its crystalline form, was selected for X-ray crystallographic study, with a view to establishing the mode of attachment of the cyclopentadienyl group to the metal. This work is believed to be the first reported crystallographic structure of a cyclopentadienylsodium complex.

**Preparation**

The compound was prepared by the reaction of equimolecular proportions of cyclopentadienylsodium and tetramethylethylenediamine (TMED) in tetrahydrofuran (THF). The product was recrystallised from hot benzene as chunky, colourless plates, which decompose immediately on exposure to air, turning dark brown and then black.

Characteristic absorptions in its infrared spectrum and a singlet absorption in the \( ^1\text{H} \) n.m.r. spectrum, due to the cyclopentadienyl protons, indicated a pentahapto interaction between the cyclopentadienyl groups and metal atoms.
The preparation and spectroscopic characterisation of the compound was undertaken by Aoyagi and Wade, 1976.

**Crystal Data**

The compound crystallised as colourless platelets which rapidly darkened on exposure to air. For the purpose of data collection, the crystals were sealed in quartz capillary tubes. The crystal selected had dimensions of 0.40 x 0.35 x 0.35 mm.

Preliminary studies using the Weissenberg and precession methods established the unit cell as orthorhombic. The conditions limiting reflections were

<table>
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<th>hkl</th>
<th>No conditions</th>
<th>h00 (h = 2n)</th>
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</thead>
<tbody>
<tr>
<td>0kl</td>
<td>l = 2n</td>
<td>0k0 No conditions</td>
</tr>
<tr>
<td>h0l</td>
<td>l = 2n</td>
<td>00l (l = 2n)</td>
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<tr>
<td>hk0</td>
<td>h = 2n</td>
<td></td>
</tr>
</tbody>
</table>

and these defined the space group as Pcca.

More accurate unit cell dimensions were obtained from a least-squares treatment of the positions of twelve high order reflections, measured on a four-circle diffractometer.

$$\text{Na}(\text{C}_5\text{H}_5)(\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2)$$

- \(M = 204.3\)
- \(a = 15.961\text{Å}\)
- \(b = 8.949\text{Å}\)
- \(c = 18.408\text{Å}\)
- \(Z = 8\)
- \(D_c = 1.031 \text{g.cm}^{-3}\)

Absorption coefficient for MoKα radiation = 9.6 cm⁻¹.

**Data Collection**

The intensity data were collected on a four-circle diffractometer as previously described, using a 0-2θ scan technique. Each reflection was scanned in eighty steps of 0.01° with a counting time of three seconds per step, and a background count of sixty seconds at the beginning and end of each scan. Three standard reflections were measured every forty reflections, and were used to place the data on a common scale.
Three equivalent octants of reciprocal space were scanned up to a limit of $\theta = 20^\circ$, to give after averaging a total of 1234 unique reflections of which 771 were classed as observed reflections having net counts greater than $a$.

The data was corrected for Lorentz and polarisation effects, but not for absorption.

**Solution And Refinement**

The structure was solved by the symbolic addition procedure, using a multi-solution program. A set of normalised structure factors were calculated and signs were given to 170 of these with $|E|$ greater than 1.5. The program initially chose three reflections to define the origin, and these were arbitrarily given positive signs. A further four reflections were chosen, the signs of which were varied systematically so that each of the sixteen possible combinations was used together with the origin determining reflections as a starting set for the symbolic addition procedure. These reflections together with a summary of the results are shown in Table 8.1.

The most self-consistent set corresponds to set 10 which has a consistency index of 0.85. Three other sets have a high consistency index, namely sets 9, 12 and 14, with values of 0.81, 0.81 and 0.79. At the end of each cycle, the signs of the reflections in the starting set are recalculated from the signs of the remaining reflections, although no sign changes were made. In each of the last three sets, a change in sign of one member of the starting set, makes them all equivalent to set 10.

An E-map was computed using the phases estimated from set 10, and revealed the correct positions of all of the non-hydrogen atoms. In the E-map, two relatively large peaks lay on mutually perpendicular 2-fold axes, at the positions $(0.25, 0.0, 0.125)$ and $(0.0, 0.30, 0.25)$, and with peak heights of 5.8 and 5.7. These two peaks were attributed to the sodium atoms. The remaining peaks which occurred in general positions had heights varying from 1.1 to 2.0, against a general background of peak heights up to 1.

All of the atoms were included in two cycles of least-squares refinement, using the block diagonal approximation, at the end of which the $R$-value was 0.134. A further cycle of refinement in which all atoms were given anisotropic temperature factors, further reduced the $R$-value to 0.125. A further difference map showed peaks due to the hydrogen atoms.
Table 8.1

Na(C₅H₅)(Me₂NCH₂CH₂NMe₂)

Symbolic Addition Procedure

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Results

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<th>Set No.</th>
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<th>Changes</th>
<th>Cycles</th>
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<th>No. -</th>
<th>Consistency Index</th>
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<td>84</td>
<td></td>
<td>0.531</td>
</tr>
</tbody>
</table>

Sets 2, 3, 4 → 1
11, 13, 16 → 15
9, 12, 14 → 10
These atoms were placed at their calculated positions and allotted isotropic temperature factors which were allowed to refine. A further refinement cycle now reduced the $R$-value to 0.10. Further refinement using full matrix least-squares saw the $R$-value converge to its final value of 0.087. The parameter shifts in the final cycle were all less than 0.3$\sigma$. A difference synthesis calculated from the final structure factors showed no peaks greater than 0.2$e$.Å$^{-3}$.

An empirical weighting scheme was used in the initial stages of refinement, but was replaced in the final stages by one based on counting statistics as described earlier. The optimum value for $P$ was 0.12 as determined by an even distribution of $w\Delta^2$ as a function of $|Fo|$. The unobserved reflections were not included in the refinement.

The weighting analysis is given in Table 8.8, and the final atomic and thermal parameters are given in Tables 8.2 and 8.3.

Atomic scattering factors were taken from International Tables, Vol. III.

Structure factors are listed in Table 8.9.

**Description And Discussion of The Structure**

The structure, Figure 8a, consists of puckered chains of sodium atoms, each with a chelating TMED molecule attached, and linked by pentahapto cyclopentadienyl groups. Since the sodium atoms lie on perpendicular 2-fold axes, the chain puckering occurs in two mutually perpendicular planes. Each sodium atom is surrounded by a distorted tetrahedral arrangement of two nitrogen atoms from the same TMED group, and two pentahapto cyclopentadienyl groups. The cyclopentadienyl groups are inclined at 88° to the metal-metal vectors, but the ring centres are displaced 0.11Å from these vectors.

