

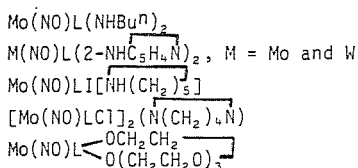
09.4-29 A PRECISION NEUTRON STUDY OF THE STRUCTURE OF TETRAAQUABIS (HYDROGEN MALEATO) ZINC(II). By A. Sequeira and H. Rajagopal, Neutron Physics Division, Bhabha Atomic Research Centre, Trombay, Bombay 400085 and M.P. Gupta, Dept. of Phys., University of Ranchi, Ranchi 834008, India.

The crystal structures of some tetraaquabis (hydrogen maleato) metal, $M(C_4H_2O_4)_2 \cdot 4H_2O$ ($M = Mn, Ni, Co, Fe, Zn$) 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 maleate (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, $P\bar{1}$, $Z = 1$, $a = 7.337(5)$, $b = 9.219(7)$, $c = 5.222(3)$ Å, $\alpha = 104.67(4)$, $\beta = 93.03(9)$, $\gamma = 108.96(9)^\circ$, $D = 1.86$, $D = 1.91$ Mg.m⁻³. The structure has been refined to final $R(\text{on } F) = 0.026$, using intensities of over 700 independent reflections recorded at a neutron wavelength of 1.036 Å. 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 Å) asymmetric intramolecular hydrogen bond connects the oxygens of the ionised and unionised 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.

09.4-30 THE STEREOCHEMISTRY OF NITROSYL[TRIS(3,5-DIMETHYLPYRAZOLYL)BORATE] COMPLEXES OF MOLYBDENUM AND TUNGSTEN
By K. Paxton, C.D. Bush and T.A. Hamor, Department of Chemistry, University of Birmingham, England:

The sterically bulky tridentate ligand $L = \text{tris}(3,5\text{-dimethylpyrazolyl})\text{borate}$, $[\text{HB}(3,5\text{-Me}_2\text{C}_3\text{HN}_2)_3]^-$ restricts the coordination of metals to which it is bonded to octahedral six-coordination. Complexes of type M or $\text{Mo}(\text{NO})\text{LXY}$ (prepared by Mrs. N. Al-Obaidi, 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 π -accepting NO, there is a tendency for $p\pi \rightarrow d\pi$ donation from the ligands X and Y ($X, Y = \text{OR}$ or NR_2) to the metal, leading to interesting chemical and electro-chemical behaviour.

The crystal structures of



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.F. Colmanet and M.F. 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 (^{99m}Tc) has found widespread use as an ideal imaging agent ($t_{1/2} = 6\text{h}$, $\gamma = 140$ keV) in diagnostic nuclear medicine. However, because of the extremely low molar concentrations involved ($\text{ca } 10^{-8} \text{ mol dm}^{-3}$) the chemistry of technetium is poorly understood. In recent years this problem has been studied by the use of long-lived technetium-99 ($t_{1/2} = 2.12 \times 10^5 \text{ y}$), which makes it possible to isolate sufficient amounts of technetium compounds for characterization by conventional chemical and spectroscopic techniques. The reaction of oxalic acid ($\text{C}_2\text{O}_4\text{H}_2$) with $[\text{AsPh}_4][\text{TcNCl}_4]$ and $[\text{AsPh}_4][\text{TcOCl}_4]$ in aqueous acetone yields crystals of $[\text{AsPh}_4]_4[\text{Tc}_4\text{N}_4\text{O}_2(\text{C}_2\text{O}_4)_6]$ and $[\text{AsPh}_4]_2[\text{TcO}(\text{C}_2\text{O}_4)_2(\text{C}_2\text{O}_3\text{OH})] \cdot 3\text{H}_2\text{O}$ respectively. The structures of these complexes have been determined.

$[\text{AsPh}_4]_4[\text{Tc}_4\text{N}_4\text{O}_2(\text{C}_2\text{O}_4)_6]$ crystallizes in the monoclinic space group $P2_1/n$ with $a = 14.433(1)$, $b = 13.229(1)$, $c = 27.020(1)$ Å, $\beta = 92.90(1)^\circ$, with $Z = 4$. Refinement with data measured with Cu K α radiation converged at $R = 0.084$ for 3839 observed terms. The structure consists of $[\text{AsPh}_4]^+$ cations and $[\text{Tc}_4\text{N}_4\text{O}_2(\text{C}_2\text{O}_4)_6]^{4-}$ anions. The anion is a cyclic tetranuclear complex $[\text{Tc}_4\text{N}_4\text{O}_2(\text{C}_2\text{O}_4)_6]^{2-}$ with C_1 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 tetradentate oxalate group and are additionally joined at an equatorial corner by a bridging oxygen atom. The strong *trans* effect exerted by the nitrido ligand is manifested by the displacement of the Tc atoms above the plane of the four oxygen atoms by 0.361 and 0.368 Å, and by the evident lengthening of the Tc-O bond *trans* to the nitrido ligand. The Tc...Tc spacings of 3.586(2) and 5.756(3) Å preclude any Tc-Tc bonding.

Monoclinic crystals of $[\text{AsPh}_4]_2[\text{TcO}(\text{C}_2\text{O}_4)_2(\text{C}_2\text{O}_3\text{OH})] \cdot 3\text{H}_2\text{O}$ belong to the space group $P2_1/c$ with $a = 16.495(3)$, $b = 14.802(2)$, $c = 21.805(4)$ Å, $\beta = 98.76(1)^\circ$ and $Z = 4$. Refinement with 5099 observed data with Mo K α radiation converged at $R = 0.058$. The technetium(V) atom is coordinated by six oxygen atoms to give a distorted octahedron. The structure of the anion is unusual in that it contains a monodentate oxalate group and that there is no lengthening of the Tc-O bond *trans* to the oxo ligand.