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New Cluster–Polyoxometalate Hybrids Derived from the Incorporation of $\{Mo_3S_4\}$ and $\{Mo_3CuS_4\}$ Units into $\{EW_{15}\}$ Cores (E = As^{III}, Sb^{III}, Te^{IV})

Maxim N. Sokolov,*[a,b] Eugenia V. Peresypkina,[a] Irina V. Kalinina,[a] Alexander V. Virovets,[a] Vladimir S. Korenev,[a] and Vladimir P. Fedin[a,b]

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A new family of hybrid chalcogenide cluster-incorporated polyoxometalates (POMs) have been prepared in which the POM standard building block $\{W_3O_4\}^{10+}$ is replaced by topologically similar chalcogenide cluster fragments $\{Mo_3S_4\}^{4+}$, $\{Mo_3S_2O_2\}^{4+}$, and $\{Mo_3CuS_4\}^{5+}$ with M–M bonds. The family includes $[EW_{15}Mo_3S_4(H_2O)_3O_{53}]^{9-}$ (E = As, Sb), $[TeW_{15}Mo_3S_4(H_2O)_3O_{53}]^{8-}$, and $[AsW_{15}Mo_3O_2S_2(H_2O)_3O_{53}]^{9-}$. The built-in sulfide ligands represent a new center of coordination for "soft" metal ions: $[AsW_{15}Mo_3S_4(H_2O)_3O_{53}]^{9-}$ reacted with Cu^+ to form a new heterometal derivative $[AsW_{15}Mo_3(CuCl)S_4(H_2O)_3O_{53}]^{9-}$. Crystal structures of $Cs_{6.5}K(NH_4)_{1.5}[\{Mo_3S_4(H_2O)_3\}AsW_{15}O_{53}]\cdot 14H_2O$ (**1**), $Cs_{5.85}Na_{3.15}[\{Mo_3S_4(H_2O)_3\}SbW_{15}O_{53}]\cdot 14.85H_2O$ (**2**), $Cs_6Na_2[\{Mo_3S_4(H_2O)_3\}TeW_{15}O_{53}]\cdot 11.7H_2O$ (**3**), $Cs_{7.15}Na_{1.85}[\{Mo_3S_4(H_2O)_2Cl\}TeW_{15}O_{53}]\cdot 11.2H_2O$ (**4**), $Cs_6(H_3O)_3[\{Mo_3O_2S_2(H_2O)_3\}AsW_{15}O_{53}]\cdot 9.85H_2O$ (**5**), and $Cs_{5.25}K_{1.75}(NH_4)_2[\{Mo_3S_4(H_2O)_3CuCl\}AsW_{15}O_{53}]\cdot 12.07H_2O$ (**6**) were determined. The highly charged isolated anions in **1**–**6** are arranged in one of the two well-known topological types – *fcc* motif. The cations and hydrate water molecules are severely disordered over the voids between the anions. The anions in **1**–**4** are involved in specific nonvalent S···S interactions with S–S distances of 2.95–3.68 Å.

Introduction

Polyoxometalates form a specific family of anionic polynuclear oxocomplexes of early-transition metals in the highest oxidation states (V, Nb, Ta, Mo, W). Their structural variety is derived from their ability to incorporate heteroatoms of about 70 other elements. The resulting heteropolymetalates display a wealth of interesting and potentially useful properties such as catalytic, redox, and magnetic properties, luminescence, and biological activity.[1,2] Apart from the incorporation of heterometals, the modification of POM structures involves the grafting of organic substituents and the coordination to organometallic moieties and preformed polynuclear and cluster (the latter case implying the presence of M–M bonds) complexes. To some degree it is also possible to substitute oxides by nitride or imido groups, fluorides, peroxides, or sulfides, or even by Cp* (Cp* = C_5Me_5). In most cases the modification of POMs by the coordination of polynuclear and cluster units implies "grafting" such units on to a preformed POM anion by the direct coordination of heterometals to nucleophilic oxygen atoms of a chosen lacunary polyoxometalate.[2] A somewhat different "fitting in" approach has been successfully employed to incorporate $\{M_2O_2S_2\}^{2+}$ units into divacant Keggin anions γ-$[SiW_{10}O_{36}]^{8-}$. The sulfur and oxygen atoms of the incorporated $\{M_2O_2S_2\}^{2+}$ units complementarily fill the places of two W and four O atoms of γ-$[SiW_{12}O_{40}]^{4-}$, which can be regarded as the "parent" structure.[3] However, in most cases such complementarity between a preformed lacunary POM and a given polynuclear unit cannot be achieved because of the nonexistence of lacunary POMs with the desired structural features. For example, the arrangement of the metal, chalcogen, and oxygen/fluoride atoms in the cluster complexes $[Mo_3O_4F_9]^{5-}$ and $[Mo_3S_4(H_2O)_9]^{4+}$ is the same as in the $\{W_3O_{13}\}^{8-}$ units, which act as standard building blocks for Keggin and Dawson-type structures (Scheme 1).[4] No stable lacunary POMs with structures complementary to the $\{M_3S_4\}$ moiety exist. The main reason for this is that the μ_3-S atom must take the place, upon incorporation, of one of the oxygen atoms of the tetrahedral units EO_4 (E = P, Si), which is not possible. The only good candidates for the incorporation of the $\{M_3S_4\}$ moiety appear to be the POMs with a Dawson-like $\{EW_{18}O_{60}\}$ core (E = Se^{IV}, Te^{IV}, As^{III}, Sb^{III}, Bi^{III}, Sn^{II})[5] because in their structures the stereochemically active lone pair of E in the $\{EW_9O_{33}\}$ subunits prevents the incorporation of the second heteroelement into the other half of the structure, which thus consists of three $\{W_3O_{13}\}$ units linked together only through common vertices without a second heteroatom. In this case the replacement of at least one such unit becomes viable (Scheme 1). We previously reported the first examples of a hybrid chalcogenide cluster-incorporated polyoxometalate in which one standard struc-

