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Crystal and Molecular Structure of Dichlorotris-(2-methylimidazole)manganese(II); a High-Spin Pentacoordinate Complex of Manganese

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Dichlorotris-(2-methylimidazole)manganese(II), $MnCl_2(2\text{-meim})_3$, is monoclinic with $a=8{\cdot}189$ (1), $b=14{\cdot}763$ (1), $c=14{\cdot}419$ Å, $\beta=108{\cdot}69$ (1)°, space group $P2_1/c$ and $Z=4$. The structure has been determined from diffractometer data, and least-squares refinement with 2397 independent reflexions has reached $R=0{\cdot}046$. A monomeric pentacoordinate structure is found, in which the coordination, though severely distorted towards square pyramidal, is essentially trigonal bipyramidal. A Cl atom and a 2-meim ligand occupy the axial positions with Mn–Cl and Mn–N distances of 2·525 and 2·249 Å respectively. For the equatorial groups the respective bonds are somewhat shorter – a Cl at 2·392 Å and two 2-meim ligands with a mean Mn–N of 2·195 Å. The molecule has approximate m (C_s) symmetry.

Introduction

Pentacoordinate transition metal complexes are unequally distributed with respect to d^n; thus d^0, d^8, and d^{10} complexes are very common, while d^5 are relatively rare. Only two pentacoordinate divalent Mn species have so far been fully analysed by single-crystal X-ray methods. They are the cations $[Mn(Me_6tren)Br]^+$ (where $Me_6tren = N[CH_2CH_2N(CH_3)_2]_3$) which is trigonal bipyramidal (di Vaira & Orioli, 1968), and $[Mn(Ph_3PO)_4I]^+$ which is square pyramidal (Ciani, Manassero & Sansoni, 1972). In addition, two other Mn complexes have only been shown to be isostructural with analogous pentacoordinate compounds of other metals (Orioli, Di Vaira & Sacconi, 1965; Pauling, Robertson & Rodley, 1965).

The title complex, $MnCl_2(2\text{-meim})_3$, has been prepared by Birdy & Goodgame (1975), and is formed irrespective of the ratio of starting materials. The fact that this complex does not involve chelating ligands means that the molecule can adopt its preferred shape with less hindrance. For an MX_2L_3 complex there are six possible idealized structures (Muetterties & Schunn, 1966): three trigonal bipyramidal with D_{3h}, C_{2v} or C_s point symmetries, and three square pyramidal (C_{2v} and two C_s). A trigonal bipyramidal configuration seemed the more likely one to be adopted as in $CuCl_2$(1,2-dimethylimidazole)$_3$ (Huq & Skapski, 1971); however, it would have been difficult to predict which ligands would be axial and which equatorial. The relative lengths of like bonds in the axial and the equatorial positions were also of interest. We have accordingly carried out a structure determination of this complex.

Experimental

Dichlorotris-(2-methylimidazole)manganese(II) crystallizes from ethanol (Birdy & Goodgame, 1975) as well formed pale yellow prisms. Preliminary photographs showed the crystals to be monoclinic, with systematic absences $h0l$: $l=2n+1$, and $0k0$: $k=2n+1$. These absences uniquely determine the space group as $P2_1/c$ (No. 14). Measurement of 22 high-angle reflexions on a diffractometer, followed by a least-squares calculation, gave $a=8{\cdot}189$ (1), $b=14{\cdot}763$ (1), $c=14{\cdot}419$ (1) Å, $\beta=108{\cdot}69$ (1)°, $U=1651{\cdot}3$ Å^3. Other crystal data are: $D_o=1{\cdot}51$ (by flotation), $D_c=1{\cdot}50$ g cm^{-3} for $Z=4$ and a molecular formula $C_{12}H_{18}Cl_2MnN_6$, $M=372{\cdot}16$, $F(000)=764$, $\mu(\text{Cu } K\alpha)=98{\cdot}4$ cm^{-1}.

