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# The Crystal Structure of μ-Oxo-bis[tetraethylenepentaamineiron(III)] Iodide

BY ALESSANDRO CODA,* BORIS KAMENAR† AND KEITH PROUT
*Chemical Crystallography Laboratory, Oxford University, 9 Parks Road, Oxford OX1 3PD, England*

AND J. ROBERT CARRUTHERS AND JOHN S. ROLLETT
*Oxford University Computing Laboratory, 19 Parks Road, Oxford OX1 3PL, England*

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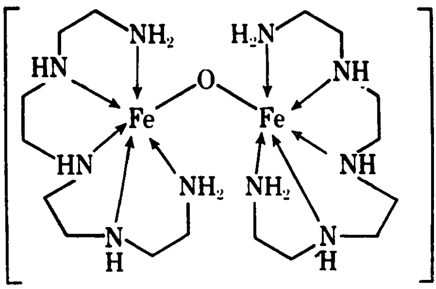
The structure of the title compound has been determined (orthorhombic, $a = 17{\cdot}33$, $b = 15{\cdot}94$, $c = 11{\cdot}68$ Å, space group *Pnn*2, four-circle diffractometer data, 1100 independent reflexions, $R = 0{\cdot}085$). The heavy-atom positions are close to those for symmetry *Pnnm*. Difficulties caused by this have been overcome by extensive constrained refinement. The $\mu$-oxo bridge is nearly linear (Fe–O–Fe 172°) and the five Fe–N bonds are unexpectedly long, in the range 2·13–2·36 Å.

## Introduction

The compound was prepared by Melby (1970) who assigned it the structure (I) from analytical evidence and from studies of the temperature variation of the magnetic susceptibility (room temperature 1·95 $\mu_B$ decreasing to 1·2 $\mu_B$ per Fe atom at 196 K). However, he was unable to correlate the infrared spectra of this and related compounds with those of the various conformers of [(tetraethylenepentaamine)CoCl]$X_2$ complexes obtained by House & Garner (1966).



(I)

The crystal structure has been determined to confirm Melby's proposal, to discover the conformation of the ligand in the complex and to investigate the low spin $Fe^{III}$–N bond lengths which are poorly characterized for 'ammine' ligands.

## X-ray structure analysis

The crystal data are: $C_{16}H_{46}Fe_2N_{10}OI_4$, $M = 1014{\cdot}0$, orthorhombic, $a = 17{\cdot}33$ (2), $b = 15{\cdot}94$ (2), $c = 11{\cdot}68$ (1) Å, $U = 3226{\cdot}2$ Å$^3$, $D_m = 2{\cdot}05$ g cm$^{-3}$, $Z = 4$, $D_{calc} = 2{\cdot}09$ g cm$^{-3}$, space group *Pnn*2 ($C_{2v}^{10}$, No. 34), from the structure analysis (systematic extinctions, $h0l$, $h+l=2n+1$; $0kl$, $k+l=2n+1$), $\mu = 383$ cm$^{-1}$ for Cu $K\alpha$ radiation, $\mu = 48$ cm$^{-1}$ for Mo $K\alpha$ radiation.

The systematic extinctions and cell dimensions were determined from oscillation and Weissenberg photographs. The cell dimensions were then refined by a least-squares procedure with a Hilger and Watts four-circle diffractometer.

The intensities used in the initial stages of the analysis were collected with Cu $K\alpha$ radiation, on the diffractometer, by the ordinate analysis technique (Watson, Shotton, Cox & Muirhead, 1970). A limit of $\theta = 60°$ was set on the sphere of reflexion by the rapid decrease of intensity with Bragg angle. For each symmetry-related set of reflexions, the r.m.s. deviation of the individual $I$ values from the mean $I$ for the set was computed. Those mean $I$ values which were less than three times the corresponding r.m.s. deviations were regarded as unobservable and 1289 independent observations were obtained. During the refinement it was felt that the effects of absorption and of the background intensity on the first set of data caused large uncertainties in the assessment of the accuracy of the analysis. To reduce this uncertainty, new data were collected on the same diffractometer which had by that time been modified to use monochromatic Mo $K\alpha$ radiation. For the Mo $K\alpha$ data the counter stepped across the reflexion peaks and was stationary for background counts. An absorption correction was calculated for each reflexion by Gaussian numerical integration (crystal size $0{\cdot}9 \times 0{\cdot}08 \times 0{\cdot}07$ mm). Some reflexions were classified as unobservable by the same process as before, and 1100 independent observations were obtained. This second set of data is that used to define the structure described here.