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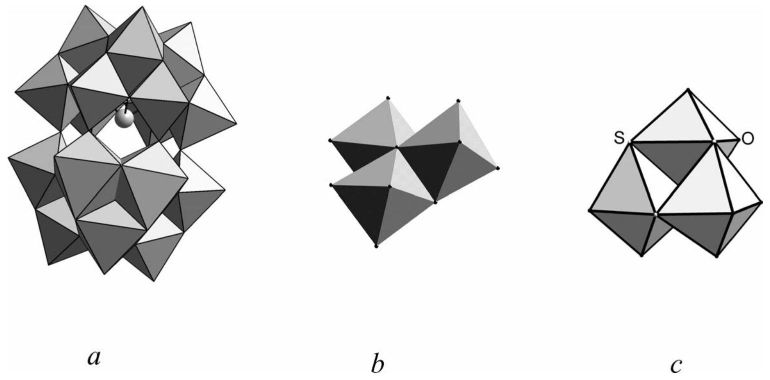
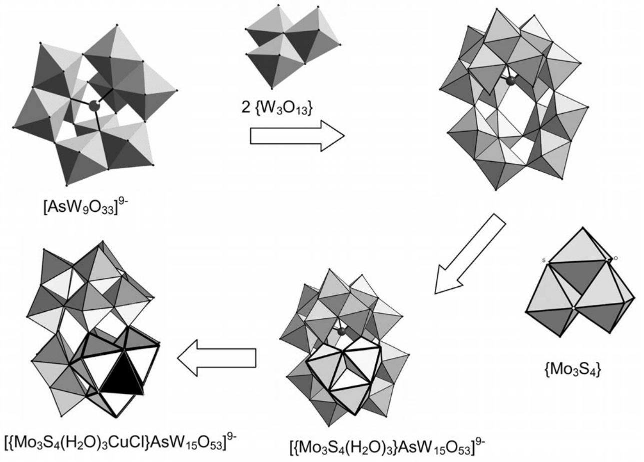
[a] Nikolayev Institute of Inorganic Chemistry SB RAS,
Prospekt Lavrentyeva 3, 630090 Novosibirsk,
Russian Federation
[b] Novosibirsk State University,
ul. Pirogova 2, 630090 Novosibirsk, Russian Federation



Scheme 1. Structural relationship between a Dawson-type structure (a) and the $\{W_3O_{13}\}^{8-}$ (b) and $[Mo_3S_4(H_2O)_9]^{4+}$ (c) building blocks.

tural unit $\{W_3O_4\}^{10+}$ in the $\{AsW_{18}O_{60}\}$ core in the Dawson-type structures is replaced by topologically similar chalcogenide cluster fragments $\{Mo_3S_4\}^{4+}$ or $\{Mo_3S_2O_2\}^{4+}$ with Mo–Mo bonds.[4] In this work we report new examples of such structures for E = Sb^{III} and Te^{IV} as well as the first successful replacement of the $\{W_3O_4\}$ unit by the cuboidal moiety $\{Mo_3CuS_4\}$ (Scheme 2).



Scheme 2. Step-by-step assembly of the anion of **6**.

Results and Discussion

Chalcogen-bridged cluster aqua complexes such as $[Mo_2O_2S_2(H_2O)_6]^{2+}$ and $[Mo_3S_4(H_2O)_9]^{4+}$ have aqua ligands easily exchangeable for highly nucleophilic oxygen atoms of lacunary POMs. A combination of chalcogenide clusters and polyoxometalates has been used for the design of polyoxothiometalate derivatives, inaccessible by direct sulfidation of polyoxometalates. Reactions between $[Mo_3S_4(H_2O)_9]^{4+}$ and monovacant $[SiW_{11}O_{39}]^{8-}$ or $[P_2W_{17}O_{61}]^{10-}$, divacant γ-$[SiW_{10}O_{36}]^{8-}$, and polyvacant $[AsW_9O_{33}]^{9-}$have been reported.[6–8] In the latter case, a 21-nuclear hybrid complex $[(H_4AsW_9O_{33})_2\{Mo_3S_4(H_2O)_5\}]^{6-}$ was obtained.[6] It has a sandwich-type structure with two protonated $[AsW_9O_{33}]^{9-}$ ligands bound to the $\{Mo_3S_4\}$ cluster core in a bidentate fashion. We found that this "sandwich" structure is not stable under hydrothermal conditions and rearranges into $[\{Mo_3S_4(H_2O)_3\}AsW_{15}O_{53}]^{9-}$ (**1**), the structure of which is a Dawson-type structure.[4] The direct hydrothermal reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with $[AsW_9O_{33}]^{9-}$ in a 1:1.5 molar ratio also led to $[\{Mo_3S_4(H_2O)_3\}AsW_{15}O_{53}]^{9-}$. The reaction clearly involves partial decomposition of some of the $[AsW_9O_{33}]^{9-}$ to furnish the tungstate necessary to achieve the As/W = 1:15 stoichiometry required in the final product. Attempts to streamline the reaction pathway by reacting $[Mo_3S_4(H_2O)_9]^{4+}$ and $[AsW_9O_{33}]^{9-}$ in a 1:1 molar ratio in the presence of another 6 equiv. of Na_2WO_4 only led to the formation of side-products, mainly $[H_2AsW_{18}O_{60}]^{7-}$.[5a] The Sb analogue, $[\{Mo_3S_4(H_2O)_3\}SbW_{15}O_{53}]^{9-}$ (**2**), was similarly obtained from $[Mo_3S_4(H_2O)_9]^{4+}$ and $[SbW_9O_{33}]^{9-}$ (Figure 1). Moreover, $[TeW_9O_{33}]^{8-}$, generated in situ from TeO_3^{2-} and WO_4^{2-},[9,10] gave the expected Te analogues, $[\{Mo_3S_4(H_2O)_3\}TeW_{15}O_{53}]^{8-}$ (**3**; Figure 2, a) and $[\{Mo_3S_4(H_2O)_2Cl\}TeW_{15}O_{53}]^{9-}$ (**4**; Figure 2, b). Our attempts to include in this family the derivatives of Sn^{II} and Se^{IV} have so far remained unsuccessful. In the reactions involving $[Mo_3S_4(H_2O)_9]^{4+}$ and in situ generated $[SnW_9O_{33}]^{10-}$ or $[SeW_9O_{33}]^{8-}$,[9] only simple Dawson-type polyoxometalates, $[H_2SnW_{18}O_{60}]^{8-}$ and $[H_3SeW_{18}O_{60}]^{5-}$, were detected. On the other hand, a mixed oxido–sulfido cluster core $\{Mo_3O_2S_2\}^{4+}$ could also be incorporated by the reaction of the aqua complex $[Mo_3O_2S_2(H_2O)_9]^{4+}$ with $[AsW_9O_{33}]^{9-}$ in a 1:2 molar ratio to give $[\{Mo_3S_2O_2(H_2O)_3\}AsW_{15}O_{53}]^{9-}$ (**5**). Even more important is the fact that the three μ_2-sulfur atoms of the $\{Mo_3S_4\}$ cluster unit incorporated into the Dawson-type framework retain their ability to coordinate a low-valent, chalcophilic metal ion to form the cuboidal units $\{Mo_3M'S_4\}$.[11] In this way we were able to isolate a unique hybrid cluster–POM complex, $[\{Mo_3S_4(H_2O)_3CuCl\}AsW_{15}O_{53}]^{9-}$ (**6**; Figure 3), from the hydrothermal reaction of $[(\{H_4AsW_9O_{33}\}_2\{Mo_3S_4(H_2O)_5\})_2]^{12-}$ with CuI (in the presence of excess Cl^-). Because the $\{Mo_3S_4\}$ cluster functionality is known to incorporate more than 20 transition and post-transition metals to give heterometal cuboidal clusters with remarkable catalytic properties,[12] the preparation of **6** provides a new way to make water-soluble, hydrolytically stable catalysts based upon chalcogenide clusters.