A crystal, 0·19 × 0·24 × 0·15 mm, was mounted with **c** parallel to the φ axis of a Siemens off-line automatic four-circle diffractometer. Reflexion intensities were measured with Cu $K\alpha$ radiation ($\lambda=1{\cdot}5418$ Å) at a take-off angle of 3·0°, a Ni β-filter, and a Na(Tl)I scintillation counter. The θ–2θ scan technique was employed with a 'five-value' measuring procedure: one side of peak, background, full peak, background on other side of peak, other side of peak (Allen, Rogers & Troughton, 1971). 2400 independent reflexions were measured to $\theta=60°$, and of these 197 were considered to be 'unobserved' as the net count of each was less than $2{\cdot}58\sigma$. The 1,11,0 reflexion was monitored as a reference every 50 reflexions: its net count did not alter noticeably over the period of data collection (*ca* 4 days). The data were scaled by use of the reference reflexion, and Lorentz and polarization corrections applied. At a later stage the data were corrected for absorption by the Gaussian integration method (Busing & Levy, 1957), with a 12 × 12 × 12 grid, and with crystal path lengths determined by the vector analysis procedure of Coppens, Leiserowitz & Rabinovich (1965).

Solution and refinement of the structure

The origin-removed Patterson synthesis presented a curious problem – three internally consistent sets of vector peaks could be found to give possible Mn atom positions, although only one independent Mn was known to be present. Since there was little to choose

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between the three solutions, a few cycles of least-squares refinement were carried out on each to give almost identical R values in the range 0·54–0·56. The solution giving the worst R was the only one for which a difference synthesis gave plausible positions for the Cl atoms. The remaining non-hydrogen atoms were now located without difficulty from the next difference synthesis, and isotropic refinement gave R = 0·112.

Refinement with anisotropic thermal parameters reduced R to 0·058. Application of an absorption correction and refinement as previously caused R to increase marginally to 0·059. (The correction was checked and no mistake could be found; we can only surmise that absorption errors had in some way been partly compensated by other factors.) The H atoms were located from a difference synthesis, and when they were included as fixed atom contributions with isotropic temperature factors of their parent C atoms R diminished to 0·052. Further full-matrix refinement in which a weighting scheme was introduced, and three strong low-angle reflexions thought to be suffering from extinction were removed, reduced R to its final value of 0·046. The final difference synthesis was featureless.

In the later stages of refinement the weighting scheme was that suggested by Hughes (1941) where $w=1$ for $F<F^*$, $\sqrt{w}=F^*/F$ for $F \geq F^*$, with $F^*=85$ as the optimum value. Scattering factors of Cromer & Waber (1965), and for H of Stewart, Davidson & Simpson (1965), were used, while the anomalous dispersion corrections for Mn and Cl were those given by Cromer (1965). The July 1970 version of the X-RAY 63 System (Stewart, 1964) was used for the solution and refinement of the structure. Calculations were performed on the University of London CDC 7600 computer, while the structural illustrations were drawn with the Imperial College CDC 6400.

Atomic coordinates of the non-hydrogen atoms are given in Table 1, while Table 2 lists the coefficients in the expression for the anisotropic temperature factor $\exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\right]$ and the root-mean-square amplitudes of vibration along the principal axes of the thermal ellipsoid. The unrefined coordinates of the H atoms are listed in Table 3.*

Table 1. *Atomic coordinates with estimated standard deviations in parentheses*

	x	y	z
Mn(1)	0·19805 (8)	0·19865 (4)	0·22097 (5)
Cl(1)	0·31466 (13)	0·30912 (7)	0·12409 (8)
Cl(2)	0·26869 (14)	0·28779 (7)	0·36706 (8)
N(11)*	0·0773 (5)	0·0837 (3)	0·2780 (3)
C(12)	0·0026 (6)	0·0130 (3)	0·2256 (3)
N(13)	−0·0459 (6)	−0·0474 (3)	0·2819 (3)
C(14)	−0·0014 (8)	−0·0125 (4)	0·3755 (4)
C(15)	0·0743 (7)	0·0675 (3)	0·3721 (4)
C(16)	−0·0264 (8)	−0·0023 (4)	0·1199 (4)
N(21)	0·3851 (5)	0·0983 (3)	0·2053 (3)
C(22)	0·4633 (6)	0·0341 (3)	0·2682 (3)
N(23)	0·5178 (5)	−0·0320 (3)	0·2205 (3)
C(24)	0·4775 (7)	−0·0077 (4)	0·1242 (4)
C(25)	0·3950 (6)	0·0729 (3)	0·1150 (4)
C(26)	0·4903 (8)	0·0323 (4)	0·3742 (4)
N(31)	−0·0599 (4)	0·2339 (3)	0·1226 (3)
C(32)	−0·2043 (6)	0·2441 (3)	0·1430 (3)
N(33)	−0·3386 (5)	0·2534 (3)	0·0603 (3)
C(34)	−0·2768 (6)	0·2483 (4)	−0·0171 (3)
C(35)	−0·1056 (6)	0·2370 (3)	0·0215 (3)
C(36)	−0·2250 (6)	0·2467 (4)	0·2410 (4)

