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), MnCl₂(2-meim)₃, is monoclinic with a = 8.189 (1), b = 14.763 (1), c = 14.419 Å, β = 108.69 (1)°, space group P2₁/c and Z = 4. The structure has been determined from diffractometer data, and least-squares refinement with 2397 independent reflections has reached R = 0.046. 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 (C₃) symmetry.

Introduction
Pentacoordinate transition metal complexes are unequally distributed with respect to dⁿ; thus d⁰, d⁸, and d¹⁰ complexes are very common, while d² complexes 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(Me₆tren)Br]⁺ (where Me₆tren = N(CH₂CH₂N(CH₃)₂)₆) which is trigonal bipyramidal (di Vaira & Orioli, 1968), and [Mn(P₃H₅O)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, MnCl₂(2-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 MX₂La complex there are six possible idealized structures (Muetterties & Schunn, 1966): three trigonal bipyramidal with D₃h, C₃ᵥ or C₃ point symmetries, and three square pyramidal (C₄ᵥ and two C₃). A trigonal bipyramidal configuration seemed to be 'unobserved' as the net count of each was less than 2.58σ. The 1,11,0 reflexion was monitored as a 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 θ = 60°, and of these 197 were considered to be 'unobserved' as the net count of each was less than 2.58σ. 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).

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 P2₁/c (No. 14). Measurement of 22 high-angle reflexions on a diffractometer, followed by a least-squares calculation, gave a = 8.189 (1), b = 14.763 (1), c = 14.419 (1) Å, β = 108.69 (1)°, U = 1651.3 Å³. Other crystal data are: D₀ = 1.51 (by flotation), Dₐ = 1.50 g cm⁻³ for Z = 4 and a molecular formula C₃₇H₁₈Cl₂MnN₆, M = 372.16, F(000) = 764, μ(Cu Kα) = 98.4 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. Reflection intensities were measured with Cu Kα radiation (λ = 1.5418 Å) at a take-off angle of 3°, a Ni β-filter, and a Na(Tl)I scintillation counter. The 0–2θ 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 θ = 60°, and of these 197 were considered to be 'unobserved' as the net count of each was less than 2.58σ. 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 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.)

In the later stages of refinement the weighting scheme was that suggested by Hughes (1941) where \( w = 1 \) for \( F < F^* \), \( w = F^*/F \) 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 \( \exp \left[ -\left( \beta_{11} h^2 + \beta_{22} k^2 + \beta_{33} l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl \right) \right] \) 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.*

