Short review

Structures of polymetallaorganosiloxanolates — a novel class of organosilicon metal complexes [*]

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Abstract

Single crystal X-ray diffraction studies have revealed the nature and structure of eight types (I–VIII) of polymetallaorganosiloxanolates, representatives of a novel class of the organosilicon metal complexes. Most of the complexes (types I–VII) have sandwich structures with a layer of metal cations between two macrocyclic siloxanolate ligands. In type VIII a single such ligand envelops four inner Cu^{2+} ions to form a globular species.

Keywords: Metal organosiloxanolates; Macrocyclic ligands; Crystal structure; Molecular structure; X-ray diffraction

Polymetallaorganosiloxanolates (denoted below by PMOS) are metal complexes with organosiloxanolate ligands and contain the $M-O_M-Si$ units of metal atoms M and silanolate oxygen atoms O_M, the $Si-O_c-Si$ units containing the siloxane oxygen atoms O_c, and Si–C bonds to organic radicals. Thus, PMOS are intermediate between mineral silicates and organosilicon compounds proper.

Recently PMOS of a novel type have been obtained in our Institute by A.A. Zhdanov and coworkers [1]. Organosiloxanolates of alkali metals [2] are first prepared by reaction of alkali metal hydroxides with silsesquioxanes $[RSiO_{3/2}]_n$, then an exchange reaction with transition metal, copper or lanthanide chlorides, accompanied by a profound transformation of the siloxanolate ligands, affords various PMOS. The latter contain M^{2+} or M^{3+} cations, coordinated by macrocyclic organosiloxanolate ligands, and often also alkali metal ions and small anions, viz. Cl^-, OH^-, O^{2-}, and numerous donor solvent molecules, usually but not always coordinated to metal atoms. Therefore most PMOS have a rather complicated composition, though their molecular structures are quite straightforward,

very attractive architecturally, and in principle fairly simple.

Up to the present our single crystal studies have revealed the existence of eight types of PMOS and established their structures.

PMOS of type I [4], involving Mn, Co, Ni and other bivalent transition metals, are sandwich-like anionic complexes, built of two parallel co-axial 12-membered macrocyclic siloxanolate ligands, separated by the cationic moiety, a planar layer of six M^{2+} ions (Fig. 1). The ligands have a regular all-*cis* configuration and a distorted crown conformation and coordinate to the transition metal ions through their 12 μ_2-bridging olate atoms O_M in a chelate fashion. The complexes studied have an isostructural cylindrical metallasiloxanolate core surrounded by Ph groups on the Si atoms and donor solvent molecules (usually, alcohols) coordinated to the metal atoms through their donor O_s oxygens. Additional stabilization of these PMOS by inclusion of the μ_6-Cl^- anion in the centre of the cationic moiety is especially interesting. Thus, this small encapsulated anion is coordinated in a planar slightly distorted hexagonal arrangement by six M^{2+} ions [5]. The M^{2+} ions are coordinated in a distorted octahedral manner by four O_M atoms in the equatorial plane and an O_s in the proximal and a Cl^- in the distal apical positions. The anion charge (−1) is compensated by the outer Na^+ cation.

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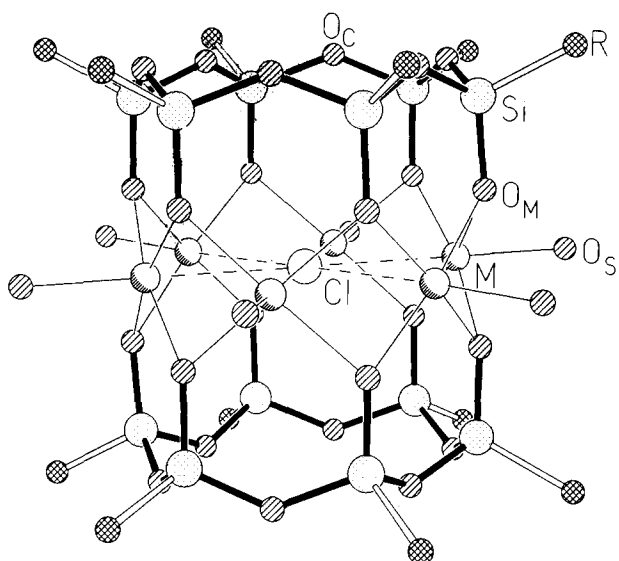Fig. 1. The structure of the metallasiloxanolate framework of PMOS of type I (M = Mn, Co, Ni) and II (M = Cu, the encapsulated Cl⁻ anion is absent). Ph substituents of siloxanolate ligands and alkyl groups of coordinated solvent (alcohols) molecules are not shown.