* The atoms of the 2-meim ligands are numbered (*mn*) where *m* is ligand number, and *n* is the atom number within each ligand.

Table 2. *Anisotropic thermal parameters* (Mn, Cl × 10^5; N, C × 10^4) *and root-mean-square amplitudes of vibration* (Å)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Min.	Inter.	Max.
Mn(1)	758 (12)	212 (3)	332 (4)	−8 (5)	116 (5)	−10 (3)	0·150	0·154	0·183
Cl(1)	977 (19)	264 (5)	411 (6)	−40 (8)	258 (8)	12 (5)	0·158	0·178	0·197
Cl(2)	1326 (21)	277 (5)	326 (6)	−24 (8)	79 (9)	−42 (4)	0·159	0·183	0·218
N(11)	127 (7)	29 (2)	38 (2)	−16 (3)	22 (3)	−2 (2)	0·159	0·192	0·213
C(12)	126 (9)	28 (2)	44 (3)	−13 (4)	23 (4)	−2 (2)	0·162	0·203	0·210
N(13)	191 (9)	31 (2)	60 (3)	−36 (3)	42 (4)	1 (2)	0·144	0·236	0·264
C(14)	260 (14)	45 (3)	47 (3)	−33 (5)	51 (5)	2 (3)	0·178	0·221	0·298
C(15)	183 (11)	37 (3)	39 (3)	−23 (4)	31 (4)	−5 (2)	0·178	0·192	0·249
C(16)	287 (15)	42 (3)	55 (4)	−48 (5)	46 (6)	−14 (3)	0·174	0·231	0·314
N(21)	125 (7)	27 (2)	41 (2)	10 (3)	25 (3)	4 (2)	0·166	0·191	0·207
C(22)	116 (9)	28 (2)	46 (3)	10 (4)	19 (4)	5 (2)	0·160	0·197	0·211
N(23)	157 (8)	32 (2)	58 (3)	34 (3)	34 (4)	7 (2)	0·142	0·229	0·254
C(24)	207 (12)	42 (3)	50 (3)	27 (5)	52 (5)	1 (2)	0·172	0·214	0·270
C(25)	158 (10)	30 (2)	49 (3)	22 (4)	38 (4)	9 (2)	0·161	0·196	0·243
C(26)	229 (13)	49 (3)	47 (3)	31 (5)	21 (5)	7 (3)	0·183	0·240	0·303
N(31)	77 (6)	33 (2)	39 (2)	−3 (3)	16 (3)	2 (2)	0·155	0·185	0·199
C(32)	95 (8)	35 (2)	42 (3)	−2 (4)	15 (4)	4 (2)	0·174	0·188	0·212
N(33)	71 (7)	59 (3)	47 (3)	0 (3)	6 (3)	5 (2)	0·147	0·220	0·255
C(34)	106 (9)	65 (3)	35 (3)	1 (4)	8 (4)	6 (2)	0·168	0·200	0·270
C(35)	101 (9)	46 (3)	35 (3)	2 (4)	18 (4)	1 (2)	0·172	0·184	0·227
C(36)	98 (9)	79 (4)	50 (3)	6 (5)	35 (4)	3 (2)	0·158	0·218	0·296

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31259 (14 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Fractional coordinates of the* H *atoms*

The atoms are numbered so that the first two digits correspond to those of the parent atom.