The $-M(C_5H_5)M(C_5H_5)M(C_5H_5)$-chain structure of Na$(C_5H_5)(Me_2NCH_2CH_2NMe_2)$ may be compared with the chain structures of In$(C_5H_5)$ (Frasson, Menegus and Panattoni, 1963), Pb$(C_5H_5)_2$ (Panattoni, Bombieri and Croatto, 1966), Ga$(C_5H_5)(CH_3)_2$ (Mertz, Zettler, Hausen and Weidlein, 1976), Zn$(C_5H_5)CH_3$ (Aoyagi, Shearer, Wade and Whitehead, 1978) and Tl$(C_5H_5)$ (Frasson, Menegus and Panattoni, 1963).

In Na$(C_5H_5)(Me_2NCH_2CH_2NMe_2)$, the two distinct Na-Na-Na angles of 128° and 119° (Table 8.5) define the degree of puckering of the chain and reflects the distorted tetrahedral co-ordination of the
Figure 8b

View of the Sodium Chain

Angle at Sodium 119°
Figure 8a

View of the Sodium Chain

Angle at Sodium 128°
sodium atoms. These angles may be compared with angles of 118° and 121° in Pb(C₅H₅)₂ and 137° in In(C₅H₅).

The chelating TMED groups have nitrogen–nitrogen separations of 3.03(1) and 3.04(1)Å (Table 8.4), and both subtend an angle at sodium of 70.5°. The smallness of this angle illustrates the restricted bite of this particular ligand, and also emphasises the importance of metallic radius in determining whether TMED chelates or bridges, as found in the potassium fluorenyl complex, K(C₁₃H₉)(TMED)₂ (Stucky, 1974).

The sodium–nitrogen separations of 2.618(9) and 2.628(7)Å are intermediate in value between the observed Na–N separation of 2.50Å in sodium azide, NaN₃ (Pringle and Noakes, 1968), 2.49Å in Na(C₁₂H₄N₄) (Konno and Seito, 1974), 2.61Å in N(CH₂CH₂OH)₃NaI (Voegele, Fischer and Weiss, 1974), 2.46Å in N(CH₂CH₂OCH₃)₃NaI (Voegele, Thierry and Weiss, 1974) and the theoretical Na–N values calculated for various complexed sodium cations (Rao, Randhawa, Reddy and Chakravorty, 1978). These calculated values include 2.8Å in Na(NH₃)⁺, 2.8Å in Na(pyridine)⁺ and 2.9Å in Na(NH₃)₄⁺.

The chelation of TMED to the sodium atoms produces 5–membered rings, both of which are found to be non-planar (Table 8.7). Within the TMED molecules, the carbon–carbon distances are 1.432(15) and 1.429(12)Å, and the nitrogen carbon distances range from 1.442(15) – 1.477(10)Å and 1.449(13) – 1.463(12)Å respectively.

This structure is consistent with an ionic model of the bonding in terms of Na(TMED)⁺ cations and C₅H₅⁻ anions and may be compared with the structures of Zn(C₅H₅)CH₃ and Ga(C₅H₅)(CH₃)₂. These compounds also have chain structures, but with a greater degree of covalency in the metal–cyclopentadienyl bonding, which may be reflected in the distortion of the cyclopentadienyl ring from pentahapto geometry namely, 65° inclination to the metal–metal vectors in Zn(C₅H₅)CH₃ and 50° inclination in Ga(C₅H₅)(CH₃)₂.

The sodium–cyclopentadienyl carbon distances range from 2.856(15) to 2.963(12)Å for Na(1), and from 2.829(14) to 3.033(12)Å for Na(2). A comparison may be made between these values and relative distances found in the magnesium complexes, Mg(C₅H₅)Br[(C₂H₅)₂N(CH₂)₂N(C₂H₅)₂] (Johnson, Toney and Stucky, 1972) and Mg(C₉H₇)₂ (Atwood and Smith, 1974).
The latter two compounds are considered to possess a degree of covalency in the metal – cyclopentadienyl bonding, and the magnesium – carbon distances of 2.55 and 2.43Å respectively, can be regarded as \( \pi \)-type interaction distances. These values differ by 0.33 and 0.21Å from the value of 2.22Å, attributed to an electron-deficient Mg – C bridging interaction (Atwood and Smith, 1974). If the sodium – carbon distance of 2.63Å found in Na(C\(_5\)H\(_5\)) (Weiss and Sauermann, 1970), can be considered as representative of a bridging Na – C interaction, then a corresponding increase in this value, would give a predicted \( \pi \)-type Na – C interaction in the order of 2.9Å. The observed Na – C distances in the Na(C\(_5\)H\(_5\)) TMED complex are of this order, and this may be interpreted as implying a degree of covalency in the sodium – carbon bonding.

A further comparison can be made between the metal – sodium and metal – nitrogen distances observed in Na(C\(_5\)H\(_5\)) TMED and the magnesium complex, Mg(C\(_5\)H\(_5\))Br \{C\(_2\)H\(_5\))\(_2\)N(C\(_2\)H\(_5\))\(_2\)\}. In the magnesium complex the mean Mg – N distance is 2.61Å, and the mean Mg – C distance is 2.55Å giving a difference (Mg – N) – (Mg C) of 0.29Å.

In the sodium complex, the mean Na – N distance is 2.62Å and the mean Na – C distance is 2.92Å with a difference (Na – N) – (Na – C) of 0.30Å, in very good agreement with the value above.

The cyclopentadienyl groups are planar within experimental error, and the ring carbon – carbon distances range from 1.37(2) to 1.40(2)Å, with a mean value of 1.38(1)Å. This value appears shorter than the mean C – C distances in other metal – cyclopentadienyl complexes in which the degree of covalency is thought to be greater, such as 1.43Å in Fe(C\(_5\)H\(_5\))\(_2\) (Bohn and Haaland, 1965), 1.42Å in Mg(C\(_5\)H\(_5\))\(_2\) (Haaland, Lusztyk, Novak, Brunvoll and Starowieyski, 1974), 1.43Å in Ni(C\(_5\)H\(_5\))\(_2\) (Hedberg and Hedberg, 1970) and 1.41Å in Be(C\(_5\)H\(_5\))\(_2\) (Wong, Lee, Chao and Lee, 1972), and is a further indication as to the anionic character of the cyclopentadienyl rings.

