New Strategies for the Generation of Large Heteropolymetalate Clusters: The β-*B*-SbW$_9$ Fragment as a Multifunctional Unit

Michael Bösing, Ina Loose, Heinrich Pohlmann and Bernt Krebs*

Abstract: Proceeding from the α-*B*-SbW$_9$O$_{33}$ fragment **1**, various novel large heteropolyanions ($[Na_2Sb_8W_{36}O_{132}(H_2O)_4]^{22-}$ (**2**), $[Sb_2W_{22}O_{74}(OH)_2]^{12-}$ (**3**) and $[Sb_2W_{20}M_2O_{70}(H_2O)_6]^{(14-2n)-}$ (**4**); $M^{n+} = Fe^{3+}, Co^{2+}, Mn^{2+}, Ni^{2+}$) have been obtained in crystalline form by systematic synthesis. Their unexpected structures have been studied by X-ray diffraction: **2**, **3** and **4** contain β-SbW$_9$ units connected to each other by Sb^{3+} ions, WO_2/WO_2OH groups, and $WO_2/M^{n+}(H_2O)_3$ groups, respectively. Structural details and especially the systematic synthesis strategy for the formation of these interesting polytungstates are discussed in order to explain the unusual behaviour of **1** in aqueous solution under different reaction conditions.

Keywords
antimony · heteropolyanions · polyoxometalates · synthesis design · tungsten

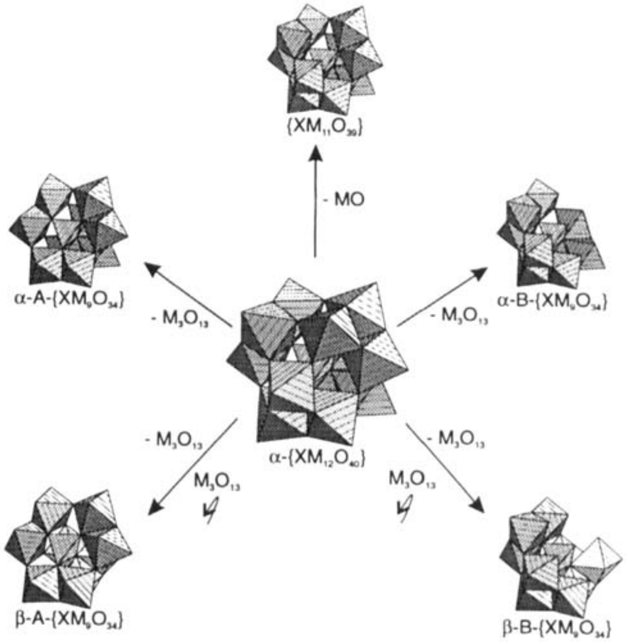
Introduction

The chemistry of the early transition elements, particularly tungsten, molybdenum and vanadium, in aqueous solution is dominated by the formation of polyoxoanions. The first compounds of this remarkable class of metal–oxygen clusters were reported over 150 years ago, and new anions with interesting topologies and/or different heteroelements are still being discovered.[1] Owing to their unusual properties (high charges and ionic masses, oligomeric cluster structures, high solubility, etc.) some of these polyanions have applications in chemical analysis, catalysis and medicine.[2–4] At present more than 70 different elements have been reported as constituents of heteropolyanions. Nonetheless, some types of anions are preferred due to their particular stability, for example the well-known Keggin, Dawson, Anderson and Dexter–Silverton structures.[5] Formally their formation can be described as exemplified by Equation (1).[6] The driving force for this behaviour (even for the

$$12\{MoO_4\}^{2-} + \{HPO_4\}^{2-} + 23\,H^+ \longrightarrow [PMo_{12}O_{40}]^{3-} + 12\,H_2O \qquad (1)$$

generation of the relatively simple α-Keggin structure type anions $[XM_{12}O_{40}]^{n-}$ with an extremly high formation tendency, Scheme 1) is still not clearly understood.[7]

Complex, largely unknown reaction mechanisms are responsible for these self-organisation processes; this makes a straightforward reaction route for their syntheses difficult, even in some apparently simple cases. Beyond this, there are larger more or less labile anions produced from subunits of these structures that have not yet been synthesised by a systematic scheme; examples are derivatives of lacunary polyoxometalates in which one or more metal atoms have been discarded, specifically complexes of XM$_{11}$[8–13] or XM$_9$[14–16] units (Scheme 1).



Scheme 1. The α-Keggin structure and its relationship to some deficient (lacunary) species. For α-*A*-XM$_9$O$_{34}$ and XM$_{11}$O$_{39}$ the effective interconversion reactions are reversible, whereas for the three other XM$_9$O$_{34}$ anions the arrows represent only a structural relationship. The reverse conversion of β-*A*-XM$_9$O$_{34}$ and α-*B*-XM$_9$O$_{34}$ to the Keggin anion is, however, possible.

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A suitable method of preparation seems to be the production of large highly negatively charged (and therefore soluble) intermediate subunits. These transferable units can then be stabilised by electrophilic protection groups or joined together in polycondensation reactions.[17, 18] An example of this useful strategy is the dimerisation of the molybdoarsenate $[(AsOH)_3(MoO_3)_3(AsMo_9O_{33})]^{7-}$. After protonation, the monomeric fragment reacts as a stable intermediate of $[AsMo_9O_{33}]^{9-}$ to give the dimeric anion $[(AsOH)_6(MoO_3)_2(O_2Mo{-}O{-}MoO_2)_2(AsMo_9O_{33})_2]^{10-}$.[19] According to this general idea, we report here a strategy for the systematic synthesis of large Sb-containing polymetalate clusters with the ability to fix various transition-metal elements.