A Patterson synthesis indicated, in space group *Pnnm*, the positions of four $I^-$ ions with $z = 0$ and $\frac{1}{2}$ on the mirror planes and an Fe atom at a general position. An $F_{obs}$ synthesis in this symmetry was computed with the heavy-atom phases. It proved impossible to find sites for the lighter atoms which corresponded to

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* Permanent address: Istituto di Cristallografia, via A. Bassi 4, 27100 Pavia, Italy.

† Permanent address: Laboratory of General and Inorganic Chemistry, Faculty of Science, The University, Ulica socijalističke revolucije 8, 41000 Zagreb, Yugoslavia.

an acceptable chemical structure that could be refined in space group *Pnnm* to give good agreement with $F_{\text{obs}}$.

The $F_{\text{obs}}$ synthesis showed more maxima than would have been expected for the number of light atoms in the structure. Some could be excluded from further consideration because they represented diffraction effects near the $I^-$ ions and attempts were made to select sites from the remaining peak positions to give trial structures in space group *Pnn*2. Refinement of reasonable trial structures gave some measure of agreement but the resulting atomic positions were unacceptable in terms of interatomic distances and vibrational amplitudes. A systematic attempt was made to break the false symmetry by constructing a model of symmetry *Pnn*2. The positional parameters for the model were for pairs of sites related by the mirror plane of *Pnnm* (and some sites on this mirror plane). These positions were selected from the 55 highest peaks remaining after some had been rejected on the grounds of proximity to the $I^-$ ions. The asymmetry was introduced by assigning a C scattering factor to each site and giving occupation numbers (individual scale-factors) of zero to every site except one. This one site (not on the mirror plane) was given an occupation number of unity. The occupation numbers were then refined by five cycles of least-squares calculations. Because of the close approach to *Pnnm* symmetry the early normal matrices were nearly singular and fractional shift factors, which were increased gradually from 0·05 to 1·0, were used to prevent any shift from exceeding unity. An $F_{\text{obs}}$ map based on the phases for the final set of structure factors revealed the sites of all but three of the C, N and O atoms. A further set of structure factors followed by calculation of another $F_{\text{obs}}$ map gave a complete trial structure.

Refinement of this trial structure led to distances and angles surrounding the Fe atoms which were not unreasonable but could be much improved if the *y* coordinates of the two Fe atoms were interchanged, a change which would correspond to the alternative resolution of an ambiguity produced by the pseudo-symmetry of the structure. The change was made and further refinement was carried out with anisotropic thermal parameters for all atoms and with the help of constraints (Waser, 1963; Rollett, 1969) on the C–C and C–N distances, the C–C–N and C–N–C angles and the bond-stretching amplitudes for the C–C, C–N, N–Fe and Fe–O bonds. The refinement produced an *R* of 0·096 with acceptable distances and vibrations for all except the Fe–O bonds. The Fe and O vibrations were, however, such that they could not be reconciled with reasonable stretching amplitudes for the Fe–O bonds.

At this point the second, improved, set of data collected with Mo $K\alpha$ radiation became available. With the new data a refinement was carried out in which the I and Fe atoms were given anisotropic vibration parameters while the C, N and O atoms were given isotropic. The C–C distances were set to 1·504 ± 0·006 Å, the C–N distances to 1·483 ± 0·003 Å, the C–C–N angles to 108·7 ± 0·2° and the C–N–C angles to 114·5 ± 0·4°. These dimensions and standard deviations were derived by calculating the means and standard deviations of the corresponding dimensions in a number of other crystal structures containing similar ligands.