A trend has been observed for transition metal \( \pi \)-cyclopentadienyl complexes which relates the metal – ring centre distance, with the metallic radius of the metal atom (Johnson, Toney and Stucky, 1972). In the case of Na(C\(_5\)H\(_5\)) TMED, the sodium atoms lie 2.68Å from the centre of the cyclopentadienyl ring, and this distance cannot be fitted into such a scheme.
Non-bonding Contacts

Non-bonding contacts occurring within a chain are given in Table 8.6.

Two contacts occur between adjacent cyclopentadienyl rings and these involve atoms C(1) ... C(2\text{II}) with a separation of 3.825\,\text{Å}, and C(1) ... C(5\text{IV}) with a separation of 3.925\,\text{Å}. These interactions are probably the cause of the 0.11\,\text{Å} displacement of the cyclopentadienyl ring centres away from the metal–metal vectors.

Several contacts occur between nitrogen and the cyclopentadienyl carbon atoms, and also between the methyl carbon atoms. No contacts less than 4\,\text{Å} occur between the chains.
Figure 8c

Projection on the [0 1 0] Plane

Na(\text{C}_5\text{H}_5) \text{TMED}
### Table 8.2: \( \text{Na}(\text{C}_5\text{H}_5)(\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2) \)

**Final Atomic Co-ordinates And Their Estimated Standard Deviations**

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<th>(y/b)</th>
<th>(z/c)</th>
</tr>
</thead>
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Table 8.3  \( \text{Na(C}_5\text{H}_5\text{(CH}_3\text{)}_2\text{NCH}_2\text{CH}_2\text{N(CH}_3\text{)}_2} \)  

Anisotropic Thermal Parameters (Å²) And Their Estimated Standard Deviations (both \( \times 10^4 \))

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Table 8.5  \( \text{Na}\{\text{C}_5\text{H}_5\}\{\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2\} \)

**Final Bond Angles And Their Estimated Standard Deviations**

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The intermolecular contacts refer to the position of atom A in the original co-ordinates list, and atom B as obtained from this using the symmetry operations given.

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Table 8.7  \( \text{Na}(\text{C}_5\text{H}_5)(\text{Me}_2\text{NCH}_2\text{NMe}_2) \)

**Mean Planes**

**Plane 1**

\[-11.4229X + 4.6557Y + 8.5779Z = 0.8669\]

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**Plane 2**

\[14.5768X + 0.000Y - 7.4982Z = -1.8745\]

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**Plane 3**

\[13.6626X - 4.6264Y + 0.000Z = 3.4156\]

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The superscripts II and IV refer to equivalent positions \((0.5-x, -y, z)\) and \((-x, y, 0.5-z)\).

\(X, Y, Z\) refer to fractional co-ordinates along the unit cell axes and \(P\) refers to the distance of the atom from the mean plane.

Atoms marked * are not included in the mean plane calculations.
Table 8.8  \( \text{Na(C}_5\text{H}_5\text{)}(\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2) \)

**Analysis of Variance**

| \( |F_0| \) Ranges | \( N \) | \( \sum_{w} \Delta^2/N \) | \( R \) |
|-----------------|--------|-----------------|-----|
| 5 - 8           | 146    | 0.56            | 0.344 |
| 8 - 11          | 173    | 0.71            | 0.203 |
| 11 - 14         | 127    | 0.89            | 0.110 |
| 14 - 24         | 170    | 1.02            | 0.055 |
| 24 - 175        | 155    | 0.73            | 0.036 |
Table 8.9

$\text{Na(C}_5\text{H}_5\text{)}\text{TMED}$

**Final Values of the Observed and Calculated Structure Factors**
CHAPTER NINE

THE CRYSTAL STRUCTURE

OF

Zn(C₅H₅)CH₃
Introduction

The structure described and discussed in this section, relates to a cyclopentadienylzinc derivative in which the zinc is involved in multi-centre bonding to carbon.

The crystal structures of several cyclopentadienyl-group II metal complexes have been reported, namely, biscyclopentadienylberyllium (Wong, Lee, Chao and Lee, 1972, Haaland and Novak, 1974), dicyclopentadienylmagnesium (Bunder and Weiss, 1975), dicyclopentadienylcalcium (Zerger and Stucky, 1974) and also of a cyclopentadienylmercury derivative (Ph$_3$P C$_5$H$_4$Hg)$_2$ (Holy, Baenziger, Flynn and Swenson, 1976). The intervening group IIIB metals, zinc and cadmium, appear to have been neglected, and although several cyclopentadienylzinc derivatives have been synthesised (Strohmeier and Landsfeld, 1960) and various spectroscopic studies reported (Lorberth, 1969, Brunvoll, Cyvin and Schafer, 1970), the present work is believed to be the first reported crystallographic study of a cyclopentadienylzinc derivative.

Previous to this work, the ability of zinc to participate in multi-centre bonding to carbon, could only be inferred from indirect studies, namely, the degree of association of bisphenylethynylzinc (Jeffery and Mole, 1968), the observation of intramolecular metal-double bond interactions, in the cyclisation of di-5-hexenylzinc (St. Denis, Oliver, Dolzine and Smart, 1974), studies of the rates of alkyl group exchange reactions of zinc alkyls (Oliver, 1970) and of the spectroscopic studies of other alkenylzinc compounds (St. Denis, Oliver and Smart, 1972).

Preparation

The compound was prepared from the reaction of methylzinc iodide and sodium cyclopentadienide in tetrahydrofuran, giving colourless needle-shaped crystals, which redissolved readily in tetrahydrofuran. Cryoscopic measurements on the solution, suggested the presence of monomeric units of Zn[C$_5$H$_5$]CH$_3$. The infrared and $^1$H n.m.r. spectra of the solution was consistent with a pentahapto co-ordination of the cyclopentadienyl groups, such as would allow full use of the metals valence shell atomic orbitals, the cyclopentadienyl groups functioning as five electron ligands.

The preparative and spectroscopic work on this compound was undertaken by Aoyagi and Wade, 1977.
Crystal Data

The compound crystallised as white, air-sensitive needles which were sealed in quartz capillary tubes for the purpose of data collection. The crystal selected had dimensions of $0.16 \times 0.26 \times 0.42\,\text{mm}$, with elongation along the $c$-axis.

Preliminary studies using the precession method showed the unit cell to be orthorhombic. The conditions limiting reflections were:

\begin{align*}
    h + k &= 2n \\
    k &= 2n \\
    h &= 2n (l = 2n) \\
    h + k &= 2n \\
    h &= 2n \\
    k &= 2n \\
    l &= 2n
\end{align*}

and these established the space group as either $Cmcm$ or $Cmc21$.