	x	*y*	*z*
H(13)	−0·111	−0·108	0·258
H(14)	−0·018	−0·043	0·436
H(15)	0·125	0·111	0·432
H(161)	−0·075	0·060	0·095
H(162)	−0·111	−0·052	0·091
H(163)	0·086	−0·014	0·105
H(23)	0·583	−0·090	0·253
H(24)	0·501	−0·045	0·069
H(25)	0·349	0·110	0·051
H(261)	0·625	0·035	0·410
H(262)	0·441	−0·024	0·397
H(263)	0·436	0·089	0·397
H(33)	−0·466	0·260	0·057
H(34)	−0·347	0·253	−0·090
H(35)	−0·018	0·232	−0·018
H(361)	−0·100	0·237	0·288
H(362)	−0·304	0·196	0·251
H(363)	−0·273	0·308	0·255

Description of the structure and discussion

The structure of a five-coordinate species represents a very fine balance of factors, such as the steric requirements of the ligands, the *d*-electron distribution of the metal atom, the amount of π-bonding, and crystal packing forces. Thus the structure of trigonal bipyramidal $[\text{Mn}(\text{Me}_6\text{tren})\text{Br}]^+$ (Di Vaira & Orioli, 1968) is dictated by the conformation of the polyamine, while the square pyramidal cation $[\text{Mn}(\text{Ph}_3\text{PO})_4\text{I}]^+$ (Ciani *et al.*, 1972) results from a blocking of the sixth coordination position by the phenyl rings of the phosphine oxide ligands.

Fig. 1 shows the molecular structure of $\text{MnCl}_2(2\text{-meim})_3$, in which the central Mn atom has a distorted trigonal bipyramidal coordination. [The diagram also shows the thermal vibration ellipsoids (Johnson, 1965) of the non-hydrogen atoms.] A Cl atom and a 2-meim group are axial, and the equatorial positions are occupied by the other Cl and two 2-meim. Thus this compound has a structure different from that of $\text{CuCl}_2(1,2\text{-dimethylimidazole})_3$, which is also trigonal bipyramidal but with less distortion, and in which the equatorial positions are occupied by two Cl atoms and a 1,2-dimethylimidazole group (Huq & Skapski, 1971).

An approximate *m* (C_s) symmetry is found for the title complex, where the 'mirror plane' comprises the two Cl atoms, a 2-meim ligand (1*n*), and the central metal atom (Fig. 2). The most important distances, both intra- and intermolecular, and bond angles are given in Table 4. There is a difference between the axial and the equatorial bond lengths: Mn–Cl(axial) is 2·525 Å as against Mn–Cl(equatorial) 2·392 Å, and Mn–N(axial) is 2·249 Å, while the Mn–N(equatorial) distances are 2·194 and 2·196 Å.

From the bond angles given in Table 4 it can be seen that the trigonal bipyramidal coordination is considerably distorted from the ideal geometry. Thus the axial–metal–axial angle is 168°, while the three equatorial angles are 110, 119, and 131°. Nevertheless TBP is a better description than square pyramidal. In the latter case, for instance, the apical atom would be Cl(2) and the two *trans* basal–metal–basal angles, which should be equal, are then 168 and 131°. Hoskins & Whillans (1972/1973) have carried out calculations of potential energy based on interligand repulsion in order to predict likely bond angles in pentacoordinate species. They used simplified models of geometry intermediate between square pyramidal and trigonal bipyramidal. For a case where the axial–metal–axial angle is 170° and one of the equatorial angles is 110° they predict the other two equatorial angles to be 117 and 133°, a

Table 4. *Interatomic distances* (Å) *and bond angles* (°) *with estimated standard deviations in parentheses*

(*a*) Intramolecular

Mn(1)–Cl(1)	2·525 (1)	Mn(1)–N(11)	2·249 (4)	Mn(1)–N(21)	2·194 (4)	Mn(1)–N(31)	2·196 (3)
Mn(1)–Cl(2)	2·392 (1)						