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

<table>
<thead>
<tr>
<th>( \beta_{11} )</th>
<th>( \beta_{22} )</th>
<th>( \beta_{33} )</th>
<th>( \beta_{12} )</th>
<th>( \beta_{13} )</th>
<th>( \beta_{23} )</th>
<th>Min.</th>
<th>Inter.</th>
<th>Max.</th>
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<tr>
<td>Mn(1)</td>
<td>758 (12)</td>
<td>212 (3)</td>
<td>322 (4)</td>
<td>-8 (5)</td>
<td>116 (5)</td>
<td>-10 (3)</td>
<td>0.150</td>
<td>0.154</td>
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<tr>
<td>Cl(1)</td>
<td>977 (19)</td>
<td>264 (5)</td>
<td>411 (6)</td>
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<td>258 (8)</td>
<td>12 (5)</td>
<td>0.158</td>
<td>0.178</td>
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<tr>
<td>Cl(2)</td>
<td>1326 (21)</td>
<td>277 (5)</td>
<td>326 (6)</td>
<td>-24 (8)</td>
<td>79 (9)</td>
<td>-42 (4)</td>
<td>0.159</td>
<td>0.183</td>
</tr>
<tr>
<td>N(11)*</td>
<td>127 (7)</td>
<td>29 (2)</td>
<td>38 (2)</td>
<td>-16 (3)</td>
<td>22 (3)</td>
<td>-2 (2)</td>
<td>0.159</td>
<td>0.192</td>
</tr>
<tr>
<td>C(22)</td>
<td>126 (9)</td>
<td>28 (2)</td>
<td>44 (3)</td>
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<td>23 (4)</td>
<td>-2 (2)</td>
<td>0.162</td>
<td>0.203</td>
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<td>C(23)</td>
<td>191 (9)</td>
<td>32 (2)</td>
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<td>39 (3)</td>
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<td>0.192</td>
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<td>C(16)</td>
<td>287 (15)</td>
<td>42 (3)</td>
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<tr>
<td>N(21)</td>
<td>125 (7)</td>
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<td>41 (2)</td>
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<td>28 (2)</td>
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<td>19 (4)</td>
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<tr>
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<td>32 (2)</td>
<td>58 (3)</td>
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<td>34 (4)</td>
<td>7 (2)</td>
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<td>0.229</td>
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<tr>
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<td>27 (5)</td>
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<td>C(25)</td>
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<td>49 (3)</td>
<td>22 (4)</td>
<td>38 (4)</td>
<td>9 (2)</td>
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<td>C(26)</td>
<td>223 (13)</td>
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<td>47 (3)</td>
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<td>21 (3)</td>
<td>7 (3)</td>
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<td>0.240</td>
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<tr>
<td>N(31)</td>
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<td>33 (2)</td>
<td>39 (2)</td>
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<td>2 (2)</td>
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<td>0.185</td>
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<td>C(32)</td>
<td>95 (8)</td>
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<td>42 (3)</td>
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<td>4 (2)</td>
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<td>0.188</td>
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<tr>
<td>N(33)</td>
<td>71 (7)</td>
<td>59 (3)</td>
<td>47 (3)</td>
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<td>6 (3)</td>
<td>5 (2)</td>
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<td>0.220</td>
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<tr>
<td>C(34)</td>
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<td>8 (4)</td>
<td>6 (2)</td>
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<td>0.200</td>
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<td>C(35)</td>
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<td>46 (3)</td>
<td>35 (3)</td>
<td>2 (4)</td>
<td>18 (4)</td>
<td>1 (2)</td>
<td>0.172</td>
<td>0.184</td>
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<tr>
<td>C(36)</td>
<td>98 (9)</td>
<td>79 (4)</td>
<td>50 (3)</td>
<td>6 (5)</td>
<td>35 (4)</td>
<td>3 (2)</td>
<td>0.158</td>
<td>0.218</td>
</tr>
</tbody>
</table>
Intramolecular 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 CuCl2(1,2-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 (C2) symmetry is found for the title complex, where the 'mirror plane' comprises the two Cl atoms, a 2-meim ligand (ln), 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 3. Fractional coordinates of the H atoms

<table>
<thead>
<tr>
<th>H(13)</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>-0.111</td>
<td>-0.108</td>
<td>0.258</td>
</tr>
<tr>
<td>H(14)</td>
<td>-0.018</td>
<td>-0.043</td>
<td>0.436</td>
</tr>
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<td>H(15)</td>
<td>0.125</td>
<td>0.111</td>
<td>0.432</td>
</tr>
<tr>
<td>H(161)</td>
<td>-0.075</td>
<td>0.060</td>
<td>0.095</td>
</tr>
<tr>
<td>H(162)</td>
<td>-0.111</td>
<td>-0.052</td>
<td>0.091</td>
</tr>
<tr>
<td>H(163)</td>
<td>0.086</td>
<td>-0.014</td>
<td>0.105</td>
</tr>
<tr>
<td>H(23)</td>
<td>0.583</td>
<td>-0.090</td>
<td>0.253</td>
</tr>
<tr>
<td>H(24)</td>
<td>0.501</td>
<td>-0.045</td>
<td>0.069</td>
</tr>
<tr>
<td>H(25)</td>
<td>0.349</td>
<td>0.110</td>
<td>0.051</td>
</tr>
<tr>
<td>H(261)</td>
<td>0.625</td>
<td>0.035</td>
<td>0.410</td>
</tr>
<tr>
<td>H(262)</td>
<td>0.441</td>
<td>-0.024</td>
<td>0.397</td>
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<tr>
<td>H(263)</td>
<td>0.436</td>
<td>0.089</td>
<td>0.397</td>
</tr>
<tr>
<td>H(33)</td>
<td>-0.466</td>
<td>0.260</td>
<td>0.057</td>
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<td>H(34)</td>
<td>-0.347</td>
<td>0.253</td>
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<td>H(35)</td>
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<td>0.232</td>
<td>-0.018</td>
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<tr>
<td>H(361)</td>
<td>0.100</td>
<td>0.237</td>
<td>0.288</td>
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<td>H(362)</td>
<td>-0.304</td>
<td>0.196</td>
<td>0.251</td>
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<tr>
<td>H(363)</td>
<td>-0.273</td>
<td>0.308</td>
<td>0.255</td>
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### Table 4. Interatomic distances (Å) and bond angles (°) with estimated standard deviations in parentheses