In addition, the differences in Fe–O bonded distances, in the mean square vibrational amplitudes of C and N atoms joined by covalent bonds, and of Fe and O atoms along the directions of the bonds joining them were constrained to be zero with standard devia-

Table 1. *Final atomic parameters with standard deviations in parentheses*

For anisotropic thermal motion the temperature factor *T* is give by $T = \exp\{-2\pi^2[U(11)h^2a^{*2} + U(22)k^2b^{*2} + U(33)l^2c^{*2} + 2U(23)klb^*c^* + 2U(13)hla^*c^* + 2U(12)hka^*b^*]\}$.

| | *x*/*a* | *y*/*b* | *z*/*c* | $U_{\text{iso}}$ |
|---|---|---|---|---|
| O(1) | 0·132 (2) | 0·746 (1) | 0·499 (2) | 0·048 (4) |
| N(11) | 0·017 (3) | 0·657 (3) | 0·627 (3) | 0·061 (8) |
| N(12) | 0·101 (2) | 0·674 (2) | 0·826 (4) | 0·062 (7) |
| N(13) | 0·220 (2) | 0·645 (2) | 0·680 (3) | 0·063 (7) |
| N(14) | 0·214 (2) | 0·822 (2) | 0·702 (3) | 0·065 (7) |
| N(15) | 0·057 (2) | 0·844 (2) | 0·707 (4) | 0·064 (8) |
| N(21) | 0·110 (3) | 0·903 (3) | 0·381 (3) | 0·069 (9) |
| N(22) | 0·156 (2) | 0·832 (2) | 0·176 (4) | 0·069 (7) |
| N(23) | 0·259 (2) | 0·754 (2) | 0·316 (3) | 0·065 (7) |
| N(24) | 0·138 (2) | 0·637 (3) | 0·287 (3) | 0·060 (7) |
| N(25) | 0·014 (2) | 0·744 (2) | 0·292 (4) | 0·056 (8) |
| C(11) | −0·023 (2) | 0·644 (3) | 0·738 (4) | 0·061 (8) |
| C(12) | 0·036 (2) | 0·615 (3) | 0·825 (4) | 0·062 (7) |
| C(13) | 0·173 (2) | 0·640 (3) | 0·875 (3) | 0·062 (7) |
| C(14) | 0·215 (2) | 0·592 (2) | 0·784 (4) | 0·063 (7) |
| C(15) | 0·291 (2) | 0·697 (2) | 0·673 (3) | 0·064 (7) |
| C(16) | 0·280 (2) | 0·773 (2) | 0·747 (4) | 0·064 (7) |
| C(17) | 0·181 (2) | 0·883 (3) | 0·785 (4) | 0·064 (7) |
| C(18) | 0·107 (2) | 0·916 (2) | 0·737 (4) | 0·064 (8) |
| C(21) | 0·090 (2) | 0·946 (3) | 0·273 (4) | 0·069 (8) |
| C(22) | 0·150 (3) | 0·924 (2) | 0·184 (4) | 0·069 (8) |
| C(23) | 0·228 (2) | 0·801 (3) | 0·124 (3) | 0·068 (7) |
| C(24) | 0·290 (2) | 0·799 (3) | 0·215 (4) | 0·067 (7) |
| C(25) | 0·274 (2) | 0·662 (2) | 0·316 (4) | 0·064 (7) |
| C(26) | 0·216 (2) | 0·620 (3) | 0·241 (4) | 0·062 (7) |
| C(27) | 0·074 (2) | 0·623 (3) | 0·205 (3) | 0·058 (7) |
| C(28) | 0·001 (2) | 0·656 (2) | 0·256 (4) | 0·057 (7) |

Table 1 (*cont.*)