						Mean	
N(11)–C(12)	1·318 (6)	N(21)–C(22)	1·327 (6)	N(31)–C(32)	1·315 (7)	N(*m*1)–C(*m*2)	1·320
C(12)–N(13)	1·348 (7)	C(22)–N(23)	1·349 (7)	C(32)–N(33)	1·345 (5)	C(*m*2)–N(*m*3)	1·347
N(13)–C(14)	1·379 (7)	N(23)–C(24)	1·368 (7)	N(33)–C(34)	1·366 (7)	N(*m*3)–C(*m*4)	1·371
C(14)–C(15)	1·342 (8)	C(24)–C(25)	1·355 (7)	C(34)–C(35)	1·342 (6)	C(*m*4)–C(*m*5)	1·346
C(15)–N(11)	1·386 (7)	C(25)–N(21)	1·382 (7)	C(35)–N(31)	1·385 (6)	C(*m*5)–N(*m*1)	1·384
C(12)–C(16)	1·483 (8)	C(22)–C(26)	1·473 (8)	C(32)–C(36)	1·477 (8)	C(*m*2)–C(*m*6)	1·478

Cl(1)–Mn(1)–Cl(2)	95·99 (4)	Cl(2)–Mn(1)–N(11)	95·96 (10)	N(11)–Mn(1)–N(21)	86·05 (15)
Cl(1)–Mn(1)–N(11)	168·03 (10)	Cl(2)–Mn(1)–N(21)	118·83 (9)	N(11)–Mn(1)–N(31)	88·32 (13)
Cl(1)–Mn(1)–N(21)	88·80 (11)	Cl(2)–Mn(1)–N(31)	110·44 (11)	N(21)–Mn(1)–N(31)	130·72 (14)
Cl(1)–Mn(1)–N(31)	86·88 (11)				

Mn(1)–N(11)–C(12)	124·5 (3)	Mn(1)–N(21)–C(22)	127·8 (4)	Mn(1)–N(31)–C(32)	129·1 (3)
Mn(1)–N(11)–C(15)	129·5 (3)	Mn(1)–N(21)–C(25)	122·2 (3)	Mn(1)–N(31)–C(35)	124·6 (3)
C(12)–N(11)–C(15)	105·9 (4)	C(22)–N(21)–C(25)	106·8 (4)	C(32)–N(31)–C(35)	105·8 (3)
N(11)–C(12)–N(13)	110·5 (4)	N(21)–C(22)–N(23)	109·6 (4)	N(31)–C(32)–N(33)	110·6 (4)
N(11)–C(12)–C(16)	127·0 (5)	N(21)–C(22)–C(26)	127·0 (5)	N(31)–C(32)–C(36)	127·1 (4)
N(13)–C(12)–C(16)	122·5 (4)	N(23)–C(22)–C(26)	123·5 (4)	N(33)–C(32)–C(36)	122·3 (5)
C(12)–N(13)–C(14)	107·8 (4)	C(22)–N(23)–C(24)	108·5 (4)	C(32)–N(33)–C(34)	107·8 (4)
N(13)–C(14)–C(15)	105·9 (5)	N(23)–C(24)–C(25)	106·2 (5)	N(33)–C(34)–C(35)	106·2 (4)
C(14)–C(15)–N(11)	109·9 (4)	C(24)–C(25)–N(21)	108·9 (4)	C(34)–C(35)–N(31)	109·6 (5)

Table 4 (*cont.*)

(*b*) Intermolecular

N(13)···Cl(2$^{\mathrm{i}}$)	3·370 (4)	N(13)–H(13)–Cl(2$^{\mathrm{i}}$)	153
N(23)···Cl(1$^{\mathrm{ii}}$)	3·230 (4)	N(23)–H(23)–Cl(1$^{\mathrm{ii}}$)	155
N(33)···Cl(1$^{\mathrm{iii}}$)	3·356 (5)	N(33)–H(33)–Cl(1$^{\mathrm{iii}}$)	151

Superscripts refer to atoms in the following positions:
(i) $-x, y-\frac{1}{2}, \frac{1}{2}-z$; (ii) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iii) $x-1, y, z$.