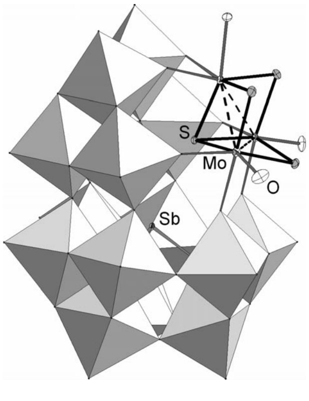


Figure 1. The structure of anion $[\{Mo_3S_4(H_2O)_3\}SbW_{15}O_{53}]^{9-}$ (**2**) in polyhedral view. The cluster fragment $\{Mo_3S_4(H_2O)_3\}$ and the Sb atom are shown as ellipsoids at the 50% probability level. Dashed lines show the Mo–Mo bond in the cluster core.

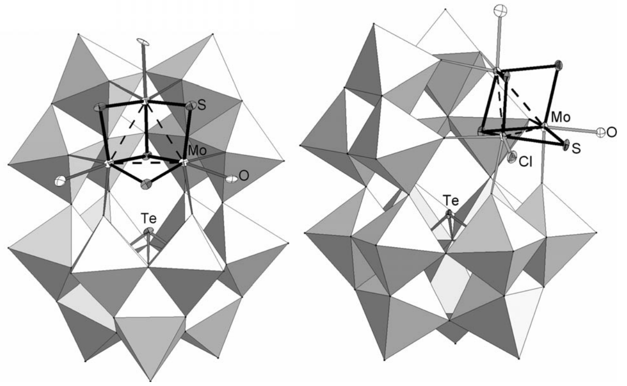


Figure 2. The structures of the Te-containing Dawson-like anions $[\{Mo_3S_4(H_2O)_2Y\}TeW_{15}O_{53}]^{9-}$ [X = H_2O (**3**) and Cl (**4**)] in polyhedral view. Cluster fragments $\{Mo_3S_4(H_2O)_3\}$ (a) and $\{Mo_3S_4(H_2O)_2Cl\}$ (b) and the Te atoms are shown as ellipsoids at the 50% probability level. Dashed lines show the Mo–Mo bond in the cluster core.

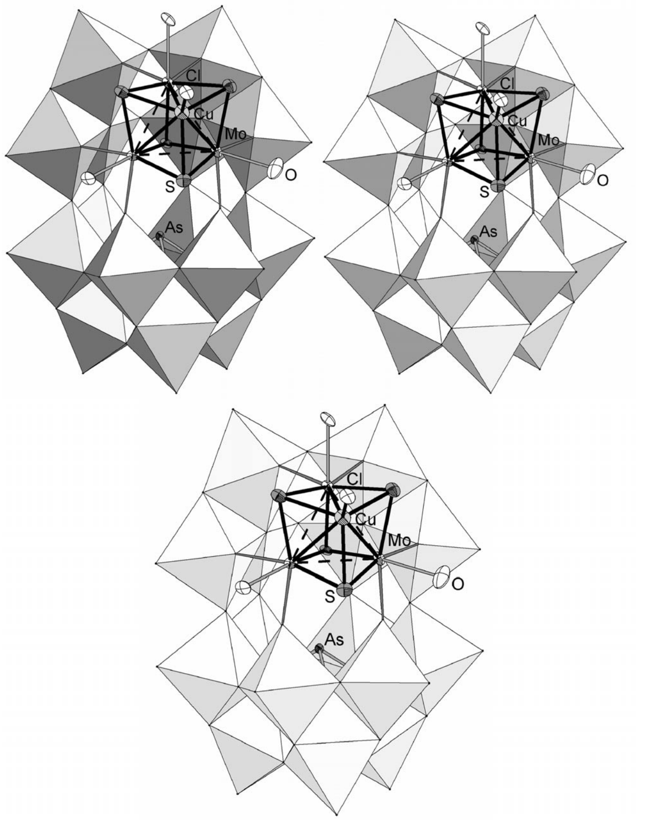


Figure 3. The structure of anion $[\{Mo_3S_4(H_2O)_3CuCl\}AsW_{15}O_{53}]^{9-}$ (**6**) in polyhedral view. Cluster fragment $\{Mo_3S_4(H_2O)_3CuCl\}$ is shown as ellipsoids at the 50% probability level. Dashed lines show the Mo–Mo bond in the cluster core.