More accurate unit cell dimensions were obtained from a least-squares treatment of the positions of twelve high order reflections, measured on a four-circle diffractometer.

\[
\text{Zn}[\text{C}_5\text{H}_5]\text{CH}_3
\]

\[
\begin{array}{c}
    M = 145.49 \\
    a = 8.944(2)\,\text{Å} \\
    b = 7.044(2)\,\text{Å} \\
    c = 9.476(2)\,\text{Å} \\
    Z = 4 \\
    D_m = 1.60\,\text{g. cm}^{-3} \\
    D_c = 1.60\,\text{g. cm}^{-3}
\end{array}
\]

Absorption coefficient for MoK$_\alpha$ radiation = 38.57 cm$^{-1}$.

Data Collection

The intensity data were collected on a Hilger and Watts four-circle diffractometer using MoK$_\alpha$, Zr-filtered radiation.

A $\theta$-2$\theta$ scanning technique was employed consisting of eighty steps of $0.01^\circ$. A counting time of three seconds per step was chosen together with a background count of sixty seconds measured at the beginning and end of each scan. Three intense reflections were chosen as standards and measured after every forty reflections.
These standard reflections were used to calculate a scale factor enabling the data to be placed on a common scale.

Two equivalent octants $hkI$ and $hkI$ of reciprocal space were scanned, up to a limit of $\theta = 25^\circ$. After averaging, a total of 300 unique reflections were obtained of which 250 were classed as observed reflections, having net counts $\geq 2.5 \sigma$. The data was corrected for Lorentz and polarisation effects and also for absorption.

**Solution And Refinement**

The structure was solved through the use of the Patterson function which for both the centric and non-centric space groups takes the form

$$P(u,v,w) = \frac{8}{V} \sum_{0}^{a} \sum_{0}^{b} \sum_{0}^{c} |F_{hkl}|^2 \cos 2\pi u \cos 2\pi v \cos 2\pi w$$

The function was calculated over one-eighth of the unit cell and sharpened by using as coefficients the products $|F_o||E|$.

Since the unit cell contains four formula-units, certain constraints are placed upon the positions of the zinc and methyl carbon atoms, and of the cyclopentadienyl groups. In the centric case, both the zinc and methyl carbon atoms must occupy 4-fold special positions, whereas in the non-centric case both atoms must lie on the single mirror plane at $x = 0$. Certain constraints are also imposed upon the position of the cyclopentadienyl group, and in the non-centric case, one atom must lie on the mirror plane.

In the vector map, a large peak was observed at the position $(0.0, 0.1825, 0.50)$ with a peak height of 435 with respect to the origin peak of 999. The zinc atom was placed at the position $(0.0, 0.0912, 0.25)$ and for both space groups, a related zinc atom would be situated at the position $(0.0 - 0.0912, 0.75)$, derived by the 2-fold screw axis along $c$, and in the centric case, by the centre at the origin. In both cases, this results in a centrosymmetric arrangement of the zinc atoms, and in the centric space group, the zinc atoms would occupy the 4-fold positions resulting from the intersection of the two mirror planes.

The position of the zinc atom was refined using least-squares methods, and an electron density difference map computed, based upon the phasing of the zinc atoms. This map which is consequently centrosymmetric, revealed a well defined peak of height $4.6 e. \, \AA^{-3}$ at the position $(0.0, 0.3734, 0.25)$ and this was interpreted as being due to the methyl carbon atom.
Further peaks were observed with heights ranging from 3.8 to 4.6 e. Å⁻³, but as these were poorly defined, an attempt was made to improve the resolution by computing a further electron density difference map based upon the refined positions of both the zinc and methyl carbon atoms. With anisotropic temperature factors allotted to both atoms, refinement resulted in an R-value of 0.205.

Since the zinc and methyl carbon atoms are centrosymmetric, then the computed electron density is also centrosymmetric and shows the symmetry of the centric space group Cm cm. Careful examination of the map revealed three peaks in the asymmetric unit, elongated along an arc in a plane passing through the origin and perpendicular to the mirror plane at x = 0. This plane also contains the 2-fold axis parallel to a, which passes through the origin. The elongation of the peaks was attributed to there being several closely spaced atoms per peak, and the atomic positions were selected so that 5-membered rings were generated in two distinct orientations.

Orientation A

In orientation A, one atom lies on the mirror plane at x = 0; whilst in orientation B, one atom lies on the 2-fold axis parallel to a.

For either orientation the cyclopentadienyl groups lie mid-way between the zinc atoms and therefore act as bridging units.

Refinement In The Non-centric Space Group

A cyclopentadienyl group with orientation A satisfies the symmetry requirements of space group Cm cm21. With anisotropic temperature factors for the zinc and methyl carbon atoms, and isotropic temperature factors for the cyclopentadienyl carbon atoms, the R-value becomes 0.0643. With anisotropic temperature factors for the cyclopentadienyl carbon atoms, the R-value became 0.0546.
With MoKα radiation, the zinc atoms make an anomalous contribution to the scattering, which results in different values of the structure factors calculated for the arrangement described above, and the alternate arrangement in which the y and z co-ordinates of the cyclopentadienyl carbon atoms have been reversed in sign. In this latter configuration, R-values of 0.0645 and 0.0549 were obtained corresponding to isotropic and anisotropic temperature factors being attributed to the cyclopentadienyl carbon atoms. These values are in very close agreement with the values obtained previously. Electron density difference maps computed for both arrangements showed small peaks (0.5 - 0.75 e. Å⁻³) lying in positions mid-way between the ring carbon atoms, and strongly suggested the possibility of disordering in the cyclopentadienyl groups, and that the space group was the centric Cm cm.

Refinement In The Centric Space Group

In the centric space group Cm cm, cyclopentadienyl groups may be positioned with orientation A or with orientation B. For either orientation the centre of symmetry at the origin would generate a second 5-membered ring, resulting in disordering of the cyclopentadienyl groups.

The structure was refined for both orientations with anisotropic temperature factors for the zinc and methyl carbon atoms, and isotropic temperature factors for the cyclopentadienyl carbon atoms.