Table 5. *Planarity of groups of atoms in the structure and distances* (Å) *from the least-squares planes*

Equations of the planes are expressed as $Px+Qy+Rz=S$ in direct space.

$$7{\cdot}07x-6{\cdot}69y-0{\cdot}97z=-0{\cdot}28$$

N(11)	0·003	C(12)	−0·002	N(13)	0·005
C(14)	−0·004	C(15)	−0·001	C(16)	−0·002

Not defining plane: Mn(1) 0·142

$$7{\cdot}03x+7{\cdot}02y-1{\cdot}30z=3{\cdot}14$$

N(21)	−0·007	C(22)	0·009	N(23)	−0·008
C(24)	0·004	C(25)	−0·002		

Not defining plane: Mn(1) −0·638, C(26) 0·049

$$1{\cdot}03x+14{\cdot}64y-0{\cdot}09z=3{\cdot}35$$

N(31)	−0·002	C(32)	−0·004	N(33)	0·002
C(34)	−0·002	C(35)	0·004	C(36)	0·003

Not defining plane: Mn(1) −0·262

$$4{\cdot}71x+10{\cdot}23y-8{\cdot}59z=1{\cdot}06$$

Mn(1)	0·008	Cl(2)	−0·002	N(21)	−0·003
N(31)	−0·003				

Not defining plane: Cl(1) 2·519, N(11) −2·228

$$-6{\cdot}78x+6{\cdot}65y-0{\cdot}71z=-0{\cdot}17$$

Mn(1)	−0·009	Cl(1)	0·004	Cl(2)	0·001
N(11)	0·004				

Not defining plane: N(21) −1·934, N(31) 2·045

$$0{\cdot}15x+7{\cdot}59y+11{\cdot}63z=3{\cdot}52$$

Cl(1)	0·312	N(11)	0·354	N(21)	−0·334
N(31)	−0·332				

Not defining plane: Mn(1) 0·582, Cl(2) 2·968

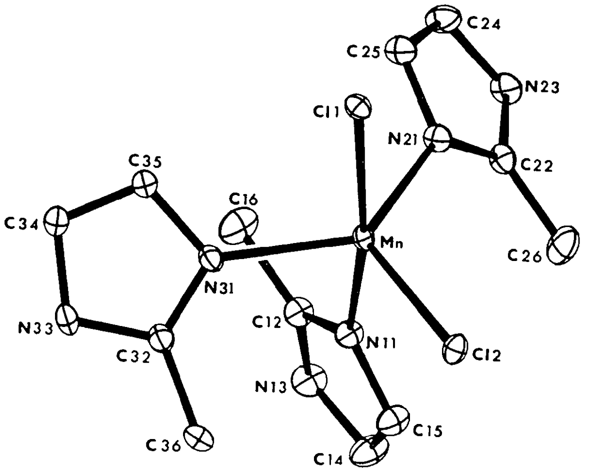

Fig. 1. The molecular structure of $MnCl_2(2\text{-meim})_3$. Thermal vibration ellipsoids are scaled to enclose 20% probability.

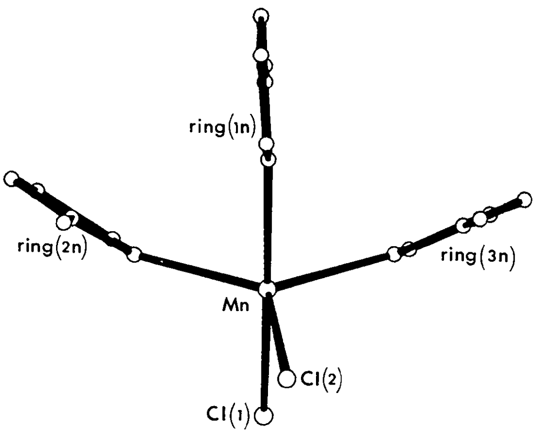

Fig. 2. A view of the molecule showing that the planes of the three imidazole rings are nearly coaxial, and that the molecule has approximate *m* symmetry. Note the pronounced bending at the N(1) position of ring (2*n*).

