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COMMUNICATIONS

Reverse-Keggin Ions: Polycondensation of Antimonate Ligands Give Inorganic Cryptand

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Polyoxometalates (POMs) have been known since the early nineteenth century. Recently, the work of Müller,[1] Pope,[2] and others[3] has generated some of the most extraordinary inorganic architectures based on these molecules including some of the largest polymetallic compounds known and some of the most beautiful, such as the icosidodecahedron.[1b] Potential applications of POMs have been suggested in areas as diverse as catalysis and anti-HIV treatment.[4,5]

The Keggin ion,[6] of general formula $[EM_{12}O_{40}]^{x-}$, is probably the most well-known POM. It is known for a range of M (Mo, W, V, Ti) and a wider range of E (P, As, Sb, Bi, Co, Cu, Fe); in all cases, the p-block element, E, is found surrounded by a tetrahedral coordination sphere of O atoms at the center of the molecule, with the twelve d-block elements, M, arranged in a truncated tetrahedron about this central p-block atom. Recently, Bino et al. reported the first Fe(III) Keggin ion,[7] using fluoride ligands in terminal sites, in place of the terminal oxides found in traditional Keggins. The central atom was iron(III).

We have been using phosphonates as ligands for making polymetallic complexes[8] and shown they can be used for linking together metal cages. We became interested in the idea that, for heavier members of the N-group, condensation of the REO_3H groups might generate larger poly-oxygen donor ligands, which might in turn lead to new structural types. Therefore, we have begun exploring the chemistry of phenylantimonate, "$PhSbO_3H_2$". The synthesis of phenylantimonate was reported in 1920 by Schmidt.[9] The preparation is from aniline and $SbCl_3$ followed by acid hydrolysis. The resulting white powder is not crystalline, and literature reports tend to suggest a condensation product rather than isolated $PhSbO_3H_2$ in the solid state.[10]

We reacted this compound with hydrated manganese(II) acetate in MeCN in the presence of pyridine or NEt_3 at 100 °C under solvothermal conditions.[11] Pale yellow crystals form which diffract poorly; synchrotron radiation was used, but the resolution is still low. Structural analyses[12] show formation of a compound of formula $[Mn(PhSb)_{12}O_{28}\{Mn(H_2O)_3\}_2\{Mn(H_2O)_2(AcOH)\}_2]$ **1** (Figure 1). The structure contains a central tetrahedral Mn(II) ion, which is bound to four O atoms (Figure 2a) which are each μ_4-bridging, each binding to three Sb atoms. The Sb atoms therefore lie at the vertices of a truncated tetrahedron, which is a polyhedron with triangular and hexagonal faces. Each Sb···Sb edge of the triangles is further bridged by a single O atom, while there are two μ_2-oxides on each Sb···Sb edge of the hexagons. The Sb···Sb distances within the triangles fall in the range of 3.187−3.213 Å, while the closest contacts between triangles fall in the range of 3.092−3.100 Å. Each Sb has a phenyl group attached to it, with the result that each Sb is six-coordinate (Figure 1). The structure is therefore a Keggin ion, but with the positions of the p- and d-block elements reversed; it is a reverse Keggin. This creates a position where the d-block metal ion is trapped in a tetrahedral coordination environment at the center of the cage. The orientation of the triangular Sb units is such that this is the ϵ-Keggin rather than the more common α-isomer (Figure 2a).[13]

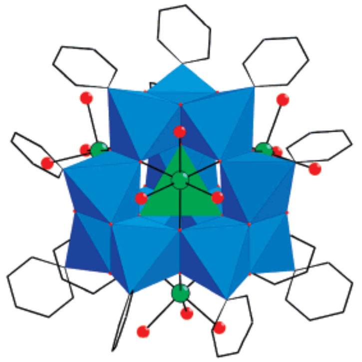

Figure 1. The structure of **1**; blue octahedra represent SbO_5C units, and the green tetrahedra at the center represents MnO_4. The capping octahedral Mn sites are shown as green circles with the terminal oxygens as red circles.