The structures of $[EW_{15}Mo_3S_4(H_2O)_3O_{53}]^{9-}$ (E = As, Sb) in **1** and **2** and of $[TeW_{15}Mo_3S_4(H_2O)_3O_{53}]^{8-}$ in **3** can be described as being derived from the $[EW_{18}O_{60}]^{9-}$ and $[TeW_{18}O_{60}]^{8-}$ prototypes, respectively, by replacement of one of the six $\{W_3O_{13}\}$ units by a topologically equivalent $\{Mo_3S_4O_7(H_2O)_3\}$ unit in the hemisphere devoid of the heterometal in such a way that one of the polar belts of the resulting Dawson-type structure will have one Mo atom, with the two other Mo atoms belonging in the equatorial belt.[4] The three μ_2-S bridges of the cluster core occupy the positions of the three μ_2-O bridges of the parent "all-oxygen, all-tungsten" structure, and the position of the capping μ_3-S matches the position occupied by one of the μ_3-O atoms in the parent structure. In $[AsW_{15}Mo_3O_2S_2(H_2O)_3O_{53}]^{9-}$ (**5**), of the two possible orientations of the incorporated $Mo_3S_2O_2{}^{4+}$ core, only one is observed in the solid state, that with the μ_2-S between the Mo atoms in the equatorial belt. As in $[H_2AsW_{18}O_{60}]^{7-}$ and its analogues,[5a] both hemispheres in $[EW_{15}Mo_3S_4(H_2O)_3O_{53}]^{9-}$ (E = As, Sb) and $[TeW_{15}Mo_3S_4(H_2O)_3O_{53}]^{8-}$ are of B-type, as defined by the way the octahedral units (15 $\{WO_6\}$ and three $\{MoO_3S_3\}$) are joined together. One important difference is, however, that the Mo atoms in **1**–**6** are in the oxidation state IV, not VI, and the three Mo–Mo bonds (Mo–Mo distance is around 2.7 Å) are present in the Mo_3 subunit. The M–M bonding is not delocalized over the rest of the POM structure: the closest Mo···W distances are as long as 3.8 Å. Incorporation of the cluster does not bring about significant changes in the lengths of the M–M bonds in **1**–**6** as compared with other known complexes with $\{Mo_3S_4\}^{4+}$, $\{Mo_3O_2S_2\}^{4+}$, and $\{Mo_3CuS_4\}^{5+}$ cores. In **6**, the Cu–S and Cu–Cl bond lengths also show no unusual features when compared with those observed in $[Mo_3(CuCl)S_4(Hnta)_3]^{2-}$ (H_3nta is nitrilotriacetic acid).[13]

Nevertheless, incorporation of the cluster units does bring strain upon the POM framework. This can be seen by comparison of the distances between the heterometal (E = As, Sb, and Te) and the μ_3-S atom of the cluster. These are, respectively, 3.65, 3.45, and 3.42 Å. In **5**, the As···S contact is even shorter than in **1**, 3.45 Å (see Tables 1 and 2). The sums of the van der Waals radii are 3.65 (As + S), 3.80 (Sb + S), and 3.86 Å (Te + S).[14] To ease this strain, two of the Mo–μ_3–S bonds, which are usually quite indifferent to the environment around Mo in the $\{Mo_3S_4\}^{4+}$ clusters, are shortened to 2.27 Å from their usual value of around 2.33–

2.34 Å.[12,15] The Mo–μ_3–S–Mo angles of 73–75° in **1**–**4** are somewhat flattened, apparently for the same reason, as compared with 71–72° in the aqua complex $[Mo_3S_4(H_2O)_9](CH_3C_6H_4SO_3)_4 \cdot 9H_2O$.[16] Shorter As–O distances {1.79(1)–1.82(2) Å vs. 1.82(2)–1.90(2) in $[H_2AsW_{18}O_{60}]^{7-}$} show that the As atom is also pushed away from S. The Sb–O and Te–O bond lengths, in contrast, are rather close to those found for the EO_3 groups in other POM structures.[10]

The mutual arrangement of the POM anions in the crystals of **1**–**4** is dictated by S···S contacts through the outward-looking μ_2-S atoms between each pair of anions in such a way that centrosymmetric dimers result, which are also routinely observed in the structures of clusters with $\{M_3Q_4\}^{4+}$ (M = Mo, W; Q = S, Se) cores.[17] However, the geometries and lengths of these nonvalent contacts differ. In **1** and **2**, two anions $[EW_{15}Mo_3S_4(H_2O)_3O_{53}]^{9-}$ (E = As, Sb) are weakly associated through four μ_2-S···μ_2-S contacts (3.36–3.49 Å, Table 1) with a distorted antiprismatic arrangement of the μ_2-S atoms (Figure 4). Pairs of $[TeW_{15}Mo_3S_4(H_2O)_3O_{53}]^{8-}$ ions in **3** are held together by five S···S contacts of 3.39–3.68 Å, and this additional contact accounts for a more regular antiprismatic arrangement of the contacting sulfur atoms (Figure 5). An interesting and unexpected trend is that upon going from E = As (**1**) and Sb (**2**) to Te (**3**) the μ_2-S···μ_2-S contacts shorten with an increase in the radius of E.

The five S···S contacts in **4** (the same as observed in **3**) are further supported by two van der Waals Cl···S contact distances of 3.70 Å and by two Cl···O(H_2O) hydrogen bonds of 3.19 Å (Figure 6). The packing of the POM ions in **5** does not involve any pairing through μ_2-S···μ_2-S interactions and the μ_2-S positions are blocked by the CuCl moiety in **6**. The specific nature of the E atom might be again one of the reasons for the lack of interaction in **5**, because in **1** (E = As) the S···S contacts are longer than in compounds with a heavier E (Sb, Te). However, the packing motifs of the highly charged anions in the crystal are almost unaffected by the presence of these interactions. In **1**, **3**, **5**, and **6** the packing of the POM anions follows a slightly distorted motif of the face-centered cubic lattice (Figure 7, Table 3). In **2** and **4** the arrangement of the anions deviates from close-packing, but it is still one of the most frequent lattice types found for organic molecular crystals.[18] Strictly speaking, this arrangement of the POM anions does not constitute a packing arrangement because some anions are involved in direct van der Waals contacts, whereas others are separated by disordered cations and solvent water molecules (Table 3). However, the cations and solvent water molecules adapt to the anionic arrangement, which is likely to be intrinsic and not cation-dictated for such large structural fragments.[19]

Table 1. Selected bond lengths [Å] and angles [°] in **1**–**3**.

