

07-Crystallography of Organometallic and Coordination Compounds

Our artificial approach consists of using metals with their different assembling properties (depending on the metal, its oxidation state, coordination number, d^n configuration, etc.) for creation of novel architectures in coordination chemistry. By an appropriate use of coordination geometry around a transition metal, binding cavities of different size between two adjacent sugar units can be planned. The structure of $[V(DAGO)_6Na_3]$ (DAGO = 1,2:5,6 di-O-isopropylidene- α -D-gluco-furanose) exemplifies the complexation of ion-pairs (Figure 1); six sugar moieties are octahedrally arranged around the vanadium atom and in three of the cavities created by pairs of sugars sodium ions are located at distances Na---O ranging from 2.24 to 2.94 Å.

Sugars can be used as ancillary ligands in the case of functionalizable centers in organometallic chemistry. The structure of the unprecedented homoleptic compound of formula $[Mo_2(DAGO)_6]$ containing a triple Mo=Mo (2.218 Å) bond is shown in Figure 2. Each Mo atom binds three sugars via their exocyclic oxygen atoms and are arranged around each Mo in such a way that bonds Mo-O form a calix with the Mo-Mo bond as stem.

Sugars act also as chelating ligands with alkali metals via oxygen atoms. Figure 3 shows the new structure of $[Li(DAGO)]_4$ with a cubic cage of four lithium atoms and four oxygen atoms, which occupy alternatively the vertices of the cube.

Figure 1

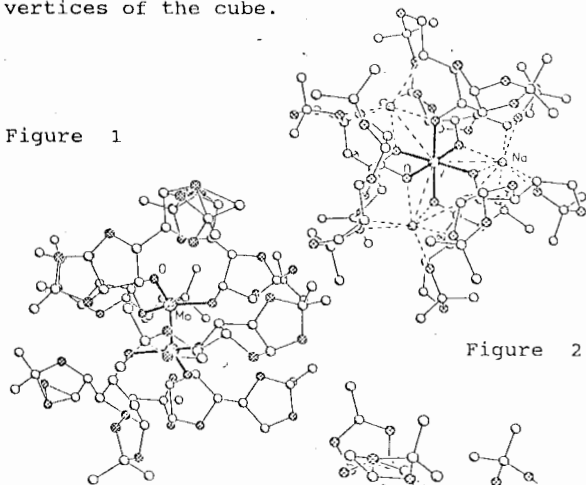


Figure 2

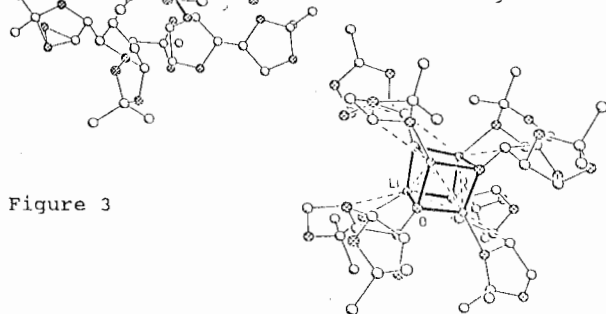
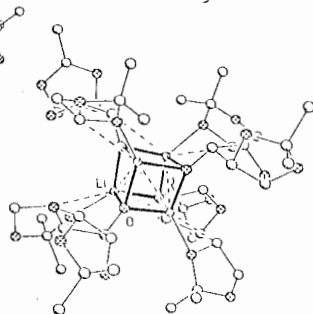
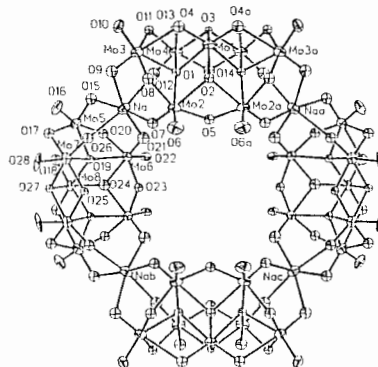


Figure 3

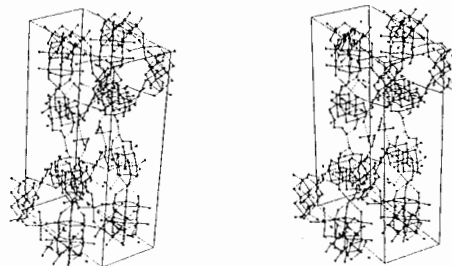


PS-07.03.11 A CYCLIC COMPLEX FORMED BY SODIUM AND HEPTAMOLYBDATE IONS: THE CRYSTAL STRUCTURE OF $(C_6H_{12}NO)_5(NH_4)_4[Na_4Mo_7O_{24}] \cdot 6CH_3OH$. By R. Hämäläinen* and U. Turpeinen, Department of Chemistry, P.O. Box 6, Vuorikatu 20, FIN-00014 University of Helsinki, Finland.

Colorless crystals of the title compound were obtained by slow evaporation of a methanol solution containing ammoniumparamolybdate, 2-dimethylaminoethanol, sodium hydroxide and NH_3 . The crystal used for data collection had approximate dimensions 0.1 x 0.1 x 0.2 mm and was sealed in a capillary. Crystal data for the title compound: $M=5300.0$, orthorhombic space group $Pm\bar{m}n$ with $a=22.275(6)$, $b=36.758(9)$, $c=11.059(6)$ Å, $Z=2$, $V=9055(4)$ Å³, $\mu(MoK\alpha)=1.96$ mm⁻¹, $F(000)=5112$, $\lambda(MoK\alpha)=0.71069$ Å, $d_{obs}=1.95$ Mgm⁻³ and $d_{calc}=1.944$ Mgm⁻³. The structure was solved by Patterson and Fourier methods using the program system SHELXTL-Plus (Sheldrick, 1990) and refined with anisotropic temperature factors for the Mo, Na and terminal O atoms of the anion group and isotropic factors for the other atoms. Hydrogen atoms were not determined. Final $R=0.078$, $R_w=0.085$ and $S=1.19$.



The configuration and the interatomic distances of the heptamolybdate group $[Mo_7O_{24}]^{6-}$ are essentially those found earlier in $M_6[Mo_7O_{24}] \cdot 4H_2O$ ($M=NH_4$ or K) (Evans, H.T., Gatehouse, B.M. & Leverett, P. (1975). *J.C.S. Dalton*, 505-514.) The sodium ions are six-coordinated with Na-O distances of 2.41(4) - 2.48(4) Å and with coordination angles between 81.3(12) and 97.4(13)°. The complex structure is stabilized by a set of hydrogen bonds involving $[Na_4Mo_7O_{24}]^{20-}$ complex anions, methanol molecules, ammonium and dimethyl-(2-hydroxyethyl)ammonium cations.



Stereoscopic view of the unit cell.

PS-07.03.12 THE CRYSTAL STRUCTURE OF 2-DIMETHYLAMINOETHANOLATO BRIDGED TETRANUCLEAR COPPER(II) 4-CHLOROBENZOATO COMPLEX: $[Cu_4(C_7H_4ClO_2)_4(C_4H_{10}NO)_4] \cdot 2CH_3OH$. By U. Turpeinen*, R. Hämäläinen and I. Mutikainen, Department of Chemistry, P.O. Box 6, Vuorikatu 20, FIN-00014 University of Helsinki, Finland.

In a systematic investigation of the reaction between Cu(II) carboxylates and 2-dialkylaminoethanols, monomeric, dimeric, tetrameric, hexameric and nonameric complexes have been synthesized and structurally characterized by X-ray crystallography (Turpeinen, U. (1985). *Finn. Chem. Lett.* 13, 73-83;