Fig. 2. The structure of type III complex (only oxygen atoms are shown in the coordinated n-BuOH molecules).

The diagonal $O_c \cdots O_c$ distances in the macrocyclic ligands are close to those in the central cavity in crown ethers. Thus, the available size of the hole in macrocycles of this type of PMOS is 2.4–3.2 Å, so that small particles (anions, but not cations, in contrast to crown ether complexes) can penetrate into the inner cavity, surrounded by 6 M^{2+} ions and 6(top) + 6(bottom) O_M atoms. Incidentally, the lone electron pairs (LEP) of the endocyclic oxygen atoms O_c do not block the entrance into the central cavity [8]. Consequently the PMOS considered could in principle act as "crowns for anions".

The neutral Cu^{2+} complex [4b,9] (Fig. 1) is a representative of PMOS of type II, which only differs from type I by the absence of the encapsulated Cl⁻ anion and the Na⁺ counterion. Therefore, all the Cu atoms have, instead of six-coordination, penta-fold tetragonal-pyramidal coordination involving 4 O_M atoms in the basal and one O_s atom of the ethanol molecule in the apical position.

The PMOS of type III [10] (Fig. 2) are represented by a complex that differs from the preceding one by replacement of the two opposite Cu^{2+} ions in the cationic moiety by K⁺ ions. However, the Cu^{2+} ions coordination is now square-planar, by 4 O_M atoms, since the apical solvent ligands are absent. The K⁺ ions have a distorted six-fold coordination (4 O_M atoms + 2 O_s atoms of solvent molecules). The − 2 charge of this complex is compensated by two outer K⁺ cations.

In the complex of type IV [11] (Fig. 3) the cationic moiety is also built of two sorts of cations: 4 Ni^{2+} + 4 peripheral Na⁺. However, in this case there are two encapsulated μ_3-OH⁻ anions joined to the cationic

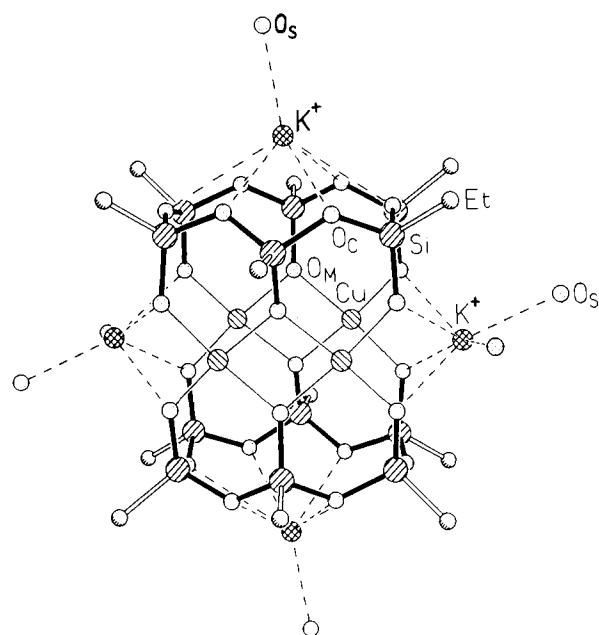layer, one from above and the other from below. The − 2 charge of this anionic complex is compensated by two outer Na⁺ cations. All the Ni^{2+} ions have a distorted octahedral coordination and all the Na⁺ ions of the cationic layer have five-fold trigonal–bipyramidal coordination. The complex is centrosymmetric, but its siloxanolate ligands are shifted relative to each other by ~ 1.5 Å to form a so-called "slipped sandwich".