Results and Discussion

Starting from the α-B-$[SbW_9O_{33}]^{9-}$ fragment **1**, we prepared a series of hitherto unknown interesting large heteropolytungstate clusters: $[Na_2Sb_8W_{36}O_{132}(H_2O)_4]^{22-}$ (**2**), $[Sb_2W_{22}O_{74}(OH)_2]^{12-}$ (**3**) and $[Sb_2W_{20}M_2O_{70}(H_2O)_6]^{(14-2n)-}$ (**4**); $M^{n+} = Fe^{3+}$, Co^{2+}, Mn^{2+}, Ni^{2+}. All these compounds were characterised by X-ray structure analyses, elemental analyses and IR absorption spectroscopy. Clusters **2**, **3** and **4** were synthesised by means of a strategy based on the general idea described in this paper. Furthermore, different intermediates (β-B-SbW_9O_{33} ($\mathbf{1^a}$), $Sb_2W_9O_{35}$ ($\mathbf{1^b}$), $SbW_{10}O_{37}$ ($\mathbf{1^c}$) and $Sb_2W_{20}O_{70}$ ($\mathbf{1^d}$)) are postulated to explain the strategy by a likely reaction mechanism.

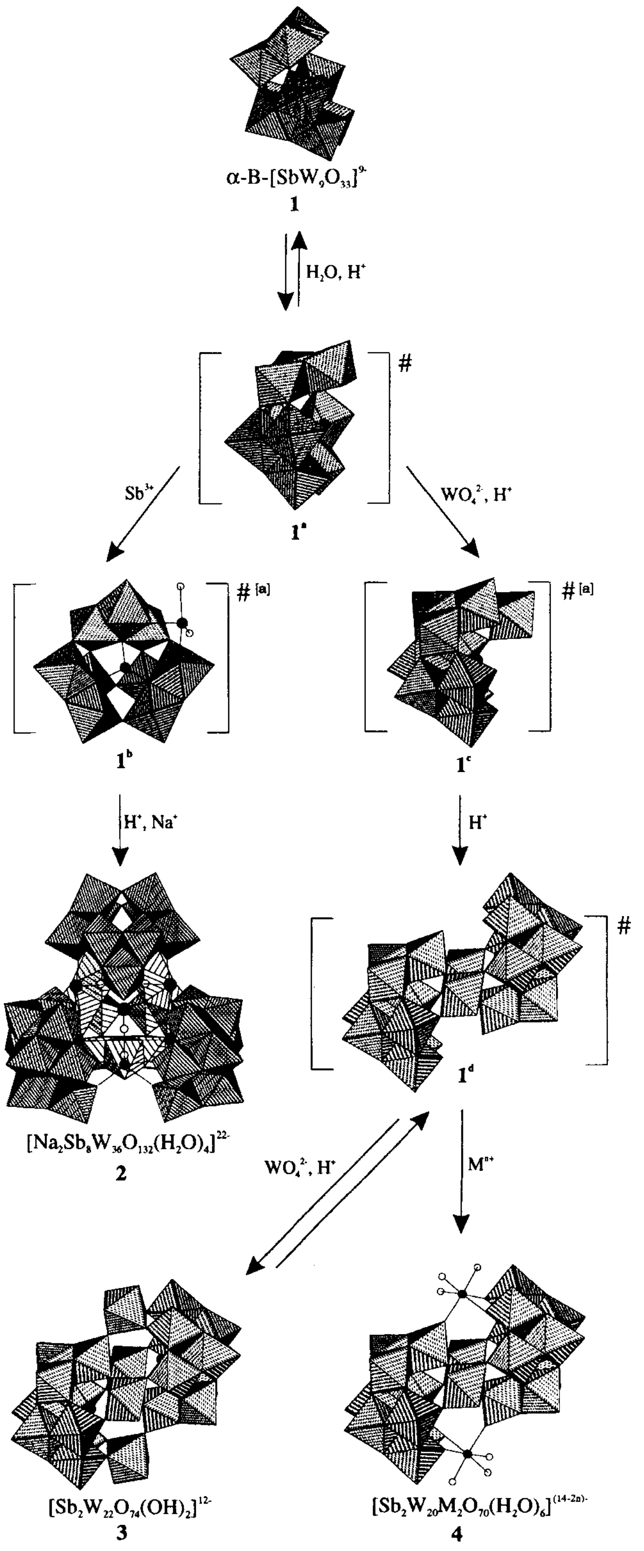
Synthesis: The syntheses of the present heteropolyanions are described clearly by Equations (2)–(5), where $M^{n+} = Fe^{3+}$, Co^{2+}, Mn^{2+}, Ni^{2+}. The strategy for generation of these compounds is illustrated in Scheme 2 and can be explained by the following reaction steps:

$$9[WO_4]^{2-} + Sb^{3+} + 6H^+ \longrightarrow \underset{\mathbf{1}}{[SbW_9O_{33}]^{9-}} + 3H_2O \tag{2}$$

$$4[SbW_9O_{33}]^{9-} + 4Sb^{3+} + 2Na^+ + 4H_2O \longrightarrow \underset{\mathbf{2}}{[Na_2Sb_8W_{36}O_{132}(H_2O)_4]^{22-}} \tag{3}$$

$$2[SbW_9O_{33}]^{9-} + 4[WO_4]^{2-} + 14H^+ \longrightarrow \underset{\mathbf{3}}{[Sb_2W_{22}O_{74}(OH)_2]^{12-}} + 6H_2O \tag{4}$$

$$[Sb_2W_{22}O_{74}(OH)_2]^{12-} + 2M^{n+} + 8H_2O \longrightarrow \underset{\mathbf{4}}{[Sb_2W_{20}M_2O_{70}(H_2O)_6]^{(14-2n)-}} + 2[WO_4]^{2-} + 6H^+ \tag{5}$$