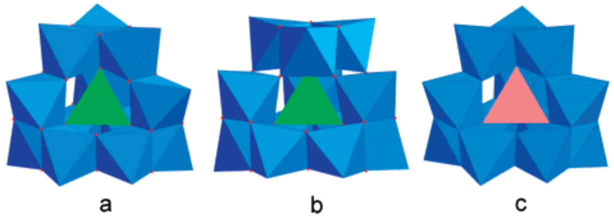

Figure 2. (a−c) Polyhedral representation of ϵ-, δ-, and ϵ-isomers of **1**, **2**, and **3**, respectively. Colors as in Figure 1, plus the pink tetrahedra in **2c** represent the ZnO_4 unit. The phenyl groups on Sb have been omitted.

The four hexagonal faces of the reverse-Keggin can coordinate to further metal sites through the bridging oxides. In **1**, these sites are occupied by two $\{Mn(H_2O)_3\}^{2+}$ and two $\{Mn(H_2O)_2(AcOH)\}^{2+}$ groups (Figure 1). These manganese sites are six-coordinate, with octahedral coordination geometries. Mn−O bond lengths for the central tetrahedral sites fall in the range of 2.076−2.109 Å, while bonds to the octahedral sites are in the range of 2.184−2.240 Å.

If we do the reaction under ambient conditions in MeCN in the presence of NaOMe and small amounts of pyridine, we crystallize $[Mn(PhSb)_{12}O_{28}\{Mn_4(H_2O)_6(C_5H_5N)_{1.5}(MeCN)_{1.5}\}]$ **2**. The connectivity of the compound is similar to that of **1**, but the orientation of the Sb_3 triangles is such that the very rare δ-isomer of the Keggin ion is found (Figure 2b).[14] The coordination number at the external Mn sites in **2** varies, with three sites five-coordinate and the fourth six-coordinate. A mixture of water, pyridine, and MeCN is bound to these external sites. Preliminary magnetic studies on **1** and **2** are

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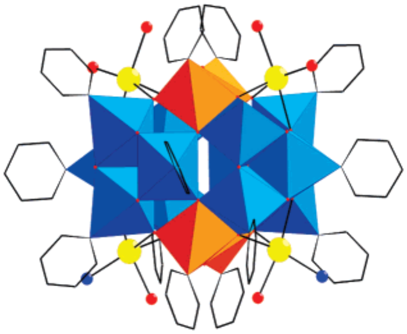

Figure 3. Repeat unit of **4**; the blue SbO_5C octahedra represent the four Sb_3 triangles of the central band, and the orange octahedra represent the Sb_2O_2 units (see text). The capping sodium atoms are shown as yellow circles coordinated to oxygen (red) and nitrogen (dark blue).

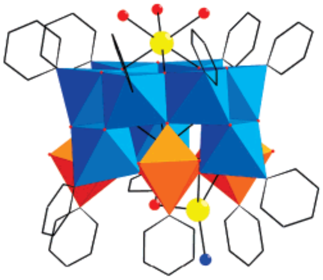

Figure 4. Repeat unit of **5** with the blue SbO_5C polyhedra representing three vertex-sharing $\{Sb_3\}$ triangles and the orange one representing the Sb octahedra linking the triangles. Other colors as in Figure 4.

consistent with high-spin Mn(II) centers, with weak anti-ferromagnetic interactions between the metal ions.

When a similar reaction is done with zinc acetate with *p*-Cl−$C_6H_4SbO_3H_2$ in solvothermal conditions similar to **1**, a further reverse-Keggin ion, $[Zn(4\text{-}Cl{-}C_6H_4Sb)_{12}O_{28}\{Zn(H_2O)\}_4]$ **3**, is formed. The core is the ϵ-reverse-Keggin as for **1** (Figure 2), but the external metal sites are four-coordinate, with each of these Zn ions bound to three oxygens from a hexagonal face of the reverse-Keggin ion, with the fourth site occupied by a terminal water ligand. While connectivity is established, refinement of the structure is very poor due to the quality of the X-ray data.