	1 (X = As)	**2** (X = Sb)	**3** (X = Te)
Mo–Mo	2.732(3)–2.764(3)	2.7346(11)–2.7580(11)	2.7365(17)–2.7682(18)
Mo–S	2.313(6)–2.305(6)	2.274(2)–2.308(2)	2.280(4)–2.322(4)
Mo–O_{H_2O}	2.204(15)–2.220(15)	2.199(7)–2.229(7)	2.190(11)–2.203(10)
Mo–μ_2-O_W	2.097(14)–2.185(16)	2.106(6)–2.125(6)	2.086(10)–2.181(10)
Mo–O	–	–	–
Mo–Cu	–	–	–
Mo–Cl	–	–	–
Cu–S	–	–	–
Cu–Cl	–	–	–
W–μ_2-O_{Mo}	1.756(14)–1.795(15)	1.782(7)–1.796(7)	1.776(10)–1.819(10)
W–μ_2-O_W	1.842(15)–2.168(15)	2.121(7)–1.836(7)	1.834(10)–2.172(9)
W–μ_3-O	2.090(15)–2.240(14)	2.070(6)–2.271(6)	2.114(11)–2.290(10)
W–μ_4-O	2.308(13)–2.417(14)	2.243(6)–2.450(6)	2.303(10)–2.446(10)
W–O_{term}	1.710(15)–1.747(16)	1.712(7)–1.735(7)	1.695(11)–1.743(10)
E–O	1.786(14)–1.808(14)	1.981(6)–1.984(6)	1.886(11)–1.906(10)
E···μ_3-S	3.649(7)	3.453(2)	3.445(4)
S···S	3.415(9) × 2	3.357(4) × 2	3.391(5) × 2
	3.490(9) × 2	3.435(4) × 2	3.403(6) × 2
			3.675(5)
S···Cl	–	–	–
Cl···O_{H_2O}	–	–	–
Mo–μ_3-S–Mo	72.91(18)–74.88(18)	73.19(7)–74.57(7)	72.98(11)–74.77(11)
W–μ_4-O–W	90.6(5)–92.0(5)	91.9(2)–94.8(2)	91.0(3)–93.1(4)
W–μ_3-O–W	94.8(5)–108.0(7)	95.2(2)–107.5(3)	94.0(4)–107.4(4)
W–μ_2-O–W	106.1(6)–122.2(8)	109.3(3)–120.5(3)	107.6(4)–127.9(6)
	141.9(8)–156.6(9)	139.6(4)–154.5(4)	138.6(6)–157.3(6)
W–μ_4-O–X	117.4(7)–119.4(7)	113.9(3)–117.8(3)	115.4(4)–116.7(5)
	132.5(7)–135.8(7)	134.9(3)–138.2(3)	139.0(5)–139.6(5)
W–μ_3-O–X	–	–	121.6(5), 122.0(5)
W–μ_2-O–Mo	146.7(8)–156.1(8)	148.1(4)–157.5(4)	147.8(5)–156.9(6)
O–X–O	95.3(6)–97.4(7)	89.9(3)–92.4(3)	90.2(4)–93.6(4)
Reference	[4]	this work	this work

Table 2. Selected bond lengths [Å] and angles [°] in **4**–**6**.

	4 (X = Te)	**5** (X = As)	**6** (X = As)
Mo–Mo	2.744(3)–2.770(3)	2.637(4)–2.743(4)	2.781(2)–2.805(2)
Mo–S	2.279(6)–2.331(7)	2.284(8)–2.357(8)	2.276(5)–2.366(5)
Mo–O_{H_2O}	2.207(18)–2.23(2)	2.19(3)–2.24(3)	2.170(12)–2.189(16)
Mo–μ_2-O_W	2.095(17)–2.200(17)	2.09(2)–2.17(2)	2.065(11)–2.148(12)
Mo–O	–	1.92(2)–2.09(2)	–
Mo–Cu	–	–	2.828(3)–2.853(3)
Mo–Cl	2.532(7)	–	–
Cu–S	–	–	2.294(5)–2.303(6)
Cu–Cl	–	–	2.300(5)
W–μ_2-O_{Mo}	1.772(17)–1.800(19)	1.77(2)–1.81(2)	1.785(12)–1.825(12)
W–μ_2-O_W	1.842(18)–2.159(16)	1.77(2)–2.15(2)	1.848(13)–2.109(13)
W–μ_3-O	2.112(17)–2.313(16)	2.07(2)–2.27(2)	2.107(11)–2.294(11)
W–μ_4-O	2.293(17)–2.497(17)	2.28(2)–2.49(2)	2.309(12)–2.399(10)
W–O_{term}	1.669(19)–1.756(17)	1.70(2)–1.88(2)	1.683(11)–1.741(11)
E–O	1.872(17)–1.885(17)	1.77(2)–1.81(2)	1.787(11)–1.811(11)
E···μ_3-S	3.422(5)	3.466(8)	3.656(4)
S···S	2.954(8)	–	–
	3.320(9) × 2		
	3.588(7) × 2		
S···Cl	3.695(9) × 2	–	–
Cl···O_{H_2O}	3.19(2)	–	–
Mo–μ_3-S–Mo	72.6(2)–74.47(19)	69.1(2)–73.7(3)	73.95(13)–75.78(15)
W–μ_4-O –W	89.5(5)–92.9(6)	88.5(7)–92.1(8)	89.9(4)–92.8(4)
W–μ_3-O –W	94.5(7)–107.8(7)	95.6(8)–107.0(10)	93.1(4)–106.6(5)
W–μ_2-O –W	109.1(7)–128.5(9)	140.8(12)–156.7(12)	109.4(6)–121.3(6)
	138.1(9)–155.7(10)	105.6(10)–125.2(13)	140.0(6)–154.1(6)
W–μ_4-O–X	114.0(8)–118.3(8)	118.0(12)–121.3(11)	118.0(6)–119.3(5)
	139.1(8)–141.0(9)	130.8(11)–135.1(11)	132.4(5)–136.2(6)
W–μ_3-O–X	122.7(8)–123.5(8)	–	–
W–μ_2-O–Mo	148.6(10)–159.0(10)	144.8(13)–159.5(13)	144.9(6)–156.5(7)
O–X–O	90.4(7)–93.6(7)	96.4(11)–98.9(11)	95.6(5)–97.7(5)
Reference	this work	[4]	this work

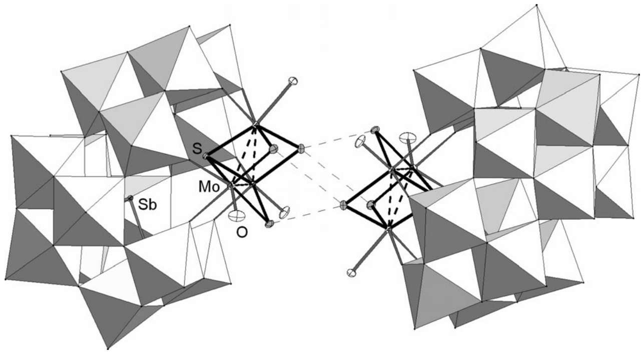


Figure 4. Dimer $[\{Mo_3S_4(H_2O)_3\}SbW_{15}O_{53}]_2^{18-}$ of **2** based on four specific nonvalent S···S contacts of 3.36–3.43 Å (thin dashed lines).