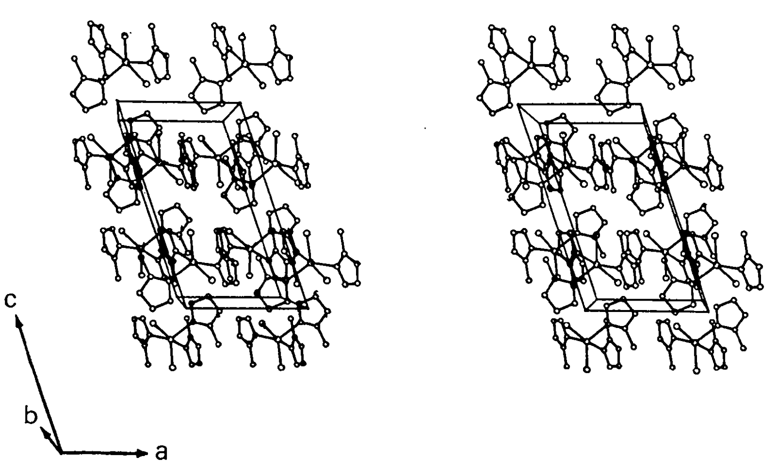

Fig. 3. A stereoscopic view showing the packing of $MnCl_2(2\text{-meim})_3$ molecules.

geometry quite similar to that found in the title complex.

Table 5 shows that the metal atom lies within the equatorial plane, Cl(2), N(21), N(31), and also within an axial plane consisting of Cl(1), N(11) and Cl(2). The angle between these two planes is 89°. This is as it should be for a trigonal bipyramid. It is, however, equally valid for a square pyramid where these planes would then be the two vertical planes. In this latter geometry there should be a third, basal, plane; which in the title complex is a poor one (even if all four 'basal' bonds were of equal length), though it is still nearly normal to the other two planes. This confirms that the geometry observed is essentially trigonal bipyramidal, but with a strong distortion towards the square pyramidal.

In the structure of $CuCl_2(1,2\text{-dimethylimidazole})_3$ the axial Cu–N bonds are appreciably shorter than the equatorial one (mean of 2·005, and 2·145 Å respectively), as is the case to a lesser extent for the Cu–Cl bonds in $[CuCl_5]^{3-}$, 2·296 and 2·391 Å respectively (Raymond, Meek & Ibers, 1968). The most common situation, however, for transition metal TBP complexes is for the axial bonds to be longer than equatorial ones, *e.g.* as in $[N_6P_6(NMe_2)_{12}CoCl]^+$ (Harrison, Paddock, Trotter & Wingfield, 1972) or the pseudo-five-coordinate complex with 2-methylimidazole ligands $[Co(2\text{-meim})_4NO_3]^+$ (Akhtar, Huq & Skapski, 1972). In the title compound the axial bonds are clearly the longer ones. The extent of the lengthening, however, is unequal. Thus the difference between the Mn–Cl bonds is quite large, while that between Mn–N bonds is relatively small.

An explanation of this difference may be sought in two possible causes, both of which may contribute to the overall effect. Firstly, with the distortion towards a square pyramidal geometry there will be a tendency for the three Mn–N lengths to equalize themselves, since all three bonds would be basal in the limiting case. Furthermore, an increase in the difference between the two Mn–Cl bonds would arise if the apical bond shortening predicted by Ballhausen & Gray (1963) for transition metal complexes operated on Mn–Cl(2); this last mechanism, however, should be viewed with some caution since many cases contrary to this prediction have been reported. A second cause may lie in the hydrogen bonding in which the Cl atoms are involved. It can be seen from Table 4 that Cl(1) takes part in two hydrogen bonds, while Cl(2) is involved in only one. Hence there may be a slight weakening of the Mn–Cl(1) bond relative to Mn–Cl(2).

There is little variation in equivalent bond lengths in the three 2-meim ligands, and in no case is the difference statistically significant. There is, however, a slight difference in the degree of planarity. Table 5 shows that ligands (1*n*) and (3*n*) are very closely planar, with an average deviation for the atoms from the least-squares plane of 0·003 Å in each case, and a maximum deviation of 0·005 Å. In (2*n*) the ring system is planar, but the methyl group is slightly, though significantly, out of the ring plane. The most striking difference between the rings, however, is in the extent to which the Mn atom lies outside the least-squares planes; for (2*n*) this deviation is *ca* 0·64 Å, which means that the coordination at N(21) is quite severely distorted from planar towards pyramidal. This distortion is best seen in Fig. 2. We have recently observed a similar pronounced bending at a donor N in the structure of a Pt complex with inosine 5'-monophosphate, $[Pt(5'\text{-}IMP)_2(NH_3)_2]^{2-}$ (Goodgame, Jeeves, Phillips & Skapski, 1975).