| | *x*/*a* | *y*/*b* | *z*/*c* | *U*(11) | *U*(22) | *U*(33) | *U*(23) | *U*(13) | *U*(12) |
|---|---|---|---|---|---|---|---|---|---|
| I(1) | 0·4808 (3) | 0·6700 (4) | 0·504 (2) | 0·075 (3) | 0·130 (5) | 0·086 (4) | −0·029 (9) | −0·029 (7) | −0·008 (3) |
| I(2) | 0·3995 (2) | 0·6358 (3) | 0·0002 | 0·043 (2) | 0·061 (2) | 0·071 (3) | 0·001 (8) | 0·032 (4) | −0·012 (2) |
| I(3) | 0·3200 (3) | 0·9239 (3) | 0·496 (2) | 0·086 (3) | 0·043 (2) | 0·106 (4) | 0·007 (9) | 0·004 (9) | −0·017 (2) |
| I(4) | 0·3644 (2) | 0·9805 (2) | 0·997 (2) | 0·065 (3) | 0·033 (2) | 0·103 (4) | −0·013 (8) | 0·00 (1) | 0·005 (2) |
| Fe(1) | 0·1242 (7) | 0·741 (1) | 0·650 (2) | 0·027 (9) | 0·11 (1) | 0·051 (5) | 0·00 (1) | 0·008 (8) | 0·050 (9) |
| Fe(2) | 0·1289 (8) | 0·761 (1) | 0·349 (2) | 0·04 (1) | 0·09 (1) | 0·038 (4) | −0·026 (9) | 0·019 (8) | 0·013 (8) |

tions of 0·02 Å, 0·0036 Å$^2$ and 0·004 Å$^2$ respectively. No constraints were placed on the positional or the vibrational relationships between the Fe and N atoms. The agreement reached at convergence was satisfactory. It was noted that both the conformation and the dimensions of the cation showed a close approach to twofold non-crystallographic symmetry about a rotation axis in a general direction in the $xy$ plane which also related I$^-$ ions close to the cation. Consequently the Fe–N distances, and the O–Fe–N, N–Fe–N and Fe–N–C angles were constrained to be equal in pairs so as to obey the twofold symmetry, with standard deviations of 0·003 Å, and 0·2° respectively. The result of these additional constraints was to reduce the maximum standard deviation for an Fe–N distance from 0·07 to 0·048 Å. Hamilton's (1965) test was applied to confirm that the change of minimization function produced by the addition of the twofold symmetry constraints was not significant. The final $R$ was 0·085.* No distance parameter deviated from the constrained value by more than 0·2 and no vibrational parameter by more than 0·5 standard deviations.

All calculations were carried out with the Oxford CRYSTALS program system (Rollett & Carruthers, 1975) on the University's ICL 1906A computer. Scattering factors and corrections for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1962). The final atomic parameters are given in Table 1. Table 2 gives the interatomic distances and interbond angles of the cation that were not fixed by constraints. Their standard deviations were calculated from the full variance–covariance matrix.

Table 2. *Interatomic distances* (Å) *and interbond angles* (°) *in the cation not fixed by constraints*

The dimensions of the two halves of the cation are equivalent by the non-crystallographic twofold axis in the $xy$ plane through O(1).

| | | |
|---|---|---|
| O(1)—Fe(1), O(1)—Fe(2) | 1·77 (1) | |
| N(11)–Fe(1), N(21)–Fe(2) | 2·32 (5) | |
| N(12)–Fe(1), N(22)–Fe(2) | 2·36 (4) | |
| N(13)–Fe(1), N(23)–Fe(2) | 2·30 (3) | |
| N(14)–Fe(1), N(24)–Fe(2) | 2·12 (4) | |
| N(15)–Fe(1), N(25)–Fe(2) | 2·13 (4) | |
| N(11)–Fe(1)–N(12), N(21)–Fe—N(22) | | 73 (1) |
| N(11)–Fe(1)–N(13), N(21)–Fe—N(23) | | 102 (3) |
| N(11)–Fe(1)–N(14), N(21)–Fe—N(24) | | 169 (1) |
| N(11)–Fe(1)–N(15), N(21)–Fe—N(25) | | 92 (4) |
| N(12)–Fe(1)–N(13), N(22)–Fe—N(23) | | 72 (1) |
| N(12)–Fe(1)–N(14), N(22)–Fe—N(24) | | 98 (4) |
| N(12)–Fe(1)–N(15), N(22)–Fe—N(25) | | 89 (1) |
| N(13)–Fe(1)–N(14), N(23)–Fe—N(24) | | 80 (1) |
| N(13)–Fe(1)–N(15), N(23)–Fe—N(25) | | 151 (2) |
| N(14)–Fe(1)–N(15), N(24)–Fe—N(25) | | 81 (1) |
| O(1)—Fe(1)–N(11), O(1)—Fe(2)–N(21) | | 88 (1) |
| O(1)—Fe(1)–N(12), O(1)—Fe(2)–N(22) | | 155 (2) |
| O(1)—Fe(1)–N(13), O(1)—Fe(2)–N(23) | | 97 (3) |
| O(1)—Fe(1)–N(14), O(1)—Fe(2)–N(24) | | 102 (5) |
| O(1)—Fe(1)–N(15), O(1)—Fe(2)–N(25) | | 109 (4) |

## Results and discussion

The crystal structure is built up from the μ-oxo-bis-(tetraethylenepentaamine)iron(III) cations (I) and isolated I$^-$ anions (Fig. 1).