The only differences between the neutral centrosymmetric Ni-complex of the next type V [12] (Fig. 4) and the preceding one are the homogeneity of the cationic moiety, built of 8 Ni^{2+} ions instead of $4Ni^{2+}$ and $4Na^+$ ions, and the encapsulation of two μ_3-O^{2-}
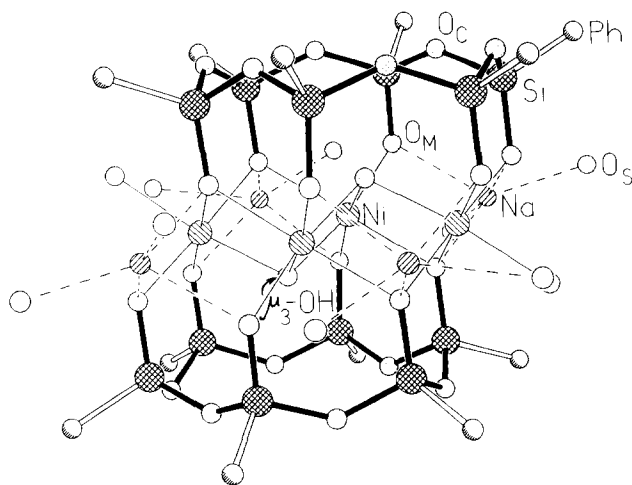

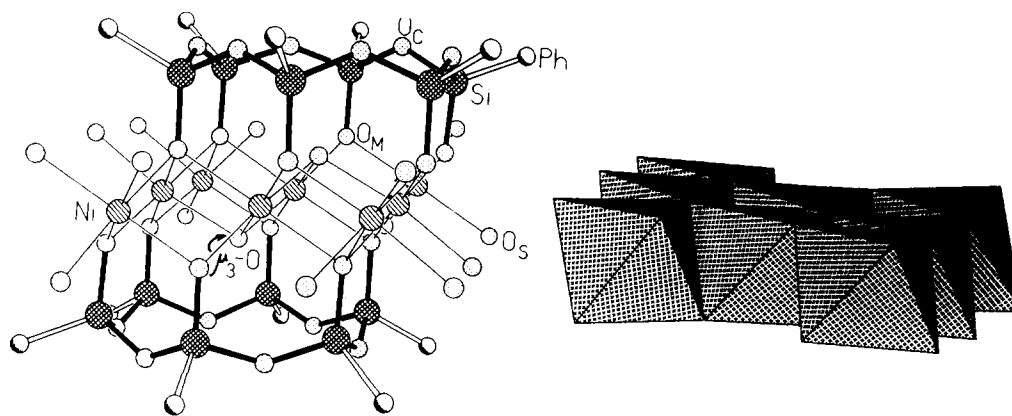Fig. 3. The structure of the metallasiloxanolate framework of PMOS of type IV.

Fig. 4. The Ni, Si, O framework in the PMOS of type V and its central Ni, O-layer.

rether than hydroxide anions. All eight Ni^{2+} ions have a slightly distorted octahedral coordination. The octahedra are fused by edges and vertices, forming the nickel–oxygen layer-like fragment $Ni_8^{2+}(O_M^-)_{12}(O^{2-})_2$ $(O_s)_{12} \equiv Ni_8O_{28}$, which is, in fact, identical to a fragment of the NiO structure [13] cut out normal to the 3-fold axis. This correspondence in principle opens a way to novel composite materials with alternating metal-oxide and silicon-oxygen layers or to silicon–oxygen coatings of metal oxide materials.