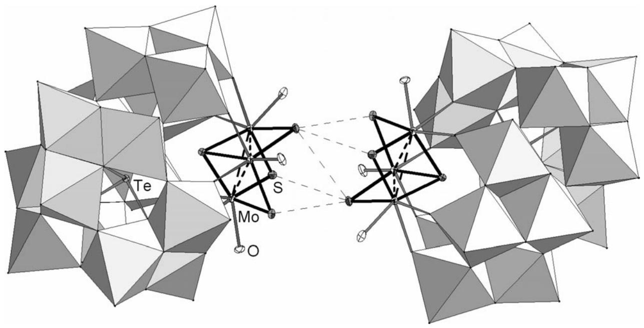


Figure 5. Dimer $[\{Mo_3S_4(H_2O)_3\}TeW_{15}O_{53}]_2^{16-}$ of **3** based on five specific nonvalent S···S contacts of 3.39–3.68 Å (dashed thin lines).

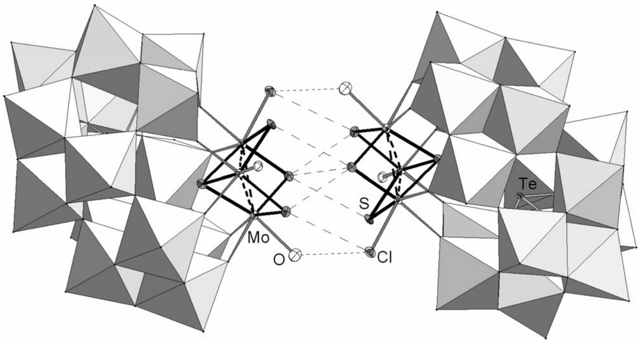


Figure 6. Dimer $[\{Mo_3S_4(H_2O)_2Cl\}TeW_{15}O_{53}]_2^{18-}$ of **4** based on five specific nonvalent S···S contacts of 3.36–3.43 Å and supported by two van der Waals Cl···S contacts of 3.70 Å (dashed thin lines) and two Cl···O(H_2O) hydrogen bonds (dotted thin lines) of 3.19 Å.

The packing of the S···S-held POM dimers themselves is always more distorted and hence plays a less important structure-forming role.[20] The presence of only one $\{M_3S_4\}$ fragment per POM precludes any further aggregation through specific S···S contacts. Thus, specific nonvalent interactions are strong enough to locally dictate the mutual orientation of the anions in the crystal structure, but not the motif of their global arrangement.

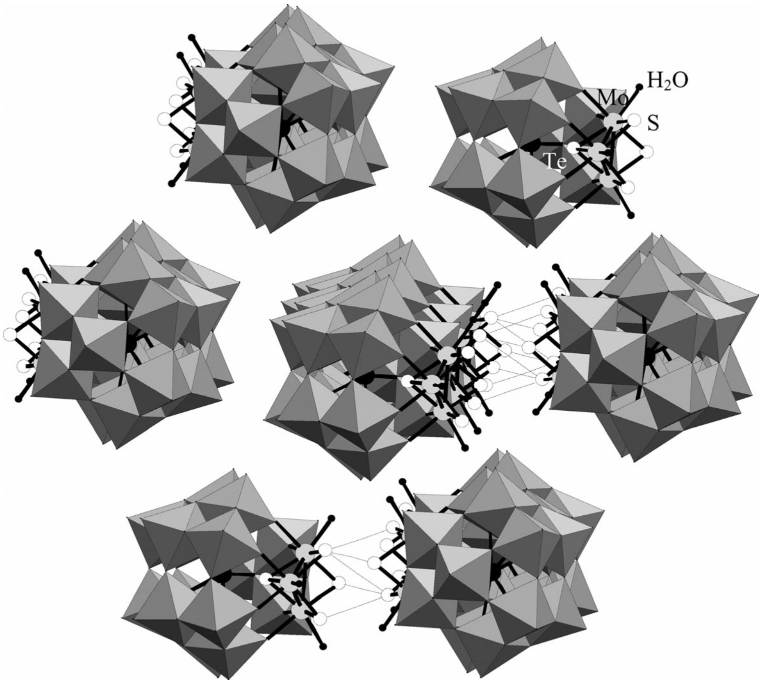


Figure 7. The fragment of the three-layered face-centered cubic motif of $[\{Mo_3S_4(H_2O)_3\}TeW_{15}O_{53}]^{9-}$ anions (WO_6 octahedrons are shown in the polyhedral representation) of **3**. Thin lines denote specific nonvalent S···S interactions linking some of the anions.

Table 3. Packing of the anions (An) in the crystals of **1**–**6**.[a]

		Isolated anions						Isolated anionic dimers		
	E	Packing Coordination sequence	Symbol of An packing motif	Uniformity	Net of direct An···An contacts Symbol of the An net motif	Dimensionality	Number of anions in the 1st coordination sphere	Packing Coordination sequence	Symbol of packing motif	Uniformity
1	As	12, 42, 92	*fcc*	0.0818	**sql**	2D	4	10, 34, 74	–[14]	0.0877
2	Sb	13, 42, 103	–[14]	0.0804	**ncj**	3D	9	12, 42, 92	*fcc*	0.0886
3	Te	12, 42, 92	*fcc*	0.0796	**svk**	3D	7	8, 26, 56	*hex*	0.0902
4	Te	13, 42, 103	–[14]	0.0799	**nci**	3D	9	12, 42, 92	*fcc*	0.1073
5	As	12, 42, 92	*fcc*	0.0818	–	3D	9	–	–	–
6	As	12, 42, 92	*fcc*	0.0806	**bct**	3D	10	–	–	–