The cyclopentadienyl carbon atoms were assigned site occupation factors of 0.5. Calculated R-values were 0.0629 for orientation A and 0.0647 for orientation B. An electron density difference map computed for each orientation, showed small peaks (0.5 e. Å⁻³) lying between the ring carbon atoms. These peaks occurred at the atomic sites selected for the alternate orientations. The appearance of these peaks led to the calculation of structure factors for a composite structure in which atoms were placed at the sites found for both orientations A and B.

The zinc and methyl carbon atom C(4) were allowed to refine, but the position of the cyclopentadienyl carbon atoms remained fixed. With isotropic temperature factors for the cyclopentadienyl carbon atoms, and occupation factors of 0.25, the R-value decreased to 0.060.
Cyclopentadienyl hydrogen atoms were then placed at their calculated positions, and a weighting scheme applied. In the final refinement, the hydrogen atom positions remained fixed but their isotropic temperature factors were refined as a common factor. The resulting $R$-values were now 0.057 for orientation A and 0.059 for orientation B. An $R$-value based on the composite structure was 0.055.

The calculated $R$-values for the three models, refined with weighting, and with calculated cyclopentadienyl hydrogen atoms, are listed below.

**Calculated $R$-values**

<table>
<thead>
<tr>
<th>Model</th>
<th>Centric Orientation A</th>
<th>Centric Orientation B</th>
<th>Centric Composite</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-value</td>
<td>0.0571</td>
<td>0.0590</td>
<td>0.0550</td>
</tr>
<tr>
<td>$R_w$-value</td>
<td>0.0711</td>
<td>0.0792</td>
<td>0.0698</td>
</tr>
</tbody>
</table>

Each model was compared by the use of statistical significance tests on the $R$-values (Hamilton, 1965), and for the composite arrangement, the number of parameters was taken as the number of parameters refined in the two orientations. At the 0.5% significance level, no significant difference was found between any of the models, suggesting that no single model was a preferred representation of the electron density.

The continued presence of small peaks lying mid-way between the ring atoms in the two orientations, strongly suggests that the cyclopentadienyl groups are highly disordered or even rotating as implied in the composite structural arrangement.

A unit weighting scheme was used in the early stages of refinement but was replaced in the final refinement by the weighting scheme

$$w = \frac{1}{\sigma^2(F) + g \cdot F^2}$$

The final value of $g$ was 0.01375.

The weighting analysis is given in Table 9.8, and the final atomic and thermal parameters are given in Tables 9.1 and 9.2. Atomic scattering factors were taken from

*Acta Cryst.*, A24 (1968) 321
*Acta Cryst.*, A24 (1968) 390
The complex components of the scattering factors for zinc were obtained from:


Structure factors are listed in Table 9.9.

Description And Discussion of The Structure

In the crystalline state, the structure consists of puckered chains of zinc atoms, each with a methyl group attached, linked by bridging cyclopentadienyl groups inclined at an angle of 65° to the zinc–zinc vectors (Figure 9a).

In the centrosymmetric space group, two distinct orientations of the cyclopentadienyl group (Orientations A and B, Figures 9b and 9c), have been considered, but the most realistic interpretation of the structure is a disordered arrangement consisting of both orientations, or possibly, rotation of the cyclopentadienyl groups. The individual orientations A and B, can however, be taken to represent the two extremes of the structure.

Small peaks lying mid-way between the ring atoms were observed in the case of ferrocene, and a disordered arrangement of the cyclopentadienyl rings was postulated in order to describe the structure (Dunitz, Orgel and Rich, 1956).

Since the cyclopentadienyl groups are inclined at 65° to the metal–metal vectors, some atoms in each ring are brought into close proximity to the zinc atoms. In orientation A, atoms C(1) A, C(2) A and C(2Ⅱ) A are closer to Zn¹, with zinc–carbon distances of 2.22, 2.65 and 2.65 Å respectively, whilst atoms C(3) A and C(3Ⅱ) A are closer to Zn, both with distances of 2.31 Å (Table 9.3).

The shorter zinc–carbon distances, 2.22 and 2.31 Å, are considered to involve strong Zn–C bonding interactions, and may be compared with the copper–carbon distances of 2.24 Å and 2.30 Å in \((\text{C}_5\text{H}_5)\text{CuP(C}_2\text{H}_5)_3\) (Delbaere, McBride and Ferguson, 1970) and \(\pi(\text{C}_5\text{H}_5)\text{CuP(C}_6\text{H}_5)_3\) (Cotton and Takats, 1970). The longer Zn–C distance of 2.65 Å, is still considered to involve some degree of bonding, and thus the cyclopentadienyl group may be regarded as contributing five electrons to the two zinc atoms.
Figure 9a

Projection on the [1 0 0] Plane

Zn(C₅H₅)CH₃
\[ \text{Zn} \left( C_{5}H_{5} \right) \text{CH}_{3} \]

**Orientation A**  
Fig. 9b

**Orientation B**  
Fig. 9c
In orientation B, atoms C(2)B and C(3)B are closer to Zn, with zinc–carbon distances of 2.25 and 2.41Å, whilst C(2)raB and C(3)raB are closer to Zn, also with distances of 2.25 and 2.41Å. As before, these distances are considered to involve zinc–carbon bonding interactions. The atom C(1)B is equidistant, 2.74Å, from both ZnI and Zn, and implies a smaller interaction. Again the cyclopentadienyl group may be regarded as contributing five electrons to the two zinc atoms.

For both orientations, each zinc atom is thus surrounded by a distorted trigonal arrangement of three ligands, a methyl group functioning as a one electron ligand, and two cyclopentadienyl groups of hapticities in the range 2 to 3, contributing five electrons between them.

The extent of displacement of the zinc atoms away from the cyclopentadienyl 5–fold axis, is reflected in the 69° inclination of the ring to the metal–metal vectors. In Zn(C5H5)CH3, this displacement is intermediate between that found in Na(C5H5)TMED, (Aoyagi, Shearer, Wade and Whitehead, 1976), where the metal atoms lie on the 5–fold axis, and in Ga(C5H5)Me2 (Mertz, Zettler, Hausen and Weidlein, 1976), where the metal atoms lie outside the ring perimeter, enabling the metal atoms to bond monohapto to the cyclopentadienyl ring. Similar displacements away from the 5–fold axis are found in crystalline Be(C5H5)2 (Wong, Lee, Chao and Lee, 1972), Ca(C5H5)2 (Zerger and Stucky, 1974), Al(C5H5)Me2 (Drew and Haaland, 1972) and in the tin complex, C5H5SnCl (Bos, Bulten and Noltes, 1975).