The structure contains a high proportion of heavy Fe and I atoms. There is also a high degree of pseudosymmetry of the light atom positions. It can be seen from Fig. 1, which displays the projection of the structure down **c**, that almost every atom of the tetraethylenepentaamine group is close to the 'mirror image'

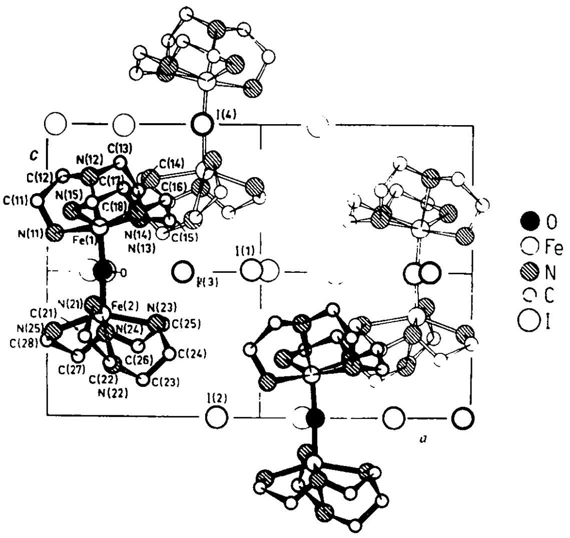

Fig. 1. μ-Oxo-bis-[tetraethylenepentaamineiron(III)] iodide: projection down **b**.

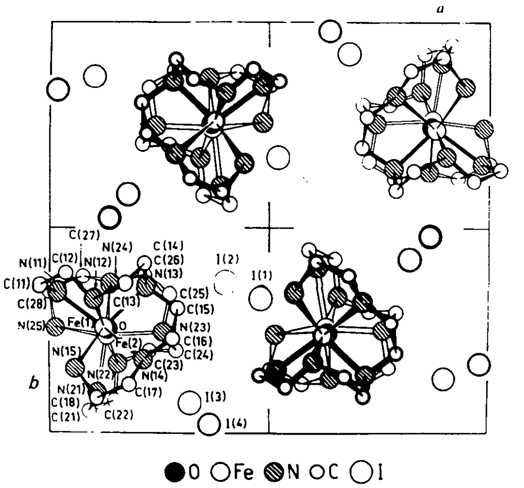

Fig. 2. μ-Oxo-bis-[tetraethylenepentaamineiron(III)] iodide: projection down **c**. The non-crystallographic twofold axis of the 'lettered' complex cation lies in the $ab$ plane at $c=\frac{1}{4}$. It bisects the line joining N(15) and N(25) and passes through the oxygen (O).

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* The list of structure factors (Mo $K\alpha$ data) has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30887 (12 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

of an atom in the group attached to the other Fe atom, if a mirror plane normal to **c** is supposed to pass through the O atom. As a result, the standard deviations of the individual bond lengths and angles are rather large, and no detailed interpretation of these dimensions will be given.

The cation is surrounded by $I^-$ anions. Figs. 1 and 2, which display projections of the structure down **c** and **b**, show that there are three $I^-$ ions in an approximately equilateral triangle coplanar with the O atom, so that each $I^-$ is equidistant from the two Fe atoms. There is also one $I^-$ ion half a unit cell along **c** from this plane, which makes contact with one Fe atom in each of two cations separated by a unit-cell translation in the **c** direction. Thus each Fe atom is in contact with four $I^-$ ions and each $I^-$ ion is in contact with two Fe atoms. Ionic bonds link chains of cations in the **c** direction, but there are no close contacts between ions of opposite signs to link the cations in the **a** and **b** directions. This lack of strong ionic binding forces is no doubt responsible for the generally high level of vibrational amplitude in the structure which contributes to the difficulty of obtaining dimensions of high precision.