It has been shown experimentally that encapsulated small anions can exchange ($Cl^- \rightleftarrows OH^-$ (type I $\rightleftarrows$ type IV), $Cl^- \rightleftarrows O^{2-}$ (I $\rightleftarrows$ V) and $OH^- \rightleftarrows O^{2-}$ (IV $\rightleftarrows$ V)), with a profound rearrangement of the cationic moieties in these PMOS sandwich structures.

The three-valent lanthanide complexes of the types VI [14] and VII [15] (Fig. 5) are in general similar to the transition metal sandwich PMOS of types I–III. However, owing to the greater size and higher charge

Fig. 5. The general view of the complex -n anions of types VI (M = La, Ox = OH⁻, n = 5) and VII (M = Nd, Gd, Dy, Ox = O²⁻, n = 6, instead of Et groups at Si atoms there are Ph groups).

of Ln^{3+} ions, there are several essential differences. First, the Ln-PMOS include two parallel and co-axial but 16-membered (rather than 12-membered) macrocyclic octadentate (rather than hexadentate) siloxanolate ligands. Secondly, the cationic moiety consists of only four Ln^{3+} cations arranged at the vertices of the square and is stabilized by encapsulation of the central anionic μ_4-OH^- or μ_4-O^{2-} ligand. The Ln-PMOS are anions, with the charge of −5 (type VI, Ln = La) or −6 (type VII, Ln = Nd, Gd, Dy), compensated by the outer K^+ or Na^+ cations. The Ln^{3+} ions have no outer solvate ligands and each is coordinated by six O_M atoms, alternately occupying terminal and μ_2-bridging positions. The coordination polyhedra of Ln^{3+} ions are monocapped trigonal prisms. The cap is the inner encapsulated anion, common for all four prisms, which are also fused by edges. The diameter of the hole in the macrocycles of these PMOS is 3.4–4.2 Å, i.e. significantly larger than that in 12-membered cyclic ligands of types I–III.

The PMOS of the last type studied, type VIII, the only structurally characterized representative of which was made by reaction of alkali metal siloxanolates with $CuCl_2$ under somewhat different conditions, have a substantially different structure [9] (Fig. 6). In this case the main structure-forming unit is the single 24-membered macrocyclic siloxanolate ligand with a horse-saddle conformation. The ligand is coordinated to four Cu atoms, arranged in the elongated tetrahedron vertices, through all of its 12 O_M atoms. The Cu atoms have now a square-planar (4 O_M) coordination, as distinct from tetragonal-pyramidal ($4O_M + O_s$) in PMOS of type II, but similar to that found in PMOS of type III. Overall the PMOS of this type have a globular structure, in which the macrocyclic ligand envelops the cationic moiety like the groove of a tennis ball in contrast to the layered sandwich structure of PMOS of all the other types studied. The PMOS of type VIII involve anions with a charge of −4 compensated by four outer Na^+ or K^+ cations, each coordinated by