The zinc atom lies 2.43Å from the centre of the cyclopentadienyl ring, and 2.22Å perpendicular to the plane of the ring, and as was found in the case of Na(C5H5)TMED, the empirical prediction method of Johnson, Toney and Stucky, 1972, again becomes invalid.

The 2.22Å distance, perpendicular to the ring plane is of interest however, in that it agrees well with the corresponding distances in other cyclopentadienyl metal complexes, namely, 2.21Å in Ga(C5H5)Me2 (Mertz, Zettler, Hausen and Weidlein, 1976), 2.21Å in C5H5MgBrEt2N(CH2)2NNEt2 (Johnson, Toney and Stucky, 1972) and 2.30Å in C5H5SnCl (Bos, Bulten and Noltes, 1975).

The –M(C5H5)M(C5H5)M(C5H5)– chain structure of Zn(C5H5)CH3
may be compared with those of In(C_5H_5) and Tl(C_5H_5) (Frasson, Menegus and Panattoni, 1963), Pb(C_5H_5)_2 (Panattoni, Bombieri and Croato, 1966), Ga(C_5H_5)Me_2 (Mertz, Zettler, Hausen and Weidlein, 1976) and with the sodium derivative, Na(C_5H_5)TMED (Aoyagi, Shearer, Wade and Whitehead, 1976).

The degree of puckering of the chain, 149° in Zn(C_5H_5)CH_3, 121° in Pb(C_5H_5)_2, 137° in In(C_5H_5) and angles of 128° and 119° in Na(C_5H_5)TMED, reflects the spatial requirements of the terminal substituents (Mertz, Zettler, Hausen and Weidlein, 1976) or of the lone pair electrons (Panattoni, Bombieri and Croato, 1976) on the metal atoms.

In both orientations, the cyclopentadienyl groups are planar within experimental error (Table 9.5). The mean carbon–carbon distances are 1.406(7)Å for orientation A and 1.391(10)Å for orientation B, and these values can be compared with 1.41(2)Å in Be(C_5H_5)_2 (Wong, Lee, Chao and Lee, 1972), 1.39(2)Å in Mg(C_5H_5)_2 (Bunder and Weiss, 1975), 1.43(3)Å in (C_5H_5)MgBrEt_2N(CH_2)_2NEt_2 (Johnson, Toney and Stucky, 1972), 1.386Å in Pb(C_5H_5)_2 (Panattoni, Bombieri and Croato, 1966) and a value of 1.39(2)Å in the calcium derivative, Ca(C_5H_5)_2 (Zerger and Stucky, 1974).

The zinc–carbon single bond distance, Zn–C(4) 1.96(1)Å is in good agreement with the zinc–carbon distances of 1.92(1)Å found in C_2H_4ZnI (Moseley and Shearer, 1966) and 1.94(1)Å found in (CH_3)_2Zn (Rundle, Olson, Stucky and Engebretson, 1963).

**Non-bonding Contacts Within The Chain**

Non-bonding contacts occurring within each individual chain are given in Table 9.6. Only the methyl carbon atoms and the cyclopentadienyl carbon atoms are involved in contacts less than 4Å. The shortest of these contacts, 3.25Å, involves atoms C(1)A and C(1)A in equivalent position (x, y, 0.5–z), and represent the position of closest contact between adjacent cyclopentadienyl rings in the same chain. Since this contact involves carbon atoms both of orientation A, then this raises the question as to whether adjacent cyclopentadienyl rings can both have this orientation.
Non-bonding Contacts Between Chains

Non-bonding contacts occurring between chains are given in Table 9.7. Up to a limit of 4 Å, these contacts occur between cyclopentadienyl carbon atoms and the shortest contact is 3.69 Å.
<table>
<thead>
<tr>
<th>Atom</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>0.0(−)</td>
<td>0.0908(2)</td>
<td>0.25(−)</td>
</tr>
<tr>
<td>C(4)</td>
<td>0.0(−)</td>
<td>0.3690(17)</td>
<td>0.25(−)</td>
</tr>
<tr>
<td>C(1)A</td>
<td>0.0(−)</td>
<td>0.1240(25)</td>
<td>−0.0785(21)</td>
</tr>
<tr>
<td>C(2)A</td>
<td>0.1297(12)</td>
<td>0.0350(18)</td>
<td>−0.0167(15)</td>
</tr>
<tr>
<td>C(3)A</td>
<td>0.0679(11)</td>
<td>−0.1085(12)</td>
<td>−0.0701(11)</td>
</tr>
<tr>
<td>C(1)B</td>
<td>0.1352(15)</td>
<td>0.0(−)</td>
<td>0.0(−)</td>
</tr>
<tr>
<td>C(2)B</td>
<td>0.0454(14)</td>
<td>0.1218(16)</td>
<td>−0.0780(13)</td>
</tr>
<tr>
<td>C(3)B</td>
<td>−0.0994(19)</td>
<td>0.0794(18)</td>
<td>−0.0504(17)</td>
</tr>
<tr>
<td>H(1)A</td>
<td>0.0(−)</td>
<td>0.2346</td>
<td>−0.1541</td>
</tr>
<tr>
<td>H(2)A</td>
<td>0.2422</td>
<td>0.0705</td>
<td>−0.0355</td>
</tr>
<tr>
<td>H(3)A</td>
<td>0.1443</td>
<td>−0.2026</td>
<td>0.1276</td>
</tr>
<tr>
<td>H(1)B</td>
<td>0.2549</td>
<td>0.0(−)</td>
<td>0.0(−)</td>
</tr>
<tr>
<td>H(2)B</td>
<td>0.0834</td>
<td>0.2212</td>
<td>−0.1523</td>
</tr>
<tr>
<td>H(3)B</td>
<td>−0.1933</td>
<td>0.1482</td>
<td>−0.0940</td>
</tr>
<tr>
<td>Atom</td>
<td>$U_{11}$</td>
<td>$U_{22}$</td>
<td>$U_{33}$</td>
</tr>
<tr>
<td>-------</td>
<td>------------</td>
<td>------------</td>
<td>------------</td>
</tr>
<tr>
<td>Zn</td>
<td>713(10)</td>
<td>317(9)</td>
<td>422(8)</td>
</tr>
<tr>
<td>C(4)</td>
<td>807(88)</td>
<td>475(71)</td>
<td>570(76)</td>
</tr>
<tr>
<td>C(1)A</td>
<td>531(45)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(2)A</td>
<td>527(30)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(3)A</td>
<td>318(20)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(1)B</td>
<td>302(28)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(2)B</td>
<td>426(32)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(3)B</td>
<td>534(31)</td>
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<td></td>
</tr>
<tr>
<td>H(1)A</td>
<td>1204(394)</td>
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</tr>
<tr>
<td>H(2)A</td>
<td>1204(394)</td>
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</tr>
<tr>
<td>H(1)B</td>
<td>1209(460)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(2)B</td>
<td>1209(460)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(3)B</td>
<td>1209(460)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 9.3  