Scheme 2. Suggested reaction route with likely postulated intermediates ($\mathbf{1^a}$, $\mathbf{1^b}$, $\mathbf{1^c}$, and $\mathbf{1^d}$) to generate large heteropolytungstate clusters containing β-B-SbW_9 fragments (**2**, **3** and **4**) produced from **1**. [a] For the intermediates $\mathbf{1^b}$ and $\mathbf{1^c}$ only one of the two possible enantiomers is shown.

Starting fragment: The first step in the sequence of syntheses is the preparation of the starting fragment **1**. The α-B-XW_9 type of this anion is obtained from the reaction of $Na_2WO_4 \cdot 2H_2O$ and Sb_2O_3 in aqueous solution at pH 7.5. This reaction must be carried out in a nonacidic medium to avoid further condensation reactions. Besides, the unshared pair of electrons at the Sb^{3+} centre prevents condensation reactions with $[WO_4]^{2-}$ anions to form a complete spherical structure.[20] This is a basic requirement for the further steps of synthesis. Oxidation of the Sb^{III} to Sb^{V} would lead to completion of the metal–oxygen framework with formation of α-Keggin type anions. Because of its high charge, **1** tends to be stabilised by cations or to undergo further condensation reactions, depending on the pH value of the solution. We know from the X-ray structure analysis that in neutral solutions **1** is stabilised by Na^+ ions to give the dimeric product with a belt of univalent cations between the two α-*B*-SbW_9 anions. The resulting sodium compound can be isolated easily.

Generating intermediates: The second step involves the production of the hypothetical intermediates **1**^{a}, **1**^{b} and **1**^{c}. An aqueous solution of **1** contains α- and β-species of the *B*-SbW_9 anion at equilibrium.[21] As would be expected, **1** has a higher tendency to undergo condensation reactions in an acidic medium than in neutral solution. Therefore, the configuration of the α-*B*-SbW_9 anion has to be changed into a conformation that makes further protonation and condensation more likely. Formally this is an isomerisation of the α-type to the β-type anion **1**^{a}. The terminal oxygen atoms of the resulting *fac*-WO_3 group are more strongly basic than those of WO_2 and WO units and therefore offer sites for further polymerisation.[22] Probably the resulting β-*B*-SbW_9 anion is directly protonated to obey the Lipscomb rule. There are some other less condensed β-type fragments that may develop from the α-*B*-SbW_9 anion as well. For example, the SbW_7 fragment, a constitutive subunit of $[NaSb_9W_{21}O_{86}]^{18-}$,[23] could be formed, or a putative β-*B*-SbW_8 unit, which has an analogous fragment in $[As_2W_8O_{31}H]^{7-}$.[24] Nevertheless, a more acidic reaction milieu renders less condensed intermediates unlikely and, indeed, **2**, **3** and **4** consist mainly of intact β-*B*-SbW_9 subunits. This indicates the important role of this fragment as intermediate in their synthesis.

Intermediate **1**^{a} then reacts as a nucleophile with the electrophilic groups Sb^{3+}[17] or $[WO_4]^{2-}$ acting as anti-Lipscomb units[18, 25] to give the intermediates $Sb_2W_9O_{35}$ (**1**^{b}) and $SbW_{10}O_{37}$ (**1**^{c}). In both cases a pair of structurally closely related enantiomeric intermediates might be formed. In particular, the condensed SbO_2 group and the WO_4 group are placed between the protonated *fac*-WO_3 group and a WO_2 group of a neighbouring W_3O_{13} subunit in **1**^{a}. However, the formation of **1**^{b} and **1**^{c} stabilises the highly negatively charged anion **1**; it supplies enough space for further condensation reactions at the side of the anion with the lone pair of electrons at the Sb^{III} centre, a necessary condition for the generation of larger clusters.