[a] In molecular packing the coordination sequence $\{N_k\}$, $k = 1, 2, 3\ldots$, is the set of integers corresponding to the number of molecules in the first, second, and more distant coordination spheres up to the desired k.[26] fcc = face-centered cubic, hex = hexagonal primitive, sql = Shubnikov tetragonal plane net. The three-letter symbols of the nets are given according to the RCSR notation.[27] The packing modes and nets of the centroids are italicized and bold-faced, respectively. The uniformity criterion (G_3) serves to estimate the degree of distortion of the lattices. The lower the G_3 value the higher is the uniformity of the lattice. The minimum G_3 value known for 3D periodic nets is for ideal *bcc* packing (0.07854). Ideal *fcc* and *hcp* packings have G_3 = 0.07875.[28]

Conclusions

These results demonstrate that there is a real possibility of replacing the standard $\{W_3O_4\}^{10+}$ building block in classic polyoxometalate ions with topologically similar units not necessarily based upon tungsten and oxygen. In this way, new features such as metal–metal bonding, chalcogen atoms, and heterometals can be introduced and the traditional reactivity of POMs can be altered. For example, the replacement of three μ_2-S atoms for μ_2-O makes it possible for modified POMs to coordinate non-oxophilic metal centers such as Cu^+. This may open up new ways to design new catalytic systems based upon POMs and non-oxophilic noble metals in low oxidation states.

Experimental Section

General Procedures and Materials: The hydrothermal syntheses were performed in evacuated flame-sealed thick-walled glass tubes. Stock solutions of the starting aqua complexes $[Mo_3S_4(H_2O)_9]^{4+}$[21] and $[Mo_3S_2O_2(H_2O)_9]^{4+}$[22] were prepared according to published procedures. The solutions in 2 M HCl were rotaevaporated to dryness to give solid chloride salts of the aqua complexes immediately before use. Polyoxometalate complexes $K_9[AsW_9O_{33}]\cdot 19H_2O$,[23] $Na_9[SbW_9O_{33}]\cdot 19.5H_2O$[15] and $K_3(NH_4)_9[(\{H_4AsW_9O_{33}\}_2\text{-}\{Mo_3S_4(H_2O)_5\})_2]\cdot 48H_2O$[6] were prepared as described in the literature. Other reagents were of commercial quality and used as purchased.

$Cs_{6.5}K(NH_4)_{1.5}[\{Mo_3S_4(H_2O)_3\}AsW_{15}O_{53}]\cdot 14H_2O$ (1): A mixture of $K_9[AsW_9O_{33}]\cdot 19H_2O$ (1.73 g, 0.61 mmol), $[Mo_3S_4(H_2O)_9]Cl_4$ (0.31 g, 0.43 mmol), CsCl (0.57 g, 3.39 mmol), NH_4Cl (0.10 g, 1.90 mmol), and H_2O (2.5 mL) was placed in a glass tube and the pH was adjusted to 2.5 by adding drops of 1 M HCl. The tube was flame-sealed under vacuum and heated at 140 °C for 2 d. After slow cooling to room temperature and opening of the tube, brown single crystals of the product were separated by decantation from amorphous material, washed successively with a 1:1 water/ethanol mixture, ethanol, and diethyl ether, and dried in air; yield 1.97 g, 87%. IR (KBr): $\tilde{\nu}$ = 3411, 1616, 953, 844, 802, 766, 658, 476, 449 cm^{-1}. $H_{40}AsCs_{6.50}KMo_3N_{1.50}O_{70}S_4W_{15}$ (5333.00): calcd. S 2.4, K 0.7, As 1.4, Mo 5.5, Cs 16.4, W 52.2; found S 3.0, K 0.3, As 1.3, Mo 4.6, Cs 15.6, W 52.6.

$Cs_{5.85}Na_{3.15}[\{Mo_3S_4(H_2O)_3\}SbW_{15}O_{53}]\cdot 14.85H_2O$ (2): $[Mo_3S_4(H_2O)_9]Cl_4$ (0.12 g, 18.5 mmol) was added to a solution of $Na_9[SbW_9O_{33}]\cdot 19.5H_2O$ (0.8 g, 31.5 mmol) in water (30 mL) and the pH was immediately adjusted to 2.5 with 0.2 M HCl. Then the mixture was transferred into a glass tube charged with CsCl (0.05 g, 29.7 mmol). After evacuation the tube was sealed and kept at 130 °C for 2 d. After cooling a dark solution was left in the tube at room temperature. After 4 weeks, dark-brown crystals of **2** separated and were removed by decantation; yield 0.20 g (20%). IR: $\tilde{\nu}$ = 3464 (br), 1632 (s), 1485 (w), 1402 (m), 1239 (w), 1194 (w), 993 (sh), 949 (m), 894 (s), 768 (m), 749 (w), 514 (m, br) cm^{-1}. The composition and structure of the crystalline product was established by X-ray analysis.

$Cs_6Na_2[\{Mo_3S_4(H_2O)_3\}TeW_{15}O_{53}]\cdot 11.7H_2O$ (3): TeO_2 (0.133 g, 84 mmol) was dissolved in 1 M NaOH (5 mL). A solution of $Na_2WO_4\cdot 2H_2O$ (2.394 g, 7.26 mmol) in water (15 mL) was added to this solution whilst stirring and the pH was adjusted to 2.5 with 0.2 M HCl. $[Mo_3S_4(H_2O)_9]Cl_4$ (0.27 g, 42 mmol) was added to the resulting solution. The mixture was transferred into a glass tube followed by the addition of CsCl (0.05 g, 29.7 mmol). After evacuation the tube was sealed and kept at 120 °C for 2 d. After cooling a dark solution was left in the tube at room temperature. After 4 weeks, dark-brown crystals of **3** separated together with a brown amorphous powder; yield 0.22 g (10%). IR: $\tilde{\nu}$ = 3423 (br), 1742 (w), 1612 (s), 1082 (w), 968 (m), 787 (m), 753 (w), 500 (w) cm^{-1}. The composition and structure of the crystalline product were established by X-ray analysis.

