09. STRUCTURES OF ORGANIC AND COORDINATION COMPOUNDS

09.4-29 A PRECISION NEUTRON STUDY OF THE STRUCTURE OF TETRAAQUEBIS (HYDROGEN MALEATO) ZINC(II). By A. Sequin and H. Rajagopal, Neutron Physics Division, Bhabha Atomic Research Centre, Trombay, Bombay 400085 and M.P. Gupta, Dept. of Phys., University of Ranchi, Ranchi 834008, India.

The crystal structures of some tetraaquabis (hydrogen maleato) metal, M(C₄H₄O₄)₄·4H₂O (M = Mn, Ni, Co, Fe, Zn) salts have been investigated using X-rays by Gupta et al (Acta Cryst. 1984 C40, 1152) in order to study the effect of metal ions on the geometry of hydrogen maleato (HM) ion. However, the hydrogen atoms have not been precisely located. The present study has been carried out to locate the hydrogens and to elucidate the details of hydrogen bonding, particularly regarding the short intramolecular H-bond, in these isostructural salts. The title crystal is triclinic, P1, a = 7.337(5), b = 9.239(7), c = 5.322(3) A, β = 104.67(4), γ = 93.03(9), γ = 108.96(9), D = 1.86, D = 1.71 Mg.Å⁻³. The structure has been refined to final R(0) = 0.026, using intensities of over 700 independent reflections recorded at a neutron wavelength of 1.036 A. The HM ion acts as a unidentate ligand to the metal. The Zn ion is coordinated to two maleate and four water oxygens forming a distorted octahedron. A short (2.410 A) asymmetric intramolecular hydrogen bond connects the oxygens of the ionised and unisoned carboxyl groups. However, the two C=O bonds of the ionised carboxyl group have comparable lengths, indicating significant charge transfer from the carboxyl oxygen to the metal. One of the water hydrogens is involved in strong bifurcated hydrogen-bonding.


The sterically bulky tridentate ligand L = tris(5-dimethylpirazolyl)borate, (H₅B₃(5-Me₂C₃H₄N))₃⁺ restricts the coordination of metals to which it is bonded to octahedral six-coordination. Complexes of W or Mo(NO)LXY (prepared by Mrs. E. Al-Oabdi, Drs. P. Beer and C.J. Jones and Professor J.A. McCleverty of this Department) are therefore coordinatively unsaturated, the metal having, formally, a 16-electron configuration. To overcome the electron deficiency at the metal, which is further enhanced by the presence of the strongly n-accepting NO, there is a tendency for py = dm donors from the ligands X and Y (X = OR or NR₂) to the metal, leading to interesting chemical and electrochemical behaviour.

The crystal structures of

Mo(NO)L[NH₂BNH₂]
Mo(NO)L[2-C₄H₄N₂H]+, M = Mo and W
Mo(NO)L[HC₆H₄N]+
[Mo(NO)LCl]₀[NC(C₃H₄N)₂]
[Mo(NO)₂C₆H₄N]+ have been determined. The variation in the stereochemistries of these and related complexes will be discussed.

09.4-31 CRYSTAL STRUCTURES OF TWO TECHNETIUM COMPLEXES CONTAINING OXALATO LIGANDS. By S.P. Colman and M.P. Mackay, Department of Chemistry, La Trobe University, Bundoora, Victoria, Australia 3083 and J. Baldas, Australian Radiation Laboratory, Yallambie, Victoria, Australia 3085.

Technetium in its metastable form (⁹⁹Tc) has found widespread use as an ideal imaging agent (⁹⁹Tc, 140 keV) in diagnostic nuclear medicine. However, because of the extremely low molar concentrations involved (≈ 10⁻¹⁰ mol dm⁻³) the chemistry of technetium is poorly understood. In recent years this problem has been studied by the use of long-lived technetium-99 (Tc, 2.12×10⁸ y), which makes it possible to isolate sufficient amounts of technetium compounds for characterisation by conventional chemical and spectroscopic techniques. The reaction of oxalic acid (C₂O₄)₂⁻ with [AsPh₄]⁻[Tc₄N₄O₂(C₂O₄)₆] in aqueous acetone yields crystals of [AsPh₄]⁺[Tc₄N₄O₂(C₂O₄)₆(C₂H₃OH)]₄·3H₂O respectively. The structures of these complexes have been determined.

Monoclinic crystals of [AsPh₄]⁺[Tc₄N₄O₂(C₂O₄)₆(C₄H₉O₄)]·3H₂O belong to the space group P2₁/a with a = 14.423(1), b = 12.229(1), c = 27.020(1) A, β = 92.90(1), with Z = 4. Refinement with data measured with Cu Kα radiation converged at R = 0.084 for 3839 observed terms. The structure consists of [AsPh₄]⁺ cations and [Tc₄N₄O₂(C₂O₄)₆]⁻ anions. The anion is a cyclic tetracnuclear complex [Tc₄N₄O₂(C₂O₄)₆]⁻ with C₄ point symmetry. Each technetium(VI) atom is coordinated by five oxygens and one nitrogen atom to give a distorted octahedron. The octahedra are joined on a common edge by a tetradeinate oxalate group and are additionally joined at an equatorial corner by a bridging oxygen atom. The strong trans effect exerted by the nitride ligands is manifested by the displacement of the Tc atoms above the plane of the four oxygen atoms by 0.361 and 0.368 A, and by the evident lengthening of the Tc-O bond trans to the nitride ligand. The Tc...Tc spacings of 2.586(2) and 5.756(3) A preclude any Tc=Tc bonding.