<table>
<thead>
<tr>
<th>(a) Intramolecular</th>
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<tbody>
<tr>
<td>Mn(1)–Cl(1)</td>
</tr>
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<tr>
<td>N(11)–C(12)</td>
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<tr>
<td>C(12)–N(13)</td>
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<tr>
<td>N(13)–C(14)</td>
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<td>C(14)–C(15)</td>
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<td>C(15)–N(11)</td>
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<td>C(12)–C(16)</td>
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<td>Cl(1)–Mn(1)–Cl(2)</td>
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<td>Cl(1)–Mn(1)–N(21)</td>
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<td>Cl(1)–Mn(1)–N(31)</td>
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<td>C(12)–N(11)–C(15)</td>
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<tr>
<td>N(11)–C(12)–N(13)</td>
</tr>
<tr>
<td>N(11)–C(12)–C(16)</td>
</tr>
<tr>
<td>N(13)–C(12)–C(16)</td>
</tr>
<tr>
<td>C(12)–N(13)–C(14)</td>
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<tr>
<td>C(13)–C(14)–N(15)</td>
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<tr>
<td>C(14)–C(15)–N(11)</td>
</tr>
</tbody>
</table>

Mean

- Mn(1)–N(11)–Cl(2) 95.96 (10)
- Cl(1)–Mn(1)–N(11) 116.83 (9)
- Cl(1)–Mn(1)–N(21) 110.44 (11)
- Cl(1)–Mn(1)–N(31) 86.86 (11)
- Mn(1)–N(11)–C(12) 124.5 (3)
- Mn(1)–N(11)–C(15) 129.5 (3)
- C(12)–N(11)–C(15) 105.9 (4)
- N(11)–C(12)–N(13) 110.5 (4)
- N(11)–C(12)–C(16) 127.0 (5)
- N(13)–C(12)–C(16) 122.5 (4)
- C(12)–N(13)–C(14) 107.8 (4)
- C(13)–C(14)–N(15) 105.9 (5)
- C(14)–C(15)–N(11) 109.9 (4)

### Table 3. 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 

\[
[MnMe_3(tren)Br]^+ \quad \text{(Di Vaira & Orioli, 1968)}
\]

is dictated by the conformation of the polyamine, while the 

\[
[Mn(Me_6tren)Br]^+ \quad \text{(Di Vaira & Orioli, 1968)}
\]

results from a blocking of the sixth coordination position by the phenyl rings of the phosphine oxide ligands.

Table 4 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 CuCl2(1,2-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 (C2) symmetry is found for the title complex, where the 'mirror plane' comprises the two Cl atoms, a 2-meim ligand (ln), 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 (cont.)

(b) Intermolecular

\[
\begin{align*}
N(13) \cdots Cl(2') & = 3.370 (4) \\
N(23) \cdots Cl(1') & = 3.230 (4) \\
N(33) \cdots Cl(1') & = 3.356 (5)
\end{align*}
\]

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

\[
\begin{align*}
7.07x - 6.69y - 0.97z = -0.28 \\
N(11) & = 0.003 \\
C(12) & = -0.002 \\
N(13) & = 0.005 \\
C(14) & = -0.004 \\
C(15) & = -0.001 \\
C(16) & = -0.002 \\
\end{align*}
\]

Not defining plane: \(Mn(1) = 0.142\)

\[
7.03x + 7.02y - 1.30z = 3.14 \\
N(21) & = -0.007 \\
C(22) & = 0.009 \\
N(23) & = -0.008 \\
C(24) & = 0.004 \\
C(25) & = -0.002 \\
\end{align*}
\]

