

## 07-Crystallography of Organometallic and Coordination Compounds

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PS-07.03.08 STUDIES ON TRINUCLEAR CADMIUM CLUSTER COMPLEXES. SYNTHESIS AND CRYSTAL STRUCTURES OF  $[\text{NMe}_4][\text{Cd}_3(\text{SC}_6\text{H}_2\text{Pr}_3^1-2, 4, 6)_7] \cdot \text{C}_6\text{H}_{12}$  AND  $[\text{Cd}_3(\text{SC}_6\text{H}_2\text{Pr}_3^1-2, 4, 6)_8(\text{HSC}_6\text{H}_2\text{Pr}_3^1-2, 4, 6)] \cdot \text{CH}_3\text{OH} \cdot 7\text{H}_2\text{O}$ .

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By the reaction of a sterically hindered arenethiol  $2, 4, 6\text{-Pr}_3\text{C}_6\text{H}_2\text{SH}$  with  $\text{CdNO}_3 \cdot 4\text{H}_2\text{O}$ , in 3.2 to 1 ratio and in the presence of the quaternary ammonium salt  $\text{Me}_4\text{NCl}$ , the colourless salt of trinuclear cadmium cluster anion complex  $[\text{NMe}_4][\text{Cd}_3(\text{SC}_6\text{H}_2\text{Pr}_3^1-2, 4, 6)_7] \cdot \text{C}_6\text{H}_{12}$  (1) has been synthesized. The same starting materials reacted in 2 to 1 ratio and in the absence of the quaternary ammonium salt, resulting an unchanged trinuclear cadmium complex  $[\text{Cd}_3(\text{SC}_6\text{H}_2\text{Pr}_3^1-2, 4, 6)_8(\text{HSC}_6\text{H}_2\text{Pr}_3^1-2, 4, 6)] \cdot \text{CH}_3\text{OH} \cdot 7\text{H}_2\text{O}$  (2).

The crystal structures of both complexes have been determined by X-ray method. Crystals of (1) are monoclinic, space group  $P2_1/n$  with  $a=19.629$  (6),  $b=25.608$  (9),  $c=25.450$  (9) Å,  $\beta=107.54$  (3),  $V=12203$  (7) Å<sup>3</sup>,  $Z=4$ ;  $R=0.076$  for 3839 observed reflections. Crystals of (2) are triclinic, space group  $P1$  with  $a=19.792$  (10),  $b=20.508$  (12),  $c=33.97$  (2) Å,  $\alpha=85.81$  (5),  $\beta=86.77$  (5),  $\gamma=85.12$  (4),  $V=13686$  (14) Å<sup>3</sup>,  $Z=4$ ;  $R=0.0921$  for 8327 observed reflections. The core of the cluster anion of (1)  $[\text{Cd}_3(\text{SC}_6\text{H}_2\text{Pr}_3^1-2, 4, 6)_7]^-$  is formed by a defective cubane unit with three cadmium and four sulphur atoms at its vertices. Each cadmium atom exhibits tetrahedral coordination with one terminal sulphur, two doubly bridging sulphurs and one triply bridging sulphur atom. In the molecules of unchanged complex (2), three cadmium atoms are coordinated by six thiolates ( $\text{RS}^-$ ) and one thiol ( $\text{RSH}$ ) ligand. Two of three cadmium atoms have tetrahedral coordination and one is trigonal planar. There is no triply bridging ligand in this structure.

PS-07.03.09 CLOSE PACKING AND ISOSTRUCTURALISM OF ANALOGOUS  $\text{Ph}_3\text{X-X'R}_3$  COMPOUNDS ( $\text{R} = \text{Me}$ ;  $\text{X} = \text{Si, Ge, Sn}$ ;  $\text{X}' = \text{Si, Sn, Ge, Ge, Ge, Sn}$ ;  $\text{R} = \text{Et}$ ;  $\text{X} = \text{Ge, Si}$ ;  $\text{X}' = \text{Si, Ge}$  AND  $\text{R} = \text{Ph}$ ;  $\text{X} = \text{Ge, Sn, Pb}$ ;  $\text{X}' = \text{Ge, Pb, Pb, Pb}$ ). By László Párkányi and Alajos Kálmán\*, Central Research Institute for Chemistry, Hungarian Academy of Sciences, Budapest, POB 17, H-1525, Hungary.

