Molecular Configuration of the Anion $MnCl_5^{2-}$—A Square Pyramidal Pentahalide of the 3*d* Transition Series†

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Summary An *X*-ray study of the structure of $(bipH_2)MnCl_5$ [$bipH_2$ = biphenyl] shows the anion to be penta-co-ordinated by five Cl^- arranged in a square-pyramidal array about the Mn^{III} cation.

THE isolation and characterisation of transition metal derivatives with five simple monodentate ligands have been attempted by various workers.[1] We now report the structure of the species $MnCl_5^{2-}$ which was synthesized by Goodwin and Sylva[2] and confirm their assertion, on the basis of magnetic measurements,[2,3] that it was monomeric.

Crystals of $(bipH_2)MnCl_5$ are orthorhombic, space group *Pbcm*, $a = 13{\cdot}204(7)$, $b = 7{\cdot}103(5)$, and $c = 15{\cdot}339(8)$ Å; $D_m = 1{\cdot}80(2)$ g cm^{-3} (flotation in bromoform–iodoform), $D_c = 1{\cdot}81$ g cm^{-3} and $Z = 4$. The compound was prepared by a modification of the procedure given by Goodwin and Sylva[2] and the shiny black plates obtained could not be recrystallized without decomposition, which takes place *via* an internal redox reaction. Thus, it is impossible to record data without decomposition of the sample. The data collected were corrected by a decay curve obtained by monitoring two standards every hour. Data were collected by a (θ—2θ) scanning technique using a G.E. XRD-6, manually operated, quarter-circle diffractometer and Zr-filtered Mo-K_α radiation. 1193 reflections were obtained, of which 630 were considered to be observed. These were used to compute a sharpened, origin-removed, three-dimensional Patterson function from which the positions of the Mn and four independent Cl atoms were deduced. An observed Fourier synthesis phased by these atoms gave the positions of the heavy atoms of the cation. Full-matrix least-squares refinement of the data using anisotropic thermal parameters for the atoms of the anion and isotropic thermal parameters for the atoms of the cation converged to a conventional R(F) index of 0·08. Since the cation lies on a two-fold axis, with disordered NH^+ fragments and since $bipH_2^{2+}$ is isoelectronic with biphenyl, the cation was refined as though it were a biphenyl molecule. Figure 1 shows the packing of the ions in $(bipH_2)MnCl_5$. The hydrogen bonding [Cl(3)–H(2) = 2·31, Cl(1)–H(3) = 2·51, and Cl(2)–H(6) = 2·56 Å] may be responsible for the high stability of $MnCl_5^{2-}$ in this compound compared to the very unstable $(R_4N)_2MnCl_5$ salts.[4]

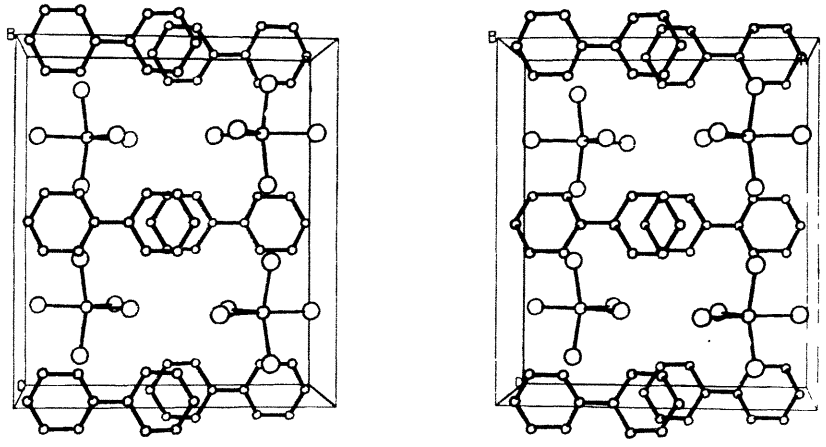

FIGURE 1. *A stereo-pair showing the packing of cations and anions in the unit cell for* $(bipH_2)MnCl_5$

Distances in Å[a]

Mn–Cl(1)	..	2·583	Mn–Cl(3)	..	2·328
Mn–Cl(2)	..	2·336	Mn–Cl(4)	..	2·241

Angles in degrees[a]

Cl(1)–Mn–Cl(2)	92·1	Cl(2)–Mn–Cl(4)	88·6
Cl(1)–Mn–Cl(3)	98·0	Cl(3)–Mn–Cl(4)	89·8
Cl(1)–Mn–Cl(4)	99·4	Cl(4)–Mn–Cl(4′)	161·1
Cl(2)–Mn–Cl(3)	169·9		

[a] E.s.d.'s for distances = 0·008 Å; for angles = 0·5°.
[b] Cl(4′) is related to Cl(4) by mirror operation.

The Table shows the most important distances and angles within the two ions. The three independent equatorial Mn–Cl bonds average 2·302 Å while the axial Mn–Cl bond is 2·583 Å long. It has been suggested[5] that all square pyramidal complexes of the transition elements have sizeable axial compressions due to strong π-bond formation between the central ion and the axial ligand but we observed the opposite effect. The bonds and angles within the cation are normal and are very similar to those of 2,2′-bipyridine;[6] however, the angle between normals to the planes of the two pyridine rings is 35·6(9)°. We feel that for non-co-ordinated bipyridine this angle is determined by forces

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such as hydrogen bonds (*vide supra*) and packing effects since there is little hindrance to rotation about the C–C single bond. Dihedral angles in related species are as follows: *trans*-2,2′-bipyridine is planar,[6] the isoelectronic molecule, biphenyl, is twisted by 45°,[7] in $(bipH_2)CoBr_4$[8] the dihedral angle between pyridine rings is 37.4° and in iodo-bis-(2,2′-bipyridyl)Cu^{II} iodide, there is one planar bipyridyl ligand and another with a twist of 10°.

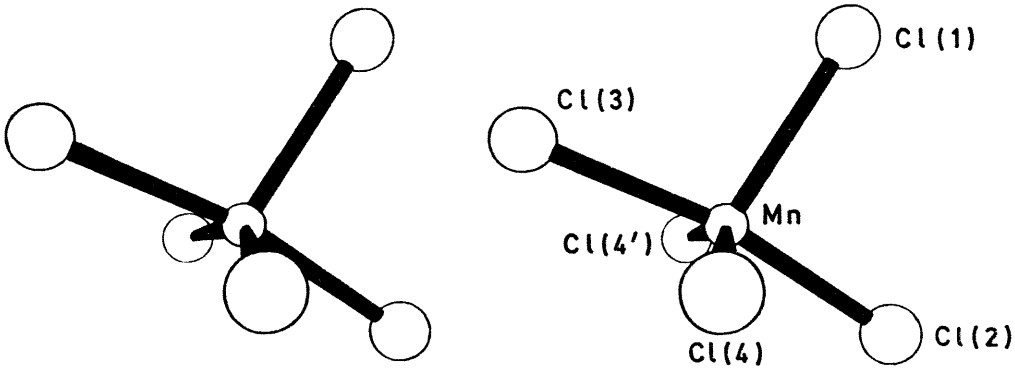

FIGURE 2. *The molecular configuration of the* $MnCl_5^{2-}$ *anion*

Figure 2, which is a stereo pair, shows the configuration of the anion in more detail.

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