In the cation the two Fe atoms are joined by the O atom with an Fe–O–Fe angle of 172°. The two halves of the cation have been made equivalent by the non-crystallographic twofold rotation axis in the *xy* plane, through the O atom, introduced in the constrained refinement. The Fe–O bonds are equivalent and 1·77 Å long; they correspond to individual $(\sigma+\pi)$ bond orders of 1·5. These bond lengths are in good agreement with those found in oxo-bridged binuclear $Fe^{III}$ complexes [see $O(FeHEDTA)_2^{2-}$: Lippard, Schugar & Walling, 1967; $O(Fesalen)_2.2C_5H_5N$: Gerloch, McKenzie & Towl, 1969; $O(Fesalen)_2.CH_2Cl_2$: Coggon, McPhail, Mabbs & McLachlan, 1971) although the bridge is more nearly linear. A pentadentate tetraethylenepentaamine chain surrounds each Fe atom so that it has a distorted octahedral coordination sphere of one O and five N atoms. In any binuclear complex the two pentadentate ligands are the same enantiomers (by the non-crystallographic twofold axis) but the *n* glide planes require that both enantiomers are present in the crystal.

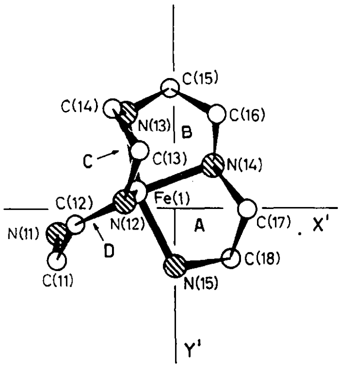

Fig. 3. The tetraethylenepentaamine ligand seen projected onto the plane N(13), N(14), N(15).

In the ligand the lengths of the C–C and C–N bonds and the C–N–C and N–C–C interbond angles were closely defined by the applied constraints. However, no constraints were applied to the torsional angles of the ligand or to the dimensions of the Fe coordination sphere. Previous work (Snow, 1972*a*,*b*) has shown that the ligand can satisfy five coordination sites of an octahedral complex with various ligand conformations whilst preserving a near regular octahedron with M–N contacts of about 2·0 Å. In the Fe complex the ligand has the *DαβR** conformation (Fig. 3) but differs from the *DαβR* conformation of the chloro(tetraethylenepentaamine)cobalt dication at ring *D*.

In the Fe compound, C(11) is on the opposite side of the mean plane of ring *D* to ring *C*, whereas in the *DαβR* Co complex the C atom corresponding to C(11) is on the same side of the mean plane of ring *D* as ring *C*. This difference in conformation is reflected in the torsion angle C(11)–C(12)–N(12)–C(13) (Table 3). The Fe–N bonds are all long (2·12–2·36 Å). The shortest Fe–N bonds, those to N(14) [N(24)], 2·12 Å, and N(15) [N(25)], 2·13 Å of ring *A*, are not significantly longer than the Fe–N bonds (2·10 Å mean) found in the $O(Fesalen)_2$ complexes (Gerloch *et al.*, 1969; Coggon *et al.*, 1971). Ring *A* has virtually the same conformation as ring *A* of the *DαβR* Co complex and might be thought of as a representative chelate system unperturbed by the π-bonded μ-oxo bridge. Not unexpectedly the longest Fe–N bond Fe(1)–N(12) [Fe(2)–N(22)], 2·36 Å, is *trans* to the μ-oxo system. This bond is somewhat longer than the Fe–N bond (2·27 Å) *trans* to the μ-oxo system in the $O(FeHEDTA)_2^{2-}$ complex (Lippard *et al.*, 1967). (The Fe atoms in the $OFe(salen)_2$

Table 3. *Dihedral angles* (°)

The dihedral angle about the bond *J–K* is the angle the bond *K–L* is rotated from the *IJK* plane. It is positive when on looking from *IJ* to *KL* the rotation is clockwise (Snow, 1972*a*).