The yields of **1**−**3** are moderate (35−40%). If we used nickel(II) in these reactions, no crystalline product was obtained using amine bases, rather we got an intractable pale green material which we believe to be a polymeric nickel antimonate of some description. If NaOMe is used as base, we can isolate cages of formula $[Na_6(PhSb)_{16}O_{38}\cdot 10H_2O\cdot 2CH_3CN]_n$ **4** and $[Na_{21}(PhSb)_{48}O_{114}]\cdot 46H_2O\cdot 4CH_3CN$ **5** in low yield. Again the major product is an intractable nickel antimonate polymer.

Compound **4** is a polymer (see Supporting Information), with one repeat unit a $\{Na_4(PhSb)_{16}O_{36}\}$ cage (Figure 3). Disordered solvent (MeCN) was accounted for with SQUEEZE.[15]

The cage contains a central band of four Sb_3 triangles, with additional Sb_2O_2 fragments at the top and bottom of the band. The core of the structure is empty, but four sodium atoms are attached to oxygen atoms on the exterior of the cage capping two adjacent triangles. The Sb atoms are present in an octahedral geometry, and the sodium ions are present in both five- and six-coordinate geometries. Na−O distances vary from 2.217 to 2.485 Å. These cages are linked into a polymer via $\{Na_2(OH)_2\}$ units.

Compound **5** is a tetramer (see Supporting Information), with the repeat unit containing 12 Sb centers (Figure 4). The structure consists of three vertex-sharing $\{Sb_3\}$ triangles, with three further Sb octahedra linking the triangles. Each $\{Sb_{12}\}$ has several Na centers attached to it. One Na is bound to three O atoms that link the $\{Sb_3\}$ triangles, and a second is found at the center of the $\{Sb_{12}\}$ fragment. A third Na is attached to the top of the polyhedron, while further Na atoms are found bound to the outside of the polyhedron. A curious feature of the structure is that one of these exterior Na sites has square planar geometry.[16] Other sodium atoms found in the cluster display varying coordination numbers (four, five, six, and nine).

It may be that the d^5 or d^{10} ions in **1**−**3** act as a template about which the reverse-Keggin ion grows. Whether we can include other transition metals within this cage is a question we are seeking to answer. These initial cages have very low solubility, and to develop the solution chemistry, we are replacing Ph with functionalized aromatic groups.

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Supporting Information Available: Detailed synthetic procedures, IR spectra, further figures, and crystallographic information (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Metal acetates and organostibonic acids (1:1 ratio) were dissolved in acetonitrile (10 mL) and reacted in presence of base (pyridine or triethylamine) in ambient conditions (for **2**) or under solvothermal conditions at 100 °C (for **1**, **3**, **4**, and **5**). For **1**−**3**, this gave the products in moderate yields. Crystals were obtained either by slow evaporation of the solvent at room temperature or directly by slow cooling of the Teflon container used for solvothermal synthesis.

(12) It is important to stress that the structures reported here contain disordered ligands and solvent-accessible voids in which solvent can be severely disordered. Details of the structural problems are given in the Supporting Information. Structural details for **1**: orthorhombic, *Pcca*, $a = 38.11$, $b = 25.37$, $c = 27.18$ Å, $R = 0.0649$. For **2**: monoclinic, $P2_1/c$, $a = 19.39$, $b = 25.82$, $c = 22.62$ Å, $\beta = 101.24°$, $R = 0.0722$. For **4**: monoclinic, $C2/c$, $a = 31.87$, $b = 17.85$, $c = 28.47$ Å, $\beta = 118.11°$, $R = 0.0671$. For **5**: triclinic, $P\bar{1}$, $a = 19.22$, $b = 21.16$, $c = 29.44$ Å, $\alpha = 104.84°$, $\beta = 100.52°$, $\gamma = 96.96°$, $R = 0.0677$. Microanalysis for **1**. Calcd: C, 26.00; H, 2.54; N, 0.0. Found: C, 26.45; H, 2.72; N, 0.0. For **2**. Calcd: C, 29.53; H, 2.50; N, 1.23. Found: C, 26.85; H, 2.65; N, 1.45.

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