Not defining plane: \(Mn(1) = 0.638, C(26) = 0.049\)

\[
1.03x + 14.64y - 0.09z = 3.53 \\
N(31) & = -0.002 \\
C(32) & = -0.004 \\
N(33) & = 0.002 \\
C(34) & = -0.002 \\
C(35) & = 0.004 \\
C(36) & = 0.003 \\
\end{align*}
\]

Not defining plane: \(Mn(1) = 0.262\)

\[
4.71x + 10.23y - 8.59z = 1.06 \\
Mn(1) & = 0.008 \\
Cl(2) & = -0.002 \\
N(21) & = -0.003 \\
N(31) & = -0.003 \\
\end{align*}
\]

Not defining plane: \(Cl(1) = 2.519, N(11) = 2.228\)

\[
-6.78x + 6.65y - 0.71z = -0.17 \\
Mn(1) & = -0.009 \\
Cl(1) & = 0.004 \\
Cl(2) & = 0.001 \\
N(11) & = 0.004 \\
\end{align*}
\]

Not defining plane: \(N(21) = 1.934, N(31) = 2.045\)

\[
0.15x + 7.59y + 11.63z = 3.52 \\
Cl(1) & = 0.312 \\
N(11) & = 0.354 \\
N(21) & = -0.334 \\
N(31) & = -0.332 \\
\end{align*}
\]

Not defining plane: \(Mn(1) = 0.582, Cl(2) = 2.968\)

Fig. 1. The molecular structure of MnCl₂(2-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 \((2n)\).

Fig. 3. A stereoscopic view showing the packing of MnCl₂(2-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 would then be the two vertical planes. In this latter it should be for a trigonal bipyramid. It is, however, equatorial plane, Cl(2), N(21), N(31), and also within plex.

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-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$_5$]$^-$, 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$_6$P$_6$(NMe$_2$)$_2$CoCl]$^+$ (Harrison, Paddock, Trotter & Wingfield, 1972) or the pseudofive-coordinate complex with 2-methylimidazole ligands [Co(2-meim)$_2$NO$_3$]$^+$ (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 (1n) and (3n) 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 (2n) 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 (2n) 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'-IMP)$_2$(NH$_3$)$_2$]$^{2-}$ (Goodgame, Jeeves, Phillips & Skapski, 1975).

Further evidence for this relative flexibility at the N(m1) position is provided by the exocyclic angles at these atoms. In (1n) the angle Mn--N(m1)--C(m5) > Mn--N(m1)--C(m2) by ca 5°, while for (2n) and (3n) 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(m2) 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(m3) 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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References

Structure Cristalline de Ag₈GeTe₆ (γ)

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γAg₈GeTe₆ cristallise dans le cube de système avec \( a = 11.566 \) Å, groupe spatial \( F₄̅₃m \), \( Z = 4 \). La structure a été résolue par Patterson et Fourier methods, et affinée par des calculs des moindres carrés à un index de résonance de 0.074. La structure consiste d'un corps rigide de Te atoms consolidé par GeTe₄ tétraédres; les Ag atoms sont désordonnés parmi les 132 autres tétraédres formés par les Te atoms.

Introduction

Des études portant sur les composés sélénés et tellurés de l'argent et des éléments du groupe IVb 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 Ag₈MX₆ où: M = Si, Ge, Sn; X = S, Se, Te. Tous ces composés présentent plusieurs phases, dont trois phases pour les tellurures. La phase \( \gamma \) de haute température est commune à tous ces composés et dans le cas des tellurures comme Ag₈GeTe₆ elle est stable à température ambiante, les points de transition étant pour ce composé situées à -29°C pour la transformation \( \gamma, \beta \) et à -52°C pour la transformation \( \beta, \alpha \).

C'est la structure de Ag₈GeTe₆(γ), phase de haute température que nous décrivons ici.

Partie expérimentale

Ag₈GeTe₆(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 relevé 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 \( F₄̅₃m \). 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 \( F₄̅₃m \), 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 Kx 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 (1/8 octant) ont été conservées soit 169 réflexions.