$Zn\left( C_{5}H_{5}\right)C_{6}H_{3}$

Final Molecular Distances ($\AA$) And Their Estimated Standard Deviations ($\AA \times 10^3$)

<table>
<thead>
<tr>
<th></th>
<th>Orientation A</th>
<th>Orientation B</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Zn$ - $C(1)$</td>
<td>3.122</td>
<td>2.736</td>
</tr>
<tr>
<td>$Zn$ - $C(2)$</td>
<td>2.808</td>
<td>3.142</td>
</tr>
<tr>
<td>$Zn$ - $C(3)$</td>
<td>2.313</td>
<td>2.983</td>
</tr>
<tr>
<td>$Zn$ - $C(4)$</td>
<td>1.959(12)</td>
<td>1.959(12)</td>
</tr>
<tr>
<td>$Zn^I$ - $C(1)$</td>
<td>2.221</td>
<td>2.736</td>
</tr>
<tr>
<td>$Zn^I$ - $C(2)$</td>
<td>2.649</td>
<td>2.250</td>
</tr>
<tr>
<td>$Zn^I$ - $C(3)$</td>
<td>3.113</td>
<td>2.409</td>
</tr>
<tr>
<td>$Zn^I$ - $C(4)$</td>
<td>1.959(12)</td>
<td>1.959(12)</td>
</tr>
<tr>
<td>$C(1)$ - $C(2)$</td>
<td>1.443(16)</td>
<td>1.388(15)</td>
</tr>
<tr>
<td>$C(2)$ - $C(3)$</td>
<td>1.386(16)</td>
<td>1.355(25)</td>
</tr>
<tr>
<td>$C(3)$ - $C(3^B)$</td>
<td>1.376(20)</td>
<td>1.471(28)</td>
</tr>
</tbody>
</table>

The superscript $I$ refers to the atom at the position $(-x, -y, -z)$

The superscript $II$ refers to the atom at the position $(-x, y, z)$

The superscript $III$ refers to the atom at the position $(x, -y, -z)$
Table 9.4  \( \text{Zn(C}_5\text{H}_5)\text{CH}_3 \)

Final Bond Angles And Their Estimated Standard Deviations

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)A</td>
<td>Zn</td>
<td>C(4)</td>
<td>85.7(1)</td>
<td></td>
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<tr>
<td>C(2)A</td>
<td>Zn</td>
<td>C(4)</td>
<td>98.0(1)</td>
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</tr>
<tr>
<td>C(3)A</td>
<td>Zn</td>
<td>C(4)</td>
<td>127.4(2)</td>
<td></td>
</tr>
<tr>
<td>C(1)B</td>
<td>Zn</td>
<td>C(4)</td>
<td>103.5(1)</td>
<td></td>
</tr>
<tr>
<td>C(2)B</td>
<td>Zn</td>
<td>C(4)</td>
<td>86.0(2)</td>
<td></td>
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<tr>
<td>C(3)B</td>
<td>Zn</td>
<td>C(4)</td>
<td>91.5(2)</td>
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<tr>
<td>C(1)A</td>
<td>C(2)A</td>
<td>C(3)A</td>
<td>106.5(9)</td>
<td></td>
</tr>
<tr>
<td>C(1)B</td>
<td>C(2)B</td>
<td>C(3)B</td>
<td>108.3(9)</td>
<td></td>
</tr>
</tbody>
</table>
**Table 9.5**  \( \text{Zn(C}_5\text{H}_5\text{)}\text{CH}_3 \)

**Mean Planes**

**Plane 1**

\[
X + 4.5546Y + 7.2282Z = 0.020
\]

<table>
<thead>
<tr>
<th>Atom</th>
<th>C(1)A</th>
<th>C(2)A</th>
<th>C(3)A</th>
<th>C(2II)A</th>
<th>C(3II)A</th>
<th>Zn*</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>-0.02</td>
<td>0.02</td>
<td>-0.01</td>
<td>0.02</td>
<td>-0.01</td>
<td>2.2</td>
</tr>
</tbody>
</table>

**Plane 2**

\[
-X + 4.5841Y + 7.1944Z = 0.0
\]

<table>
<thead>
<tr>
<th>Atom</th>
<th>C(1)B</th>
<th>C(2)B</th>
<th>C(3)B</th>
<th>C(2III)B</th>
<th>C(3III)B</th>
<th>Zn*</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>0.0</td>
<td>-0.0006</td>
<td>0.0009</td>
<td>0.0006</td>
<td>-0.009</td>
<td>2.2</td>
</tr>
</tbody>
</table>

**Angles Between Planes**

Plane 1  Plane 2  \( 0.32^\circ \)

X, Y, Z refers to fractional co-ordinates along the unit cell axes, and P refers to the distance in Å of an atom from the mean plane.

Atoms marked * are not included in the mean plane calculation.
Table 9.6  \( \text{Zn} \left( \text{C}_5 \text{H}_5 \right) \text{CH}_3 \)

Non-bonding Contacts Within The Chain (\(< 4.0 \text{Å}\))