$\text{R} = \text{Me}$ : The alternative replacement of one of Si nuclei in  $\text{Ph}_3\text{Si-SiMe}_3$  (I) (Párkányi & Hengge, 1982) with Ge atom results in two isomers  $\text{Ph}_3\text{Ge-SiMe}_3$  (II) (Párkányi, Hernandez & Pannell, 1986) and  $\text{Ph}_3\text{Si-GeMe}_3$  (III) (Pannell, Kapoor, Raptis, Párkányi & Fülöp, 1990) which remained, however, isostructural with (I). Infinite columns of head-to-tail associated molecules are located on the threefold axes of the space group  $P3$  with alternating orientation. Their similar packing can only be distinguished either by the different length or orientation of Si-Si and Si-Ge dumbbells. Recently, structure of  $\text{Ph}_3\text{Ge-GeMe}_3$  (IV) was also determined. Remaining isostructural with I-III (Fig. 1) IV provides an important link to the other related pairs, as follows.

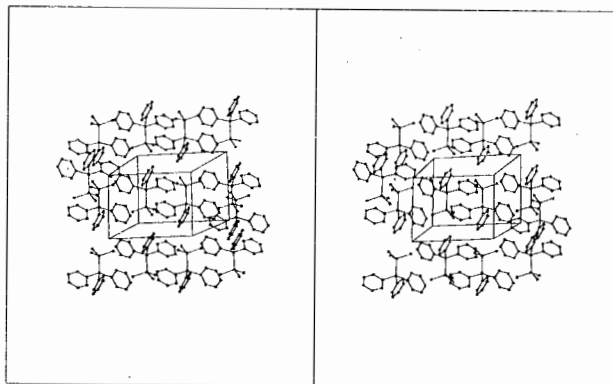
If one Ge atom in IV is replaced alternatively by Sn atom then a morphotropic phase transition (Kitaigorodskii, 1961) terminates their isostructuralism with the parent compound. The novel isomers (V) and (VI) crystallize in

pseudohexagonal orthorhombic unit cells with a common space group:  $Pna2_1$  (Pannell, Párkányi, Sharma & Cervantes-Lee, 1992). However, the new molecular array, relaxing the rigidity of the asymmetrically enlarged (Ge→Sn) molecules by dropping the  $C_3$  symmetry, retains an optimum close packing among the invariably infinite columns of the head-to-tail associated molecules. The bumps of the molecules are fitted in the hollows of the adjacent columns (oriented in the same direction) via glide planes.

$\text{R} = \text{Et}$ : The  $C_3$  molecular-symmetry-controlled packing is still sustained when the methyl groups in II and III are replaced by the larger ethyl moieties (Pannell, 1992). Now in the invariably isostructural but rhombohedral unit cells of VII and VIII (common space group  $R3$ ) there are infinite columns of the alternatively head-to-head and tail-to-tail oriented molecules. Due to the translational differences among these columns there are ethyl-ethyl, phenyl-phenyl and mixed ethyl-phenyl interactions.

$\text{R} = \text{Ph}$ : In contrast to I-VIII,  $\text{Ph}_3\text{Ge-GePh}_3$  (IX), with its  $C_i$  molecular symmetry, crystallizes in a symmetry-free unit cell (space group  $P1$ ). Nevertheless, it is pseudoisostructural with  $\text{Ph}_3\text{Pb-GePh}_3$  (X) (Kleiner & Dräger, 1984). Namely, the latter in space group  $P1$  exhibits a positional disorder of the hetero atoms. Finally, if the Ge atom of X is replaced by tin atom then once again a morphotropic phase transition gives rise to a novel packing array. The crystals of  $\text{Ph}_3\text{Pb-SnPh}_3$  (XI) are monoclinic (space group  $P2_1/n$ ) and perfectly isostructural with those of  $\text{Ph}_3\text{Pb-PbPh}_3$  (XII).

Packing similarities (i.e., packing coefficients) together with the forms and degrees of isostructurality (Kálmán, Argay, Scharfenberg-Pfeiffer, Höhne & Ribár, 1991) are discussed in details.



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PS-07.03.10 X-RAY STRUCTURES AT 120°K OF METALS ASSEMBLING SUGARS IN NOVEL ARCHITECTURES

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Sugars are the building blocks for a large number of biological molecules. The assembling strategy is dictated by nature and is appropriate for various functions of the resulting aggregates.