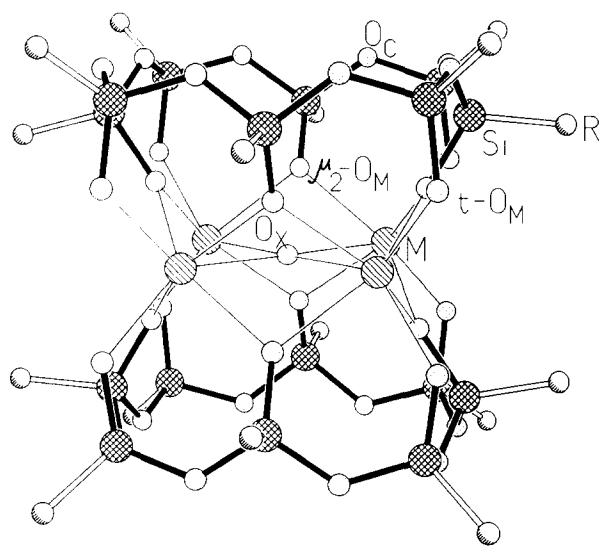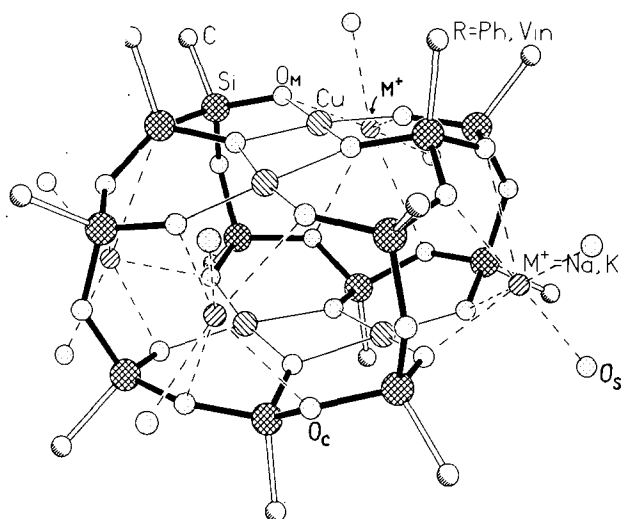Fig. 6. Copper siloxanolate framework of type VIII.

four oxygen atoms of the siloxanolate ligand and two alcohol molecules (Fig. 7).

In accordance with a coordinative-ionic character of the $M \cdots O_M$ bonds between metal cations and olate oxygens of siloxanolate ligands, the O_M atoms in most PMOS have a bridging μ_2 or μ_3 function, and the exocyclic $Si-O_M$ bonds are in general shorter (1.56–1.62 Å) than the endocyclic $Si-O_c$ bonds (1.62–1.65 Å).

The PMOS molecules are characterized by rather high internal (idealized) symmetry of the metallasiloxanolate cores. The sandwhich cylindrical complexes (types I and II) have 6/mmm symmetry, lowered in the crystals to 3, $\overline{1}$ and 1. For the types III (mmm), IV and V (2/m) the symmetry is lowered to $\overline{1}$. The high 4/mmm characteristic symmetry of types VI and VII becomes $\overline{1}$ in crystals, and for the type VIII the lowering is from $\overline{4}$2m to $\overline{4}$ or 222. The symmetry lowering observed in crystals is due to non-symmetric surround-
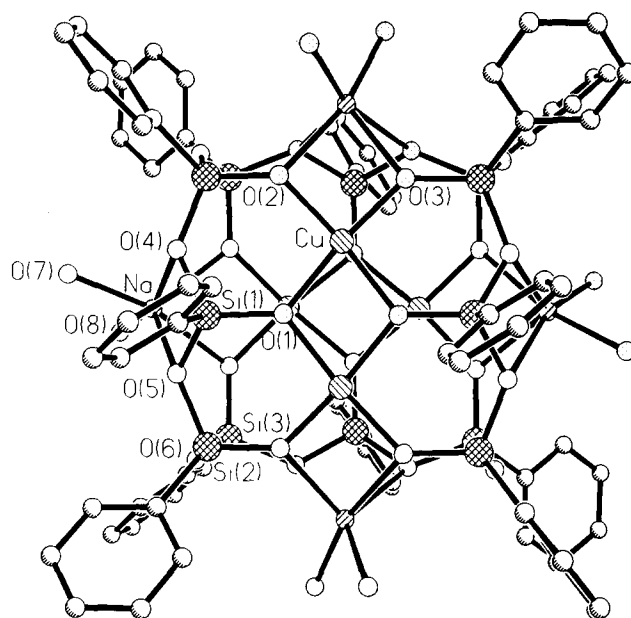

Fig. 7. The structure of the PMOS of type VIII with the $\overline{4}$ symmetry (only the oxygen O(7) and O(8) atoms of coordinated n-BuOH molecules are shown).

ing of the PMOS molecules by solvate molecules and the random orientation of organic radicals.