Condensation of intermediates: The third step in the strategy consists of stepwise condensation to form larger clusters. Intermediates **1**^{b} (two pairs of enantiomers) react after protonation at pH 6.5 to give the $[Na_2Sb_8W_{36}O_{132}(H_2O)_4]^{22-}$ anion (**2**), which combines four β-*B*-SbW_9 subunits with Na^+ and Sb^{3+} between them. The condensation results from the reaction of two $Sb^{III}-OH$ groups and two protonated WO_2 groups of each intermediate with simultaneous separation of water and formation of four $(O_5W)_2-O_2SbO_2-(WO_5)_2$ bridges. The resulting structure is stabilised by two Na^+ ions to build a distorted tetrahedral arrangement. In a similar fashion, intermediates **1**^{c} (one pair of enantiomers) react after protonation of each WO_4 group with a protonated WO_2 group of the other enantiomer to give the $[Sb_2W_{20}O_{70}]^{14-}$ ion **1**^{d}. This unknown 20-nuclear heteropolyanion[26] seems to be relatively stable and also obeys the Lipscomb rule. Another less likely possible route to **1**^{d} is formally the condensation of **1**^{a} with a speculative $SbW_{11}O_{41}$ unit. However, in a further reaction step **1**^{d} can be even better stabilised by the addition of two *fac*-WO_3 anti-Lipscomb units at pH 4.5 or by addition of two $M^{n+}(H_2O)_3$ groups ($M^{n+} = Fe^{3+}$, Co^{2+}, Mn^{2+}, Ni^{2+}) to give **3** or **4**. The resulting $[Sb_2W_{22}O_{74}(OH)_2]^{12-}$ anion (**3**) consists of two β-*B*-SbW_9 subunits connected to each other by two WO_2 groups and two WO_2OH groups, respectively.

Exchange reactions: The formation of clusters of type **3** containing transition-metal atoms can be achieved in a final step by exchange reactions. Starting from an aqueous solution of **3**, the addition of the transition-metal salts $[Fe(NO_3)_3 \cdot 9H_2O]$, $[CoCl_2 \cdot 6H_2O]$, $[Mn(NO_3)_2 \cdot 4H_2O]$ or $[NiCl_2 \cdot 6H_2O]$ leads to novel heteropolytungstates **4** with the general formula $[Sb_2W_{20}M_2O_{70}(H_2O)_6]^{(14-2n)-}$.[26, 27] The simple syntheses of these anions depend on the systematic substitution of two $M^{n+}(H_2O)_3$ groups for two relatively weakly binding *fac*-WO_2OH groups by moderate heating of the reaction solution. Obviously in this reaction **3** is reduced to the less condensed intermediate **1**^{d}, which then reacts as a nucleophile with the electrophilic transition-metal ion $[M^{n+}(H_2O)_3]$ to give stabilised anions of **4**. These heteropolytungstates are more stable in aqueous solution than anions of type **2** and **3** because of their high degree of condensation and the less negative charge of their whole anion framework.

Structural characterisation of the anions: Like many other heteropolyanions, **1**, **2**, **3** and **4** contain portions of the α-Keggin structure. This well-known cluster consists of four groups of three edge-sharing WO_6 octahedra, with corner sharing between adjacent octahedra of different groups. Removal of three adjacent corner-sharing octahedra results in an α-*A*-XW_9O_{34} anion, removal of three edge-sharing octahedra gives an α-*B*-XW_9O_{34} anion.[28] In several tungstates single crystal X-ray studies have exposed an α-*A*-XW_9 unit[29] and an α-*B*-XW_9 unit[30] (X = P, As), respectively. The present clusters all belong to the *B*-XW_9 type (**1** to the α-type and **2**, **3** and **4** to the β-type anions).

In particular, the X-ray structure analysis of the sodium salt Na_9[**1**]$\cdot 19.5H_2O$ (Table 1) reveals a novel heteropolyanion derived from the α-Keggin structure (Figure 1). The cluster consists of three corner-sharing W_3O_{13} fragments with a Sb^{III} centre linked by triply bridged oxygen atoms. Each of these groups is composed of three edge-sharing WO_6 octahedra. The tungstate framework of this α-*B*-SbW_9 structure is held together by four different types of oxygen atoms.

Fifteen oxygen atoms O_t of the cluster are terminally bonded to W^{VI} atoms with bond lengths between 1.72(1) and 1.77(1) Å. Oxygen atoms O_{W2} connecting two W^{VI} atoms have bond lengths between 1.87(1) and 2.12(1) Å, depending on the asymmetry of the bridges. This asymmetry is due to the strong *trans* effect of the terminally bonded oxo groups. Another type of oxygen atom, O_{W3Sb}, bridges three W^{VI} atoms with the Sb^{III} heteroatom and has $W-O_{W3Sb}$ bond lengths between 2.25(1) and 2.40(1) Å. Between these oxygen atoms (in the centre of the anion) the Sb^{III} atom has an average $Sb-O_{W3Sb}$ bond length of 1.98 Å. A special feature of this SbW_9 structure is the nonbonding nature of the lone pair of electrons at the Sb^{III} centre. Together with the O_{W3Sb} atoms the heteroatom has a distorted Ψ-tetrahedral coordination. Bond lengths and selected bond angles are given in Table 2. In the crystal network of **1**, two $[SbW_9O_{33}]^{9-}$ anions related to each other by a centre of inversion face each

Table 1. Crystal structure data for compounds containing the anions $[SbW_9O_{33}]^{9-}$ (**1**), $[Na_2Sb_8W_{36}O_{132}(H_2O)_4]^{22-}$ (**2**) and $[Sb_2W_{22}O_{74}(OH)_2]^{12-}$ (**3**).[37]