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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- $\alpha$ -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

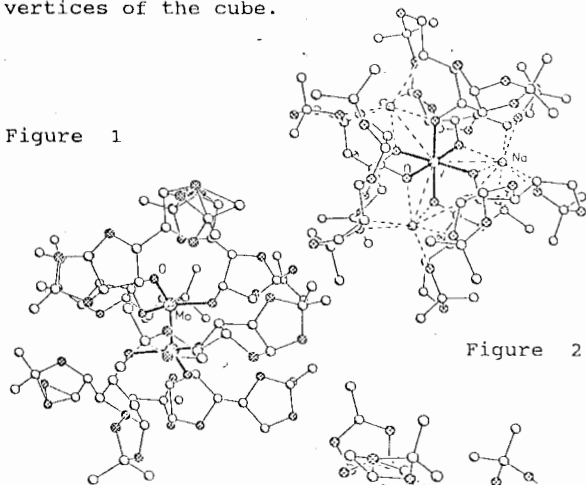


Figure 2

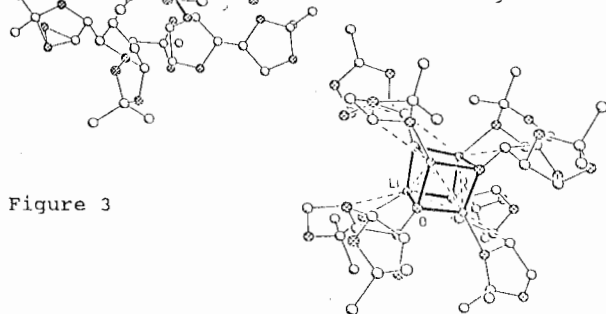
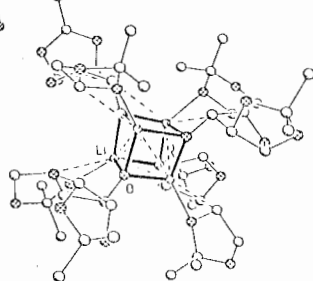
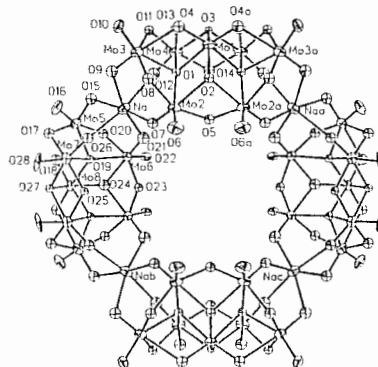


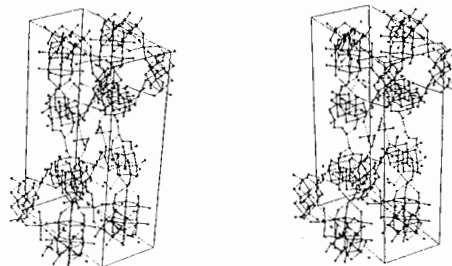
Figure 3



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,  $Z=2$ ,  $V=9055(4)$  Å<sup>3</sup>,  $\rho(MoK\alpha)=1.96$  mm<sup>-1</sup>,  $F(000)=5112$ ,  $\lambda(MoK\alpha)=0.71069$  Å,  $d_{obs}=1.95$  Mgm<sup>-3</sup> and  $d_{calc}=1.944$  Mgm<sup>-3</sup>. 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  $[Na_4Mo_7O_{28}]^{20-}$  complex anions, methanol molecules, ammonium and dimethyl-(2-hydroxyethyl)ammonium cations.



Stereoscopic view of the unit cell.

**PS-07.03.11** A CYCLIC COMPLEX FORMED BY SODIUM AND HEPTAMOLYBDATE IONS: THE CRYSTAL STRUCTURE OF  $(C_6H_{12}NO)_5(NH_4)_4[Na_4Mo_7O_{28}] \cdot 6CH_3OH$ . By R. Hämäläinen\* and U. Turpeinen, Department of Chemistry, P.O. Box 6, Vuorikatu 20, FIN-00014 University of Helsinki, Finland.

**PS-07.03.12** THE CRYSTAL STRUCTURE OF 2-DIMETHYLAMINOETHANOLATO BRIDGED TETRANUCLEAR COPPER(II) 4-CHLOROBENZOATO COMPLEX:  $[Cu_4(C_7H_4ClO_2)_4(C_4H_10NO)_4] \cdot 2CH_3OH$ . 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;