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Preparation and structure of $[Sn_8W_{18}O_{66}]^{8-}$ – a 26-nuclear stannotungstate with a hexagonal belt of six Sn(II) ions with outward-looking lone pairs

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Sn(II) acts as template in reaction with WO_4^{2-} in formate buffer, inducing the formation of decanuclear $[SnW_9O_{33}]^{10-}$ and further linking them by six Sn(II) centers to give orange 26-nuclear stannotungstate $[Sn_8W_{18}O_{66}]^{8-}$. Crystalline $[Na_{12}(OH)_4(H_2O)_{28}][Sn_8W_{18}O_{66}]\cdot 18H_2O$ (1) was isolated and structurally characterized.

Structural versatility of heteropolytungstate anions is derived from a various combinations of few important building blocks, most of which can be regarded as fragments of well-known Keggin type $[XW_{12}O_{40}]^{n-}$.[1,2] For example, removal of three W atoms gives decanuclear $\{XW_9\}$ building blocks, which can further be brought together by coordination to various metal ions to give polyoxometallates of high nuclearity (more than 20 metal atoms in a discrete anion). Thus, two $\{PW_9\}$ units are found in $[P_2W_{21}O_{71}]^{6-}$,[3] in $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$,[4] and in $[Sn_3(XW_9O_{34})_2]^{n-}$ (with Sn(II); X = P, Si),[5] three – in $[Ln_2(H_2O)_7As_3W_{29}O_{103}]^{17-}$ (Ln = La, Ce),[2] and twelve – in $[Ln_{16}As_{12}W_{148}O_{524}(H_2O)_{36}]^{76-}$.[6] Although Sn(II) can act as central atom to form B-type SnW_9 unit (B-type here means that Sn is connected with only three oxygen atoms, the fourth coordination site being occupied by the lone pair), as found in the Dawson-type anion $[H_3SnW_{18}O_{60}]^{7-}$,[7] the potential of $\{SnW_9\}$ building blocks for creation of larger heteropolyanions remains unexplored. On the other hand, the examples of $[Sn_3(XW_9O_{34})_2]^{n-}$ (X = P, n = 12; X = Si, n = 14) and $[XW_{11}O_{39}Sn]^{n-}$ show that Sn(II) can also coordinate defect Keggin-type anions.[5,8] The combination of the ability of Sn(II) to act as the central atom and as a peripheral metal ion and center for further co-ordination at the same time makes it possible to build large stannotungstates by self-assembly reactions from simple building blocks. Here we report the preparation and structure of tin-rich 26-nuclear $[Sn_8W_{18}O_{66}]^{8-}$, prepared in 40% yield from $SnCl_2$ and Na_2WO_4 in formate buffer (pH = 3.5).[9]

The anion $[Sn_8W_{18}O_{66}]^{8-}$ (symmetry D_{3h}) is built of two α-B–$SnW_9O_{33}{}^{10-}$ units, joined together by six Sn(II) cations (Fig. 1).[10] The same α-B–SnW_9 half-unit was found to be the basis of structure in $[H_3SnW_{18}O_{60}]^{7-}$.[7] The Sn(II) in this unit is three-coordinated (Sn–O 2.14(2) Å). Six more Sn(II) cations are sandwiched between two α-B–$SnW_9O_{33}{}^{10-}$ units and form a flat hexagon with non-bonding Sn ··· Sn distances of 3.586(4) Å. Each Sn(II) of this "belt" coordinates two α-B–$SnW_9O_{33}{}^{10-}$ units by four oxygen atoms (Sn–O 2.18(2)–2.28(2) Å), thus exhibiting a square pyramidal geometry with a stereochemically active, outward-looking lone pair. The same type of Sn(II) coordination was also found in $[Sn_3(XW_9O_{34})_2]^{n-}$ (X = P, n = 12; X = Si, n = 14),[5] while in recently prepared $[Sn_{1.5}(WO_2(OH))_{0.5}(WO_2)_2(XW_9O_{33})_2]^{10.5-}$ (X = Sb(III), Bi(III)) two β-B-$[XW_9O_{33}]^{9-}$ fragments are joined together by three-coordinated Sn(II), bound to two oxygen atoms of one unit and to only one such atom of the other unit. Another remarkable feature of the anion in **1** is the outward-looking lone pairs of the "belt" atoms: in $[Sn_3(XW_9O_{34})_2]^{n-}$ they are inward-looking (Sn ··· Sn 3.70–3.76 Å). Probably the difference is due to the difficulty of accommodating six lone pairs inside the flat Sn_6 hexagon. The presence of six sandwiched atoms between two XW_9 units is unusual, since the maximum number of metal ions in this position had not exceeded four so far, as in $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$, for example.

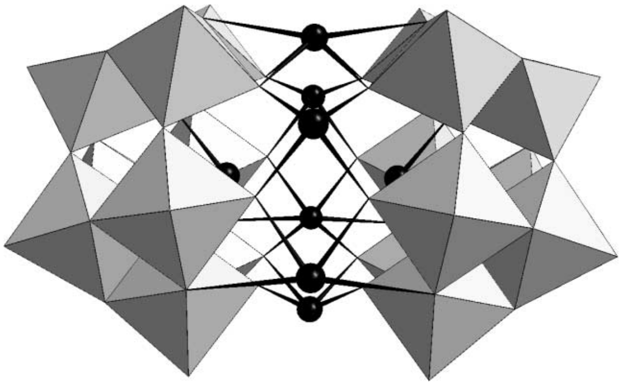

Fig. 1 The structure of $[Sn_8W_{18}O_{66}]^{8-}$ anion, Sn(II) cations are in black balls and sticks and $\{W_9\}$ fragments are grey polyheda. Distances are: W–O 1.70(2)–2.21(2) Å, Sn–O 2.14(2) Å inside $SnW_9O_{33}{}^{10-}$ units and 2.18(1)–2.28(1) Å in the 'belt' between them.

