belongs to a series of Cu(II) complexes. (F) was reported earlier (Wang, Wang, Wang & Chang, Acta Cryst., 1990, C46, 1770-1772). The coordination geometry about Cu(II) ion is all complexes, except (D), is five-coordinated and distorted square-pyramidal with four N atoms in an equatorial positions. The axial position is occupied by diethylammonium ions; triazine N atom in (A) and (C), triazine S atom in (B), water O atom in (D) and bridging oxime O atom in (F), the six-coordinated polyhedron in (E) is distorted square-bipyramidal with amine- , amine-, oxime N and bridging oxime O atom equatorial, persulphate O and another bridging oxime O atom axial. The complexes (A)-(C) are mononuclear, monomeric (E) in tetranuclear (D) and in bis mononuclear (C) is binuclear. The central part of the tetranuclear complex (E) is dodecahedron formed by four Cu, four oxime N and four bridging oxime O atoms. Present research shows that the electron and steric factors govern coordination in the axial position of Cu(II) and the oxime O atom, which participate in forming the intramolecular N-bonds in mononuclear complexes (A)-(C), or bonding with Cu(II) ions in tetranuclear (D) and binuclear (F) complexes. [Work was supported by National Science Council, Taiwan, China].

**07.03 - Metal Clusters**

**PS-07.03.02 SYNTHESIS AND STRUCTURES OF A NEW CLASS OF OCTAUCULAR MIXED-METAL CLUSTERS: [MnapO3(O2CCl2)2]Na2 (M = Cr, V, M = Mo, W; M' = Mo, M = Mo, M' = Mo) **

A new class of octanuclear cluster compounds formulated as [MnapO3(O2CCl2)2]Na2 (M = Cr, V, M = Mo, W; M' = Mo, M = Mo, M' = Mo) have been prepared and structurally characterized. The black crystals of the title compounds were obtained from the reflux reactions of M(CO)6 with Na2MoO4 (or MoCO5 with NaVO3) in propionic anhydride solution. The five intra-clustered complexes don't dissolve in many solvents such as water, most common acids (e.g., HCl), bases (e.g., NaOH) and organic solvents (e.g., DMF, THF, EtOH, CH2CN). X-ray structure analyses of them revealed the existence of a cluster anion [Cr(H2O)3]MoO3, [CrMoO3(O2CCl2)2]2-, in which the two M-O units are connected by two M' atoms through four μ 3-O (from O3) in the two M-O units and eight μ 3-O (bridging Cl3COO) bonds to form a centro-symmetric structure as shown in Fig. 1. The M-O unit is similar to the well-known M-O triclusters except for a carboxyl bridge spanning two M atoms. Bonds lengths and angles in the former are similar to the ones in the latter but M-O bond lengths (from O3) in the M-O units) become significantly ca. 0.03-0.06 Å longer. Each metal atom has distorted octahedral coordination geometry. A small range of M-O distances indicates M[Cr] rather than M[Mo] which is expected to show a much range because of John-Teller distortion, thus, by deduction the M atoms have formal oxidation states of IX, which is also supported by the similarity of the M-M distances in the five compounds to the ones in the M-O triclusters. There is an interesting nearly planar MnapMnap eight-membered cycle with Cl symmetry in the center of the structure. The deviations of the eight atoms from the least-squares plane defined by them range from ca. 0.04 to 0.2 with the average of ca. 0.14 Å, in addition there are four approximate MnapMnap planes. The long M-M distances (3.5-3.8 Å) attach to the absence of M-M bondings. Each Na atom is coordinated to five O atoms from two atoms in an uncommon distorted trigonal bipyramidal arrangement with the unusually short Na-O average distance of 2.14 Å which suggests some extent of Na-O covalent bonding; consequently, the cluster anions are connected by Na2 to constitute an infinite chain structure. So we suppose that they are best regarded as extended species rather than simple ionic complexes. This is also supported by their insolubilities in many solvents.

![The structure of [MnapO3(O2CCl2)2]Na2](image)