	Na_9[**1**]$\cdot 19.5\,H_2O$	$[N(CH_3)_4]_{10}Na_{12}$[**2**]$\cdot 26\,H_2O$	K_{12}[**3**]$\cdot 27\,H_2O$
formula	$H_{39}Na_9O_{52.5}SbW_9$	$C_{40}H_{180}N_{10}Na_{14}O_{162}Sb_8W_{36}$	$H_{56}K_{12}O_{103}Sb_2W_{22}$
M, g mol^{-1}	2862.62	11308.40	6499.60
crystal size, mm^3	$0.18 \times 0.32 \times 0.28$	$0.22 \times 0.35 \times 0.35$	$0.17 \times 0.27 \times 0.13$
crystal colour/habit	colourless plates	pale yellow plates	colourless plates
crystal system	triclinic	tetragonal	triclinic
space group	$P\bar{1}$ (no. 2)	$I\bar{4}2m$ (no. 121)	$P\bar{1}$ (no. 2)
a, Å	11.534(4)	19.190(4)	12.543(4)
b, Å	13.829(6)	19.190(4)	12.835(4)
c, Å	17.179(6)	29.377(7)	16.381(5)
α, °	66.46(3)	90	80.06(3)
β, °	82.47(3)	90	74.20(3)
γ, °	69.79(3)	90	71.31(2)
V, Å^3	2357(2)	10818(3)	2393(1)
Z	2	2	1
ρ_{calcd}, g cm^{-3}	4.03	3.47	4.51
μ, mm^{-1}	22.64	20.16	27.60
$F(000)$	2550	10024	2828
scan mode	$\theta-2\theta$	ω	$\theta-2\theta$
T, K	293	173	293
2θ range, °	$4<2\theta<54$	$4<2\theta<54$	$4<2\theta<50$
indep. reflns.	9631	3348	8473
obs. reflns. ($>2\sigma(I)$)	8633	2498	6201
variables	385	135	359
GOF on F^2	1.096	1.064	1.068
R ($>2\sigma(I)$)	R_1 [a] = 0.0494	R_1 [a] = 0.0723	R_1 [a] = 0.0684
	wR_2 [b] = 0.1250	wR_2 [b] = 0.1712	wR_2 [b] = 0.1633
R (all data)	R_1 [a] = 0.0554	R_1 [a] = 0.0990	R_1 [a] = 0.0997
	wR_2 [b] = 0.1308	wR_2 [b] = 0.1995	wR_2 [b] = 0.1876
$(\Delta/\rho)_{max}$, e$^-$ Å^{-3}	2.99	2.49	3.85
$(\Delta/\rho)_{min}$, e$^-$ Å^{-3}	-5.230	-2.806	-4.277

[a] $R_1 = \sum||F_0| - |F_c||/\sum|F_0|$. [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^4]^{1/2}$. $w_1 = 1/[\sigma^2(F_o^2) + (0.0809\,P)^2 + 33.6856\,P]$. $w_2 = 1/[\sigma^2(F_o^2) + (0.0943\,P)^2 + 21.2919]$. $w_3 = 1/[\sigma^2(F_o^2) + (0.1066\,P)^2 + 81.026\,P]$. $P = (F_o^2 + 2\,F_c^2)/3$.

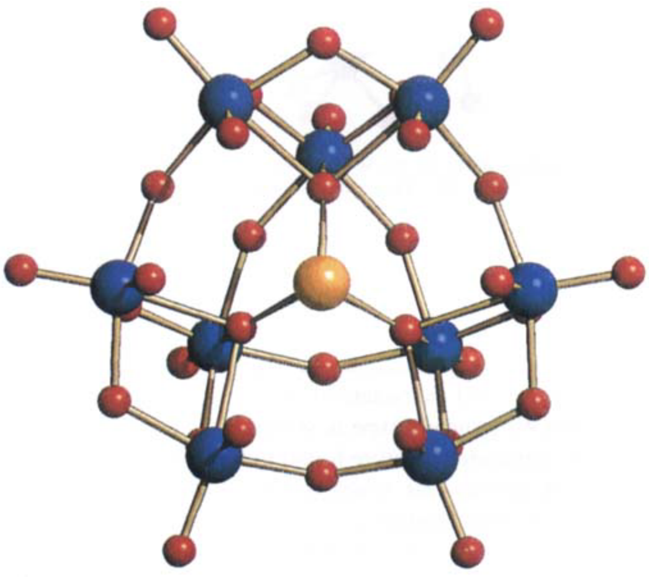


Figure 1. Structure of the $[SbW_9O_{33}]^{9-}$ anion **1** in $Na_9SbW_9O_{33}\cdot 19.5H_2O$ (W = blue, Sb = orange, O = red).

other with their open sites. A belt of six Na^+ ions connects both anions.