The Na^+ cations are connected by OH^- and H_2O into layers. Both crystallographically independent sodium atoms, Na1 and Na2, have octahedral coordination. All Na2-containing octahedra share edges forming hexagonal rings (grey cross-hatched octahedrons) similar to those in the corundum structure. The Na1-containing octahedra are aggregated into triangular units $Na_3(\mu_3\text{-}OH)(\mu\text{-}H_2O)_3$ *via* common edges. The hexagonal rings are connected to each other through the triangles which lie above (white octahedrons) and below (dark grey ones) the plane of hexagonal rings (Fig. 2). It is worth noting that recently reported cationic unit $[K_6(\mu\text{-}H_2O)_6(H_2O)_8]^{6+}$ has only discrete hexagonal rings.[11]

In the crystal the cationic layers run perpendicular to the c axis. The stannotungstate anions are found between layers and are oriented along the c axis. There is no direct coordination of Na by polyoxometallate oxygen atoms. The remaining space is filled by uncoordinated water molecules. There are some short O ··· O contacts between water molecules of the cation and oxygen atoms of the anion (2.68–2.81 Å), and between solvent water molecules (2.33–2.53 Å) which may be considered as hydrogen bonds.

Thus, one-pot self-assembly reaction gives a new stannotungstate which has six available lone pairs. That the complex is obtained in the formate, but not in the acetate buffer solutions, may indicate an importance of Sn(II)–formato complexes in the self-assembly process. Indeed, their formation both in solution and in solid state has long been reported.[12,13] Our attempts to involve Pb(II) in the same reaction have failed

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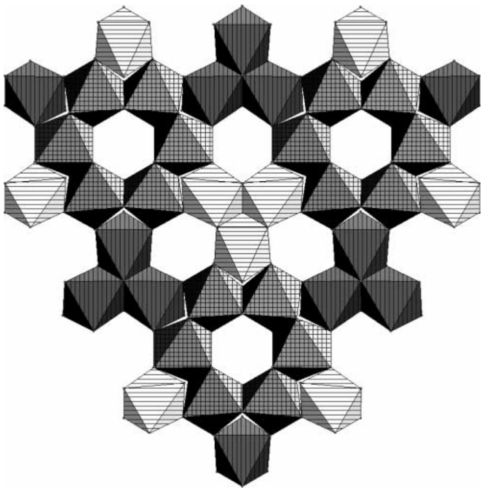

Fig. 2 Polymeric cation $[Na_{12}(OH)_4(H_2O)_{28}]^{8+}$ (viewed along *z* axis). White, medium-grey and dark-grey Na-octahedrons correspond to different levels on *z*. Distances are: Na–μ_3-OH 2.46(3) Å, Na–μ-H_2O 2.34(3)–2.54(3) Å, Na–H_2O 2.36(5) Å.

leading to a white precipitate (most likely $PbWO_4$) while preliminary data show that Ge(II) behaves similarly to Sn(II). It has been demonstrated that the lone pair at Sn(II) in $[XW_{11}O_{39}Sn]^{n-}$ and in $[Sn_3(XW_9O_{34})_2]^{n-}$ is susceptible toward electrophilic attack and oxidation.[8] Such experiments on $[Sn_8W_{18}O_{66}]^{8-}$ are under way.

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9 $[Na_{12}(OH)_4(H_2O)_{28}][Sn_8W_{18}O_{66}]\cdot 18H_2O$ (**1**). $Na_2WO_4\cdot 2H_2O$ (8.80 g, 26.7 mmol), and NaOH (4.25 g, 106.3 mmol) were dissolved in 50 ml of water. To this solution 5 ml of formic acid, and 1.67 g (7.4 mmol) of $SnCl_2\cdot 2H_2O$ were added under vigorous stirring; the solution must be brown at this stage. If the brown colour does not appear, pH must be adjusted to 3.5–4.0 by adding more formic acid. The brown solution was quickly filtered. Large orange crystals of **1** were obtained by acetone vapour diffusion into this solution. Yield 40%. IR (KBr, 4000–400 cm^{-1}): 1623 m, 932 s, 863 m, 707 s, 509 m. Raman: 958 s, 863 m, 768 w, 432 w, 355 w, 213 s. The crystals are moderately air-sensitive, and lose water quickly once taken out of mother liquor.

10 Crystal data for **1**: $H_{96}O_{116}W_{18}Sn_8Na_{12}$, M = 6487.47, hexagonal, a = 14.478(8), c = 32.08(2) Å, U = 5823.47(60) $Å^3$, T = 110 K, space group $P6_3/mmc$ (no. 194), Z = 2, D_c = 3.700 g cm^{-1}, μ(Mo-Kα) = 19.54 mm^{-1}. 42631 reflections were measured on a Bruker Smart 1000 CCD diffractometer, 2695 unique (R_{int} = 0.1191). The final $R(F) = 0.0632$, GooF = 1.137 (for 1718 $F_o \geq 4\sigma(F_o)$), $wR(F^2) = 0.1980$ (all data). The structure was solved by direct methods, and refined by full-matrix least-squares method using the *SHELXTL 5.1* programs suite.[14] Hydrogen atoms were not located. Absorption corrections were done empirically using the *SADABS* program.[15] CCDC reference numbers 218283. See http://www.rsc.org/suppdata/dt/b3/b310235a/ for crystallographic data in CIF or other electronic format.

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