<table>
<thead>
<tr>
<th>Atom A</th>
<th>Atom B</th>
<th>Equivalent</th>
<th>Cell</th>
<th>A - B(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)A</td>
<td>C(1)A</td>
<td>5</td>
<td>0, 0, 0</td>
<td>3.250</td>
</tr>
<tr>
<td>C(1)A</td>
<td>C(4)</td>
<td>1</td>
<td>0, 0, 0</td>
<td>3.559</td>
</tr>
<tr>
<td>C(1)A</td>
<td>C(4)</td>
<td>2</td>
<td>0, 0, 0</td>
<td>3.834</td>
</tr>
<tr>
<td>C(2)A</td>
<td>C(4)</td>
<td>1</td>
<td>0, 0, 0</td>
<td>3.642</td>
</tr>
<tr>
<td>C(2)A</td>
<td>C(4)</td>
<td>2</td>
<td>0, 0, 0</td>
<td>3.785</td>
</tr>
<tr>
<td>C(3)A</td>
<td>C(1)A</td>
<td>6</td>
<td>0, 0, 1</td>
<td>3.402</td>
</tr>
<tr>
<td>C(3)A</td>
<td>C(3)A</td>
<td>8</td>
<td>0, 0, 1</td>
<td>3.677</td>
</tr>
<tr>
<td>C(3)A</td>
<td>C(4)</td>
<td>2</td>
<td>0, 0, 0</td>
<td>3.785</td>
</tr>
<tr>
<td>C(3)A</td>
<td>C(2)A</td>
<td>7</td>
<td>0, 0, 0</td>
<td>3.978</td>
</tr>
<tr>
<td>C(3)A</td>
<td>C(4)</td>
<td>1</td>
<td>0, 0, 0</td>
<td>3.833</td>
</tr>
<tr>
<td>C(1)B</td>
<td>C(4)</td>
<td>2</td>
<td>0, 0, 0</td>
<td>3.719</td>
</tr>
<tr>
<td>C(2)B</td>
<td>C(1)A</td>
<td>5</td>
<td>0, 0, -1</td>
<td>3.961</td>
</tr>
<tr>
<td>C(2)B</td>
<td>C(3)A</td>
<td>6</td>
<td>0, 0, 0</td>
<td>3.511</td>
</tr>
<tr>
<td>C(2)B</td>
<td>C(3)A</td>
<td>7</td>
<td>0, 0, -1</td>
<td>3.348</td>
</tr>
<tr>
<td>C(2)B</td>
<td>C(4)</td>
<td>2</td>
<td>0, 0, 0</td>
<td>3.843</td>
</tr>
<tr>
<td>C(2)B</td>
<td>C(4)</td>
<td>1</td>
<td>0, 0, 0</td>
<td>3.586</td>
</tr>
<tr>
<td>C(3)B</td>
<td>C(1)A</td>
<td>5</td>
<td>0, 0, -1</td>
<td>3.641</td>
</tr>
<tr>
<td>C(3)B</td>
<td>C(3)A</td>
<td>7</td>
<td>0, 0, -1</td>
<td>3.932</td>
</tr>
<tr>
<td>C(3)B</td>
<td>C(4)</td>
<td>1</td>
<td>0, 0, 0</td>
<td>3.613</td>
</tr>
<tr>
<td>C(4)</td>
<td>C(1)A</td>
<td>5</td>
<td>0, 0, 0</td>
<td>3.559</td>
</tr>
<tr>
<td>C(4)</td>
<td>C(2)A</td>
<td>4</td>
<td>0, 0, 0</td>
<td>3.642</td>
</tr>
<tr>
<td>C(4)</td>
<td>C(2)A</td>
<td>5</td>
<td>0, 0, 0</td>
<td>3.642</td>
</tr>
<tr>
<td>C(4)</td>
<td>C(3)A</td>
<td>4</td>
<td>0, 0, 0</td>
<td>3.833</td>
</tr>
</tbody>
</table>
Table 9.7  
\(\text{Zn}(\text{C}_5\text{H}_5)\text{CH}_3\)

**Non-bonding Contacts Between Chains (< 4.0 Å)**

<table>
<thead>
<tr>
<th>Atom A</th>
<th>Atom B</th>
<th>Equivalent</th>
<th>Cell</th>
<th>A - B (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(2)A</td>
<td>C(2)A</td>
<td>2</td>
<td>0.5, 0.5, 0</td>
<td>3.729</td>
</tr>
<tr>
<td>C(3)A</td>
<td>C(3)A</td>
<td>2</td>
<td>0.5, 0.5, 0</td>
<td>3.915</td>
</tr>
<tr>
<td>C(1)B</td>
<td>C(2)A</td>
<td>2</td>
<td>0.5, 0.5, 0</td>
<td>3.896</td>
</tr>
<tr>
<td>C(1)B</td>
<td>C(3)A</td>
<td>2</td>
<td>0.5,-0.5, 0</td>
<td>3.831</td>
</tr>
<tr>
<td>C(2)B</td>
<td>C(2)A</td>
<td>2</td>
<td>0.5, 0.5, 0</td>
<td>3.885</td>
</tr>
<tr>
<td>C(3)B</td>
<td>C(2)A</td>
<td>3</td>
<td>-0.5, 0.5, 0</td>
<td>3.695</td>
</tr>
</tbody>
</table>

The non-bonding contacts refer to the position of atom A in the original co-ordinates list, and atom B as obtained from this, using the symmetry operations given, and refer to the cell quoted.

<table>
<thead>
<tr>
<th>Equivalent</th>
<th>Position</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(x, y, z)</td>
</tr>
<tr>
<td>2</td>
<td>(-x, -y, -z)</td>
</tr>
<tr>
<td>3</td>
<td>(x, -y, -z)</td>
</tr>
<tr>
<td>4</td>
<td>(-x, y, z)</td>
</tr>
<tr>
<td>5</td>
<td>(x, y, 0.5 - z)</td>
</tr>
<tr>
<td>6</td>
<td>(-x, -y, z - 0.5)</td>
</tr>
<tr>
<td>7</td>
<td>(x, -y, 0.5 + z)</td>
</tr>
<tr>
<td>8</td>
<td>(-x, y, -z - 0.5)</td>
</tr>
</tbody>
</table>
### Table 9.8  \[ \text{Zn(C}_5\text{H}_5\text{)}\text{CH}_3 \]

**Analysis of Variance**

<table>
<thead>
<tr>
<th>$\sin \theta$</th>
<th>0.0 - 0.18 - 0.23 - 0.26 - 0.30 - 0.32 - 0.34 - 0.37 - 0.39 - 0.41 - 0.43</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N$</td>
<td>27 28 21 30 22 23 32 27 27 13</td>
</tr>
<tr>
<td>$V$</td>
<td>190 148 130 89 104 86 128 105 146 140</td>
</tr>
</tbody>
</table>

\[
\left[ \frac{F_0}{F_{max}} \right]^{1/2}
\]

| 0.0 - 0.24 - 0.27 - 0.29 - 0.32 - 0.36 - 0.38 - 0.42 - 0.48 - 0.55 - 1.0 |
|-------------------|--------------------------------------------------------------------------|
| $N$               | 33 23 20 26 31 20 25 24 25 23                                              |
| $V$               | 162 171 127 102 131 92 85 87 101 184                                      |
Table 9.9

\[ \text{Zn(C}_5\text{H}_5\text{)} \text{CH}_3 \]

\text{Final Values of the Observed and Calculated Structure Factors}
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