The X-ray structure analysis of the mixed sodium tetramethylammonium salt $[N(CH_3)_4]_{10}Na_{12}$[**2**]$\cdot 26\,H_2O$ (Table 1)[31] shows an interesting large heteropolyanion containing four identical β-B-$[SbW_9O_{33}]^{9-}$ fragments. This tetrameric structure has crystallographic $I\bar{4}2m$ symmetry. A view of the anion along the fourfold axis is shown in Figure 2. Each of the four SbO_4 groups connecting two SbW_9 units is built of a Sb^{III} atom with Ψ-trigonal bipyramidal coordination (including the lone pair of electrons in the equatorial plane). The incomplete tungstate cage of the β-B-SbW_9 fragments consists of three edge-sharing W_3O_{13} groups with centred Sb^{III} atoms and can be derived from **1** by 60° rotation of one W_3O_{13} subunit around the $Sb-O_{W3Sb}$ binding vector. The Sb^{III} atoms in their centres are surrounded pyramidally by three oxygen atoms; the top of the pyramid is formed by the lone electron pair at the Sb atom. A special feature of **2** is the stabilisation of the metal–oxygen framework by two sodium atoms; this results in a tetrahedral formation of SbW_9 subunits. They are located at the corners of these distorted tetrahedra; Na^+ and Sb^{3+} are placed at the edges. As usual, different types of oxygen atoms connect the metal network of **2**. The first four types are equivalent to the oxygen atoms of **1** with average bond lengths of 1.74 O_t, 1.93 O_{W2}, 2.29 O_{W3Sb} and 1.97 Å for the $Sb-O_{W3Sb}$ bond length in each SbW_9 subunit. Between each of these units and the bridging Sb^{3+} ions there is an average $W-O_{WSb}$ bond length of 1.84 Å, a short bond length of 1.91(2) Å for $Sb-O_{WSb}$ (equatorial), and a relatively long bond length of 2.34(2) Å for $Sb-O_{WSb}$ (apical). The bond lengths and angles in **2** are shown in Table 2. This large anion is comparable to structures of the general formula $[M^mAs_4W_{40}O_{140}]^{(28-m)-}$; $M^{m+} = Na^+, K^+, NH_4^+, Ba^{2+}$.[32] Both structures consist of four B-XW_9 units that are cyclically connected through four bridging groups (Sb^{III} atoms or *cis*-WO_2

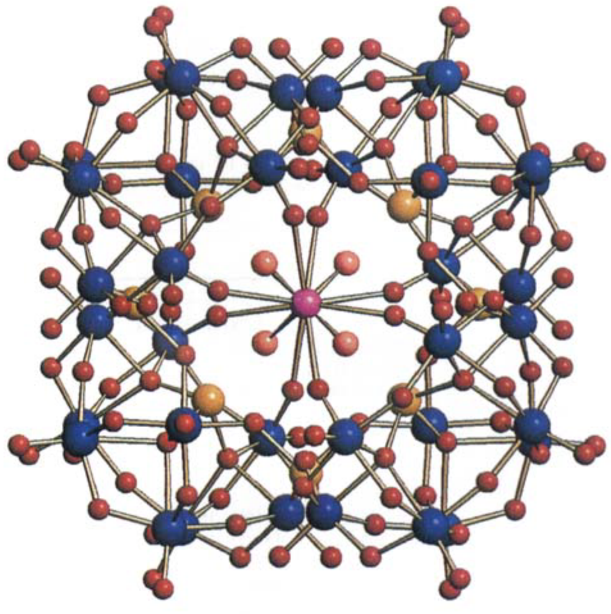


Figure 2. Structure of the large $[Na_2Sb_8W_{36}O_{132}(H_2O)_4]^{22-}$ anion **2** in $[N(CH_3)_4]_{10}Na_{12}[Na_2Sb_8W_{36}O_{132}(H_2O)_4]\cdot 26\,H_2O$ (W = blue, Sb = orange, Na = magenta, O = dark red, H_2O = light red) along the fourfold axis.

groups). The arsenatotungstate has a distorted tetrahedral structure with As atoms at the corners and M^{m+} in the centre of the anion. Unlike **2**, it is composed of α-type XW_9 fragments.[33]

The X-ray structure analysis of the potassium salt K_{12}[**3**]$\cdot 27H_2O$ (Table 1) reveals a new heteropolyanion composed of two identical β-*B*-$[SbW_9O_{33}]^{9-}$ fragments joined together by four WO_6 octahedra. These dimeric $[Sb_2W_{22}O_{74}(OH)_2]^{12-}$ anions have centres of inversion and form separate molecular units in the crystal (Figure 3). The bond lengths within each SbW_9 subunit are similar to those in **1** and **2**, with average values of 1.75 Å for $W-O_t$, 1.95 Å for $W-O_{W2}$, 2.29 Å for $W-O_{W3Sb}$ and 2.01 Å for $Sb-O_{W3Sb}$. A remarkable feature of this cluster is the existence of WO_6 octahedra without any as well as with three terminal oxygen atoms. Only a few of these so-called anti-Lipscomb polyoxometalates have been characterised,[34, 35] but this combination of rare structural properties is so far unknown elsewhere. Also the manner in which the β-*B*-XW_9 Keggin fragments are connected with one another is most uncommon. The unusual *fac*-WO_3 groups each have one terminal oxygen atom with an extremely long $W-O_t$ bond of 1.88(2) Å. For this reason, these oxo groups are assumed to be protonated and therefore to obey Lipscomb's rule.[35] Bond lengths and angles are presented in Table 2.

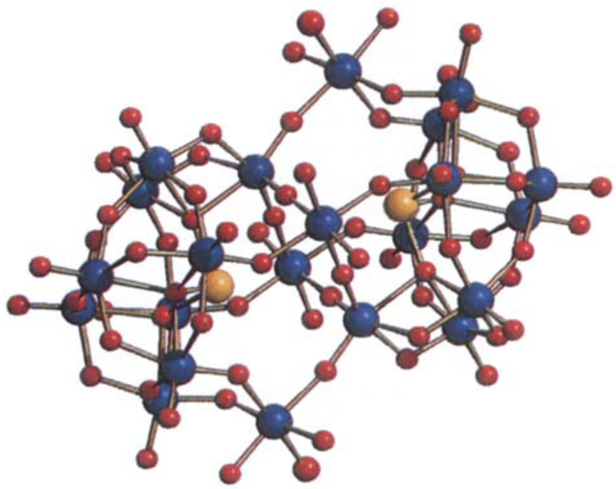


Figure 3. Structure of the $[Sb_2W_{22}O_{74}(OH)_2]^{12-}$ anion **3** in $K_{12}[Sb_2W_{22}O_{74}(OH)_2]\cdot 27H_2O$ (W = blue, Sb = orange, O = dark red, OH = light red).