The high internal symmetry of PMOS complexes along with the stereoregular structure of ligands may serve as convincing evidence for a template mechanism of PMOS formation, especially since the internal symmetries of the cationic moiety and siloxanolate ligands are usually in a good correlation and sometimes exactly coincide.

The crystals of most of the PMOS contain large quantities of solvating molecules (in some cases of different types). Most of them are directly coordinated

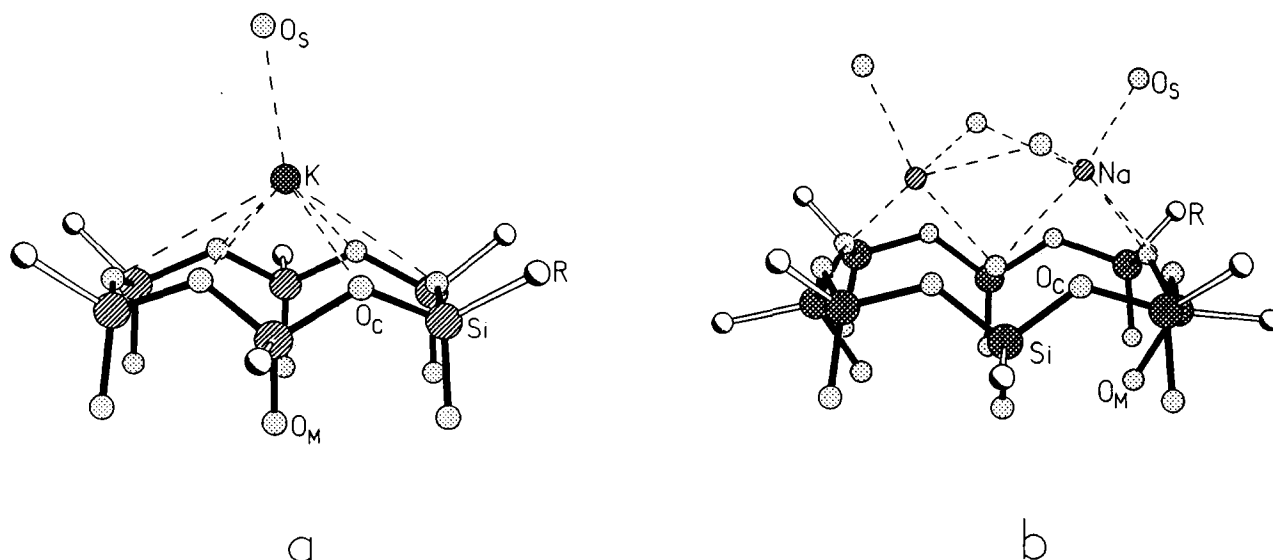a   b

Fig. 8. Coordination of the outer K^+ and Na^+ cations in the PMOS structures with the 12- (a) and 16-membered (b) siloxanolate macrocycles.
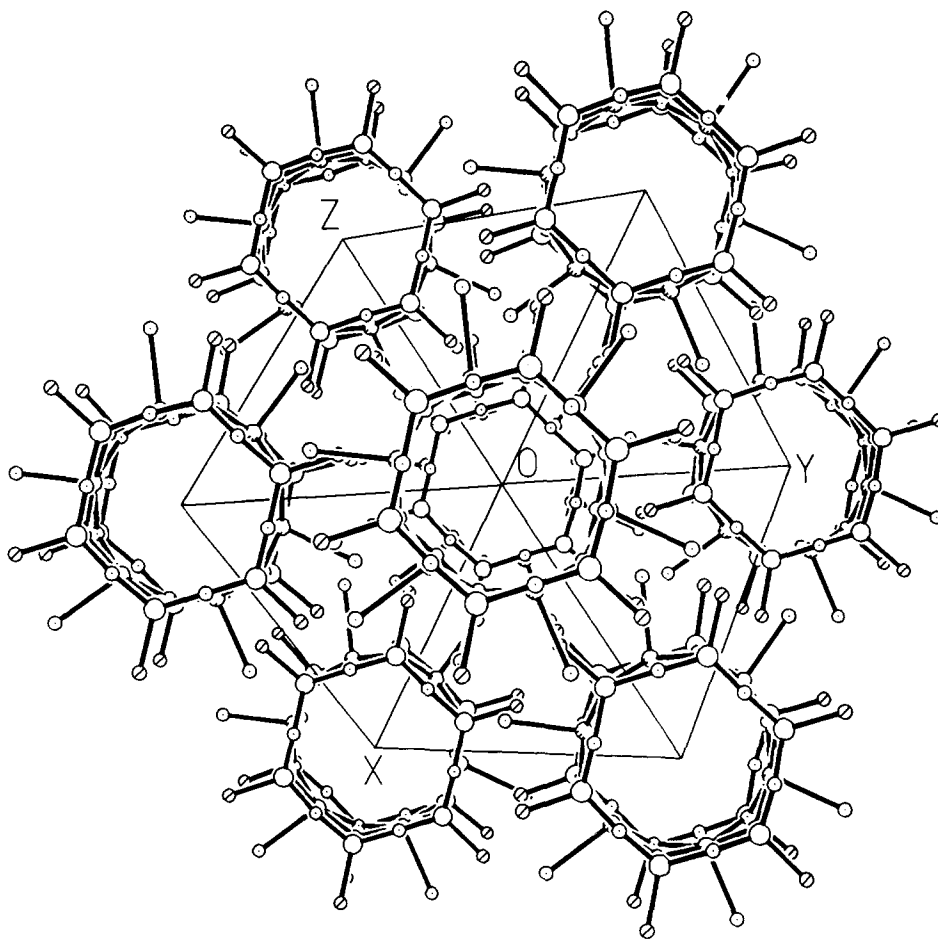
Fig. 9. The crystal structure of type II projected along the [111] direction.

to the cations in the PMOS complexes, but some have a clathrate function, filling up cavities in the packing of bulky PMOS molecules. Most of the solvating molecules contain acidic hydrogen atoms, resulting in formation of various rather complicated hydrogen bond systems in the crystals.

However, an even more important role is played by the outer alkali metal cations. Forming coordinative bonds with solvating molecules and endocyclic O_c atoms of siloxanolate ligands, these counterions link the PMOS complexes into chains, layers and 3D-frameworks. Counterion coordination by endocyclic O_c atoms of siloxanolate ligands is very similar to coordination of alkali metal cations by crown-ethers. In some cases Na^+ or K^+ ions are situated above a macrocycle plane and coordinate with all its six O_c atoms (e.g. type III, Fig. 8a). With larger sizes of macrocycles (types VI and VII) the counterions are arranged pairwise, each coordinating by only a part of the O_c atoms and being linked to each other by the bridging solvating molecules (Fig. 8b). Thus, some PMOS represent unusual molecular assemblies "crowns" for cations and "anti-crowns" for encapsulated anions (we refer to such species as "centaurs" in recognition of their dual nature).

Noteworthy is the crystal structure of the copper-containing PMOS of type II. Its hollow molecules are hexagonally packed without clathrate solvent molecules and are stacked co-axially to form infinite channels (Fig. 9), so that one can envisage the possibility that PMOS of the type might form tubular inclusion compounds.

In conclusion it should be emphasized that the peculiar molecular (and crystal) structures of the PMOS studied to date and, those PMOS molecules still to be isolated, are not only interesting and beautiful in their own right, but may turn out to be precursors of new materials with useful catalytic, magnetic and protective coating properties. In any case the structural investigations are indispensable for preparation of even more unusual and interesting PMOS.

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