Further evidence for this relative flexibility at the N(*m*1) position is provided by the exocyclic angles at these atoms. In (1*n*) the angle Mn–N(*m*1)–C(*m*5) > Mn–N(*m*1)–C(*m*2) by *ca* 5°, while for (2*n*) and (3*n*) the reverse is true. These differences may be readily explained in terms of slight intramolecular steric repulsions between Cl(2) and the three 2-meim ligands. In contrast, equivalent angles at C(*m*2) are closely similar in all three cases.

The main cohesive forces between the complex molecules arise from hydrogen bonds of the type N–H ···Cl. Every N(*m*3) atom in the structure forms one of these bonds, so that Cl(1) is involved in two while Cl(2) takes part in one. The N···Cl distances lie in the range 3·23–3·37 Å (Table 4). Fig. 3 shows the packing of the molecules as a pair of stereoscopic drawings (Johnson, 1965).

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Structure Cristalline de Ag_8GeTe_6 (γ)

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γAg_8GeTe_6 crystallizes in the cubic system with $a=11{\cdot}566$ (2) Å, space group $F\bar{4}3m$, $Z=4$. The structure was solved by Patterson and Fourier methods, and refined by least-squares calculations to an R index of 0·074. The structure consists of a rigid body of Te atoms consolidated by $GeTe_4$ tetrahedra; the Ag atoms are disordered among the 132 other tetrahedra formed by the Te atoms.

Introduction

Des études portant sur les composés sélénies et tellurés de l'argent et des éléments du groupe IV*b* ont été effectuées par Hahn, Schulze & Sechser (1965) et reprises par Gorochov (1968). Ces études par analyse thermique différentielle et diffraction des rayons X ont mis en évidence huit composés du type Ag_8MX_6 où: M = Si, Ge, Sn; X = S, Se, Te. Tous ces composés présentent plusieurs phases, dont trois phases pour les tellurures. La phase γ de haute température est commune à tous ces composés et dans le cas des tellurures comme Ag_8GeTe_6 elle est stable à température ambiante, les points de transition étant pour ce composé situés à −29 °C pour la transformation γ,β et à −52 °C pour la transformation β,α.

C'est la structure de Ag_8GeTe_6(γ), phase de haute température que nous décrivons ici.

Partie expérimentale

Ag_8GeTe_6(γ) est préparé suivant les techniques décrites par Gorochov (1968). Le produit se présente sous forme d'une masse compacte de laquelle nous pouvons extraire des cristaux noirs, durs, présentant l'éclat métallique.

Les clichés d'oscillation puis de Weissenberg et de précession rélèvent une maille cubique d'arête $a=11{,}566$ (2) Å. Toutes les réflexions observées ont des indices de même parité, ce qui indique un réseau *F*. La symétrie du groupe de Laue $m3m$ nous donne le choix entre trois groupes d'espace $Fm3m$, $F432$ et $F\bar{4}3m$. Pour essayer de lever l'ambiguïté, nous avons effectué un test de piézoélectricité qui s'est révélé positif. Nous avons donc travaillé dans le groupe spatial $F\bar{4}3m$, groupe qui a été confirmé dans la suite de notre étude.

En introduisant quatre masses formulaires par maille, nous sommes conduits à adopter une masse volumique calculée de 7,30 g cm^{-3} en bon accord avec la masse volumique expérimentale 7,22 g cm^{-3} à 20°C.

Un premier monocristal de 90 μm de dimensions moyennes a été choisi de façon à ce que l'absorption pour la radiation $K\alpha$ du molybdène ne soit pas trop importante. Les intensités des réflexions intégrées ont été recueillies sur films, puis mesurées au microdensitomètre, ces intensités ont été corrigées des facteurs géométriques de Lorentz et de polarisation puis mises en échelle absolue par la méthode de Wilson.

Puis nous avons dû, comme cela est indiqué plus loin, trouver un cristal de meilleure qualité pour achever de résoudre la structure; ce deuxième cristal de dimensions identiques au premier a été obtenu à partir d'une nouvelle préparation utilisant la méthode de transport par l'iode; les intensités de 336 réflexions ont été mesurées, seules les réflexions contenues dans l'unité asymétrique ($\frac{1}{6}$ d'octant) ont été conservées soit 169 réflexions.