Table 2. Bond lengths (Å) and angles (°) of the anions $[SbW_9O_{33}]^{9-}$ (**1**), $[Na_2Sb_8W_{36}O_{132}(H_2O)_4]^{22-}$ (**2**) and $[Sb_2W_{22}O_{74}(OH)_2]^{12-}$ (**3**) with standard deviations.

	1	**2**	**3**
$W-O_t$ [a]	1.72(1)–1.77(1)	1.67(3)–1.77(3)	1.68(2)–1.88(2)
$W-O_{W2}$ [b]	1.87(1)–2.12(1)	1.78(2)–2.09(3)	1.78(2)–2.29(2)
$W-O_{W3Sb}$ [b]	2.25(1)–2.40(1)	2.20(2)–2.38(2)	2.26(2)–2.33(2)
$W-O_{WSb}$[b]	1.78(2)–1.91(2)		
$Sb-O_{W3Sb}$ [b]	1.97(1)–1.99(1)	1.95(3)–1.99(2)	2.00(2)–2.01(2)
$Sb-O_{eq}$ [c]		1.91(2)	
$Sb-O_{ap}$ [d]		2.34(2)	
$Na-O$		2.42(3)	
$Na-O_{H2Na}$ [b]		2.43(3)	
$O-W-O_{cis}$	72(1)–106(1)	71(1)–105(1)	70(1)–105(1)
$O-W-O_{trans}$	157(1)–172(1)	155(1)–174(2)	153(1)–176(1)
$O-Sb-O_{eq}$ [c]		95(2)	
$O-Sb-O_{ap}$ [d]		165(1)	
O-Sb-O [e]	91(1)	93(1)–95(1)	89(1)–92(1)

[a] t = terminal. [b] The subscripted letters indicate the element(s) bonded. [c] eq = equatorial. [d] ap = apical. [e] Within the SbW_9 subunits.

As shown by the crystal structures of $[Sb_2W_{20}M_2O_{70}(H_2O)_6]^{(14-2n)-}$ ($M = Fe^{3+}$, Co^{2+}, Mn^{2+}, Ni^{2+}), anions of type **4**[36] are closely related to **3**. Two β-*B*-SbW_9 subunits are linked together by two corner-sharing WO_6 octahedra. Furthermore, two transition-metal atoms are bonded through two oxygen atoms of one unit and one oxygen atom of the other unit to the tungsten–oxygen framework (Figure 4). Formally the *fac*-WO_3 groups have been exchanged for transition-metal ions with three aquo ligands. This unusual formation leads to three free coordination sites at the transition-metal atoms that are completed by water molecules.

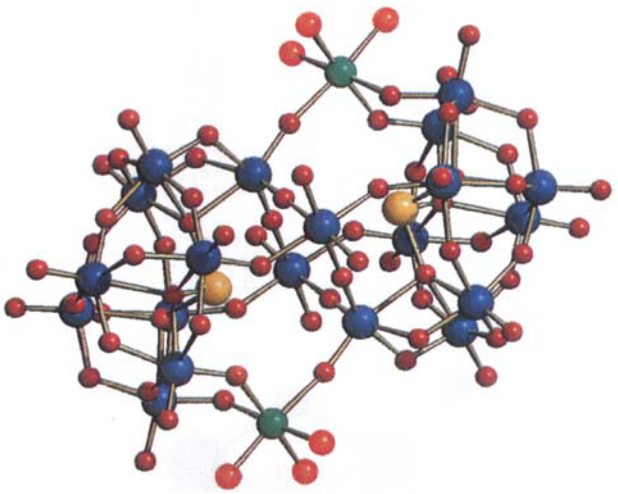


Figure 4. Structure of the $[Sb_2W_{20}M_2O_{70}(H_2O)_6]^{(14-2n)-}$ anions **4**, $M^{n+} = Fe^{3+}$, Co^{2+}, Mn^{2+}, Ni^{2+} (W = blue, Sb = orange, M = green, O = dark red, H_2O = light red).

Conclusion

A series of novel antimony-containing heteropolyanions have been prepared and characterised by X-ray structure analyses. The α-*B*-XW_9 structure type is shown in **1**; fragments of the β-*B*-XW_9 structure type were found to form the larger clusters **2**, **3** and **4**. Besides this, a new general reaction route for the synthesis of large clusters containing Keggin fragments and transition metals is proposed: stable preorganised, highly negatively charged subunits (after intramolecular reorganisation, depending on the reaction milieu) react with electrophilic groups like Sb^{3+} or *fac*-WO_3 to give stabilised intermediates. By the coupling of these intermediates larger heteropolyanions (with particular sites between the Keggin fragments for exchange reactions) can be generated. They subsequently react with various transition metals to give heteropolytungstates like **4**. This useful strategy opens a wide field in the synthesis of new polyoxometalates and has already been applied successfully to the preparation of several transition-metal-containing bismutatotungstates.[36]

Experimental Section

Crystal structure determination: Diffraction experiments were performed on a Siemens R 3 (for **1**) and a Syntex $P2_1$ diffractometer (for **2** and **3**), respectively with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) and with corrections for absorption (empirical), Lorentz and polarisation effects. The structures were solved by direct methods with the program SHELXS 86 and refined (on F^2) with SHELXL 93 by full-matrix least-squares. Oxygen atoms were refined isotropically; all other atoms were refined anisotropically. The three crystal structures exhibit the frequent appearance in this class of polyoxometalates of large disorder in the range of counterions and water molecules. Because of this, the exact formulae were determined by elemental analysis. Details of the data collection and processing, structure analysis and refinement for **1**, **2** and **3** are summarised in Table 1.

