

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 arene-thiol $2, 4, 6\text{-Pr}_3\text{C}_6\text{H}_2\text{SH}$ 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 Me_4NCl , 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) Å³, $Z=4$; $R=0.076$ 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) Å³, $Z=4$; $R=0.0921$ 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 (RS^-) and one thiol (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 ($R = \text{Me}; X = \text{Si, Ge, Sn}; X' = \text{Si, Ge, Sn}; R = \text{Et}; X = \text{Ge, Si}; X' = \text{Si, Ge}$ AND $R = \text{Ph}; X = \text{Ge, Sn, Pb}; X' = \text{Ge, Pb, Sn}$). By László Párkányi and Alajos Kálmán*, Central Research Institute for Chemistry, Hungarian Academy of Sciences, Budapest, POB 17, H-1525, Hungary.

$R = \text{Me}$: 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.

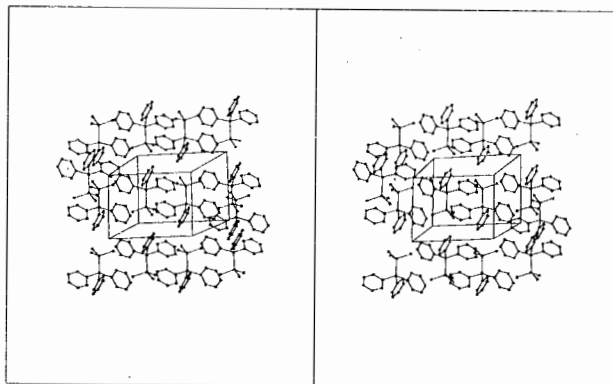
If one Ge atom in IV is replaced alternatively by Sn atom then a morphotropic phase transition (Kitaigorodskii, 1961) terminates their isostructuralism with the parent compound. The novel isomers (V) and (VI) crystallize in

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.

$R = \text{Et}$: 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.

$R = \text{Ph}$: 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.