CHEMISTRY LETTERS, pp. 51-53, 1972. Published by the Chemical Society of Japan

THE CRYSTAL STRUCTURE OF PHENANTHROLINIUM PENTACHLOROMANGANATE(III), $(phenH_2)(MnCl_5)$

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It has been established by X-ray analysis that the crystal of phenanthrolinium pentachloromanganate(III) contains $(phenH_2)^{2+}$ and square-pyramidal $(MnCl_5)^{2-}$.

The chemistry of Mn(III) is not as extensively documented as that of other valence states of the element and for the most part the stereochemistry of Mn(III) derivatives is not well established. The crystal structures of MnF_3 and of $(NH_4)_2 \cdot MnF_5$ have been reported[1,2] to contain, respectively, octahedral and tetragonally-elongated octahedral MnF_6 moieties. Recently, Goodwin and Sylva[3] reported the synthesis of phenanthrolinium pentachloromanganate(III) which they formulated as $(phenH_2)(MnCl_5)$ on the basis of elemental analysis, diffuse reflectance spectra and magnetic susceptibility measurements. Although the crystal structure of $(bipyH_2) \cdot (MnCl_5)$ has been recently reported,[4] it is important to establish the detailed geometry of $(MnCl_5)^{2-}$ with different compensating cations since it has been shown[5] that for pentahalo salts, such as $(InCl_5)^{2-}$, changes in crystal packing due to changes in cation are sufficient to cause steric changes in the anion. Shriver, et al.[5] found spectral evidence of changes between trigonal bipyramidal and square pyramidal coordination and also of distorted intermediates of these two extreme models. Therefore, it is important to determine whether these changes occur also in the case of $(MnCl_5)^{2-}$. The structure of the phenanthrolinium cation is important in itself in view of the interest in hydrogen bonding[6] in organic bases such as phenanthroline. Also, double protonation of the nitrogens in the cation should lead to strong electrostatic repulsions between the net charges remaining in the hydrogen atoms.

Such charge repulsions in rigid aromatic systems have been shown[7,8)] to lead to distortions in the planarity of the carbon-nitrogen skeleton of the molecule. As a result of these considerations, we report here the structure of (phenH_2)($MnCl_5$) which is a member of a series of structural studies[4,8,9)] of metal complexes containing organic bases as either a ligand or a cation.

Dark brown prismatic crystals were obtained by the method of Goodwin and Sylva.[3] As the crystals are highly sensitive to humidity, specimens were sealed in thin walled glass capillaries for use. Crystal data: orthorhombic, a = 17.64, b = 11.91, c = 7.34 A, Z = 4; D_c = 1.79 g.cm^{-3}, space group *P nma*. The structure was solved by Patterson and Fourier methods from visually estimated three-dimensional X-ray data recorded on Weissenberg photographs with Cu-Kα radiation. Least-squares refinement with isotropic temperature factors for all the atoms has now reached to the conventional R = 0.12 for 875 independent reflections.

The crystal structure is shown in the Figure. Three chlorine atoms, Cl(1), Cl(2), and Cl(3), lie on the crystallographic mirror plane which is perpendicular to the phenanthroline plane and bisects it. The $(MnCl_5)^{2-}$ ion is almost a regular square pyramid whose axial and average equatorial Mn-Cl bond lengths are 2.46 and 2.27 A, respectively, with the Mn atom 0.4 A above the basal plane. Qualitatively, these structural features agree with those found in the bipyridinium analogue,[4)] where the $(MnCl_5)^{2-}$ species was also found to be an axially elongated square pyramid with the Mn atom 0.36 A above the basal plane of the chlorides; however, there is a substancial difference in the Mn-Cl(axial)

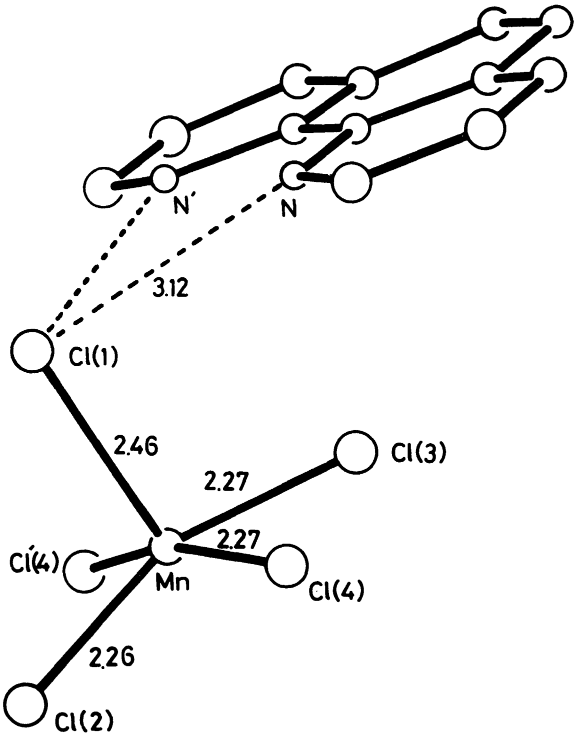
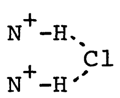


Figure Perspective drawing of the complex molecule.

distances in the two salts (2.58 A for the bipyH_2 derivative) which seems to be correlated with the Cl(axial)-N distances for the two salts (i.e., 3.40 A for the bipyH_2 salt4) v.s. 3.12 A for the phenH_2 derivative).

Since the Cl(1) is located on the mirror plane by which the two nitrogen atoms are related, the axial chlorine is symmetrically disposed with respect to these two atoms. The plane defined by Cl(1), N and N' is almost co-planar with that of the phenanthroline molecule (dihedral angle 10°) and the N-Cl(1)-N' angle is 119°. Although the hydrogen atoms were not located in difference maps, the short Cl···H bonds implied by the two Cl···N distances of 3.12 A clearly indicate the existence of symmetric  $\begin{array}{l} N^+\text{-}H\cdot \\ N^+\text{-}H\cdot \end{array}\!Cl$ bonds which are expected to minimize the electrostatic repulsion between the hydrogens of the NH^+ fragments in the phenH_2^{2+} cation.

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(Received October 13, 1971)