| *I* | *J* | *K* | *L* | This compound | Co complex* |
|---|---|---|---|---|---|
| N(11) | C(11) | C(12) | N(12)† | 54 | −38·6 |
| C(11) | C(12) | N(12) | C(13) | 160 | −86·8 |
| C(12) | N(12) | C(13) | C(14) | 83 | 98·5 |
| N(12) | C(13) | C(14) | N(13) | 50 | 47·3 |
| C(13) | C(14) | N(13) | C(15) | 91 | 73·0 |
| C(14) | N(13) | C(15) | C(16) | −80 | −101·3 |
| N(13) | C(15) | C(16) | N(14) | −61 | −15·0 |
| C(15) | C(16) | N(14) | C(17) | 162 | 160·7 |
| C(16) | N(14) | C(17) | C(18) | −170 | −169·7 |
| N(14) | C(17) | C(18) | N(15) | 53 | 50·2 |

* The equivalent dihedral angles in *DαβR* chloro(tetraethylenepentaamine)cobalt(II) (Snow, 1972).

† The dihedral angles in the other half of the cation are equivalent by non-crystallographic symmetry.

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* This trivial nomenclature was extended from that used for the trien complexes (Sargeson & Searle, 1965) by Snow, Buckingham, Marzilli & Sargeson (1969).

complexes are five-coordinate with no ligands *trans* to the μ-oxo system.) The two Fe–N contacts of intermediate length appear to be a consequence of accommodating the longest contact.

It is concluded that the conformation of the cation is well established and that there are indications of a variation in Fe–N distance with position in the tetraethylenepentaamine chain, but that further discussion of the details of the cation dimensions would not be justified on the basis of this analysis alone.

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# Electron Microscopy of the Perovskite Polytypes $Ba_4Ta_3LiO_{12}$ and $Ba_5W_3Li_2O_{15}$

By J. L. Hutchison and A. J. Jacobson

*Inorganic Chemistry Laboratory, South Parks Road, Oxford OX*1 3*QR*, *England*

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High-resolution lattice images have been obtained for the ordered perovskite polytypes $Ba_5W_3Li_2O_{15}$ (*cccch*) and $Ba_4Ta_3LiO_{12}$ (*ccch*). The lattice images can be correlated with the stacking sequence of the $BaO_3$ layers and, for $Ba_5W_3Li_2O_{15}$, with the presence of the ordered arrangement of corner-sharing $LiO_6$ octahedra.

## Introduction

The study of structural imperfections in complex oxides by high-resolution electron microscopy has received much attention in recent years. In particular, the ability of an electron microscope to generate from a thin crystal an image which closely resembles the projected structure of that crystal has led to new insights into the ultramicro-structure of complex oxides. The niobium oxide 'block' structures and a variety of 'crystallographic shear' structures have been successfully examined in this way. The structures consist of relatively open networks of corner-sharing [$MO_6$] octahedra, with centre to centre distances of 0·38 nm, comparable to the resolving power of the electron microscope. The networks are nominally one octahedron deep, and lattice images of crystals oriented with this axis parallel to the electron beam may be correlated with the actual structure in terms of dark contrast indicating areas of high projected charge density. The interpretation was possible at resolutions of 0·5–0·8 nm (Allpress, 1970; Hutchison & Anderson, 1972), although micrographs obtained at a resolution of about 0·4 nm (Iijima, 1971) were more convincing. These experimental observations which provide an empirical interpretation of image contrast have been recently confirmed by *n*-beam image calculations (O'Keefe, 1973). Much of the success of these studies of niobium oxides relies on the fact that the projected charge density, along (010), reveals channels between corner-shared octahedra, and Allpress & Sanders (1973) have suggested that other suitable systems would require such voids in projections.

In more closely packed systems, where the projected charge density is less simple, calculations have not yet been made, and only a few systems have been examined experimentally (McConnell, Hutchison & Anderson, 1974). In this work we have investigated the correlation between lattice images and crystal structure for two ordered perovskite polytypes. $ABO_3$ compounds of the perovskite type can be described in terms of $AO_3$ close-packed layers, with B cations in the $O_6$ octahedra. Many polytypes are known which differ in the ratio of the number of cubic to hexagonal stacked layers [for examples see Goodenough & Longo (1970)]. The two compounds chosen for study were eight-layer