$Na_9[SbW_9O_{33}]\cdot 19.5H_2O$ ($Na_9[\mathbf{1}]\cdot 19.5H_2O$): The salt of **1** was prepared by the reaction of $Na_2WO_4\cdot 2H_2O$ (40 g, 121 mmol) in boiling water (80 mL) and dropwise addition of Sb_2O_3 (1.96 g,6.72 mmol) dissolved in concentrated HCl (10 mL). The mixture was refluxed for 1 h and allowed to cool slowly. Colourless crystals of $Na_9[\mathbf{1}]\cdot 19.5H_2O$ were formed after evaporation of one-third of the solution volume. Yield: 28.0 g (72%); $H_{39}Na_9O_{52.5}SbW_9$ 2862.62: calcd Sb 4.22, H_2O 11.79; found Sb 4.25, H_2O 12.18; IR (KBr): $\tilde{\nu} = 920, 890$ ($W-O_t$), 767, 715 cm^{-1} ($W-O_{W2}$).

$[Na_2Sb_8W_{36}O_{132}(H_2O)_4]^{22-}$ (**2**): Solid $SbCl_3$ (1.20 g, 5.26 mmol) was dissolved in a boiling solution of $Na_9[SbW_9O_{33}]\cdot 19.5H_2O$ (15.6 g, 5.24 mmol) in water (30 mL). The resulting yellow mixture was refluxed for 1 h at pH 6–7 and allowed to cool slowly. After addition of $N(CH_3)_4Cl$ (6.8 g, 62 mmol) pale yellow microcrystals of $[N(CH_3)_4]_{10}Na_{12}[Na_2Sb_8W_{36}O_{132}(H_2O)_4]\cdot 72H_2O$ (monoclinic form) were formed over several hours. Yield: 14.5 g (91%); $C_{40}H_{272}N_{10}Na_{14}O_{208}Sb_8W_{36}$ 12137.01: calcd C 4.17, H 1.99, N 1.36, Sb 7.76, Na 3.07, H_2O 10.44; found C 4.02, H 2.06, N 1.31, Sb 8.03, Na 2.95, H_2O 10.68. Large crystals of the tetragonal modification $[N(CH_3)_4]_{10}Na_{12}[Na_2Sb_8W_{36}O_{132}(H_2O)_4]\cdot 26H_2O$ used for the X-ray investigation were obtained after several days. $C_{40}H_{180}N_{10}Na_{14}O_{162}Sb_8W_{36}$ 11308.31: calcd C 4.24, H 1.59, N 1.23, Sb 8.61, Na 2.85, H_2O 11.46; found C 4.11, H 1.65, N 1.28, Sb 8.89, Na 2.93, H_2O 11.83; IR (KBr): $\tilde{\nu} = 985$ ($W-O_t$), 900, 865, 820, 775, 745 cm^{-1} ($W-O_{W2}$).

$[Sb_2W_{22}O_{74}(OH)_2]^{12-}$ (**3**): The sodium salt of **1** (10 g, 3.49 mmol) and $Na_2WO_4\cdot 2H_2O$ (2.3 g, 6.99 mmol) were dissolved in water (10 mL) while gently heated. By dropwise addition of 1 M HCl (23.5 mL) the pH of the reaction mixture was set to 4–5; the mixture was then evaporated to one-third of its volume. After cooling, the sodium salt of **3** was formed with a yield of 6.7 g (63%). Crystals of $K_{12}[Sb_2W_{22}O_{74}(OH)_2]\cdot 27H_2O$ were obtained after recrystallisation of this compound with KCl (2.68 g, 35.9 mmol) in water (10 mL) by diffusion techniques. Yield: 4.6 g (67%); $H_{56}K_{12}O_{103}Sb_2W_{22}$ 6699.60: calcd Sb 3.70, K 7.28, H_2O 7.29; found Sb 3.77, K 7.26, H_2O 7.49; IR (KBr): $\tilde{\nu} = 950$ ($W-O_t$), 840, 800, 715 cm^{-1} ($W-O_{W2}$).

$[Sb_2W_{20}M_2O_{70}(H_2O)_6]^{(14-2n)-}$ (**4**; $M^{n+} = Fe^{3+}, Co^{2+}, Mn^{2+}, Ni^{2+}$): Salts of **4** were prepared by the reaction of stoichiometric amounts of **3** with the transition-metal salts $Fe(NO_3)_3\cdot 9H_2O$, $CoCl_2\cdot 6H_2O$, $Mn(NO_3)_2\cdot 4H_2O$ and $NiCl_2\cdot 6H_2O$ at pH 6–7 and 75° C.[36]

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[37] Further details of the X-ray investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-406489 (**1**), CSD-406488 (**2**) and CSD-406487 (**3**).