$Cs_{7.15}Na_{1.85}[\{Mo_3S_4(H_2O)_2Cl\}TeW_{15}O_{53}]\cdot 11.2H_2O$ (4): The preparation was carried as described above with the exception that the amount of $Na_2WO_4\cdot 2H_2O$ (6.75 g, 20.4 mmol) was increased twofold; yield 0.18 g (7%). IR: $\tilde{\nu}$ = 3411 (br), 1616 (s), 971 (m), 886 (sh), 815 (m), 718 (w), 638 (w), 495 (w) cm^{-1}.

Table 4. Crystal data, data collection, and structure refinement parameters for **2**–**4** and **6**.

	2	**3**	**4**	**6**
Empirical formula	$H_{35.70}Cs_{5.85}Mo_3Na_{3.15}$-$O_{70.85}S_4SbW_{15}$	$H_{29.40}Cs_6Mo_3Na_2$-$O_{67.7}S_4TeW_{15}$	$H_{26.40}ClCs_{7.15}Mo_3Na_{1.85}$-$O_{66.20}S_4TeW_{15}$	$H_{38.13}AsClCs_{5.25}CuK_{1.75}$-$Mo_3N_2O_{68.07}S_4W_{15}$
M_r	5315.09	5257.69	5394.83	5269.46
Crystal system	triclinic	triclinic	triclinic	monoclinic
Space group	$\bar{P}$	$\bar{P}$	$\bar{P}$	$P2_1/c$
a [Å]	13.1520(3)	13.1317(3)	12.5031(5)	15.4480(7)
b [Å]	15.6694(3)	13.9622(3)	13.0244(5)	14.0361(5)
c [Å]	20.8427(5)	20.4728(5)	25.9327(11)	35.3841(17)
α [°]	92.1490(10)	87.2250(10)	81.688(2)	90
β [°]	98.2390(10)	88.5780(10)	79.962(2)	96.837(2)
γ [°]	112.3640(10)	81.9470(10)	63.9840(10)	90
V [Å^3]	3911.35(15)	3711.65(15)	3725.9(3)	7617.8(6)
Z	2	2	2	4
$D_{calcd.}$ [g/cm^3]	4.513	4.704	4.827	4.595
μ [mm^{-1}]	25.667	27.137	27.620	26.541
$2\theta_{max}$ [°]	64.7	62.5	55.0	55.0
Temperature [K]	100.0(2)	100.0(2)	90.0(2)	91.0(2)
Crystal size [mm]	0.38 × 0.25 × 0.12	0.087 × 0.075 × 0.012	0.17 × 0. 04 × 0.02	0.26 × 0.24 × 0.03
Range of h,k,l	$-18 \le h \le 17$, $-23 \le k \le 15$, $-27 \le l \le 28$	$-17 \le h \le 18$, $-13 \le k \le 120$, $-29 \le l \le 28$	$-16 \le h \le 11$, $-16 \le k \le 16$, $-33 \le l \le 32$	$-20 \le h \le 19$, $-17 \le k \le 18$, $-45 \le l \le 45$
Reflections measured	48977	40941	41909	99020
Unique reflections	21193	19360	16738	17481
R_{int}	0.0302	0.0581	0.0472	0.0703
Observed [$I > 2\sigma(I)$]	17850	14456	12702	14618
Refined parameters	998	956	956	974
Restraints	0	78	438	84
R_1, wR_2 [$I > 2\sigma(I)$]	R_1 = 0.0362 wR_2 = 0.0824	R_1 = 0.0513 wR_2 = 0.1394	R_1 = 0.0661 wR_2 = 0.1489	R_1 = 0.0591 wR_2 = 0.1452
R_1, wR_2 (all data)	R_1 = 0.0469 wR_2 = 0.0866	R_1 = 0.0762 wR_2 = 0.1555	R_1 = 0.0931 wR_2 = 0.1615	R_1 = 0.0733 wR_2 = 0.1530
Goodness-of-fit on F^2	1.022	1.031	1.128	1.095
Largest diff. peak, hole [e/Å^3]	5.407/–3.954	4.692/–4.323	8.965/–4.783	5.814/–4.588

$Cs_6(H_3O)_3[AsW_{15}Mo_3O_2S_2(H_2O)_3O_{53}]\cdot 9.85H_2O$ (5): CsCl (0.03 g, 0.18 mmol) was added to a glass tube filled with a solution of $Na_9[AsW_9O_{33}]\cdot 13H_2O$ (0.08 g, 0.027 mmol) and $[Mo_3S_2O_2(H_2O)_9]Cl_4$ (0.01 g, 0.015 mmol) in H_2O (5 mL, pH adjusted to 2.7). The tube was evacuated, sealed, and heated at 140 °C for 2 d. Dark-gray single crystals of **5** were isolated after slow cooling to room temperature. They were separated manually from a large amount of amorphous material. IR (KBr): $\tilde{\nu}$ = 3411, 1624, 953, 884, 789, 766, 738, 641, 478 cm^{-1}. $H_{34.70}AsCs_6Mo_3O_{70.85}S_2W_{15}$ (5150.58): calcd. As 1.5, Mo 5.6, Cs 15.5, W 53.5; found As 1.4, Mo 5.7, Cs 15.1, W 53.4.

$Cs_{5.25}K_{1.75}(NH_4)_2[\{Mo_3S_4(H_2O)_3CuCl\}AsW_{15}O_{53}]\cdot 12.07H_2O$ (6): $K_3(NH_4)_9[(\{H_4AsW_9O_{33}\}_2\{Mo_3S_4(H_2O)_5\})_2]\cdot 48H_2O$[6] (0.3 g, 57 µmol) was dissolved in water (35 mL), and the pH was adjusted with 0.2 M HCl to 2.5. The solution was transferred to a glass tube containing CsCl (0.05 g, 0.30 mmol) and CuI (0.01 g, 57 µmol). After evacuation the tube was sealed and kept at 120 °C for 2 d. After cooling a dark solution was left in the tube at room temperature. After 4 weeks, dark-brown crystals of **6** separated; yield 0.03 g (10%). IR: 3387 (br), 1727 (w), 1606 (s), 957 (m), 786 (s), 482 (s) cm^{-1}. The composition and structure of the crystalline product were established by X-ray analysis.

X-ray Crystallography: Crystallographic data and details of structure refinement are given in Table 4. All diffraction data were collected with a Bruker X8Apex CCD diffractometer with Mo-K_α radiation (λ = 0.71073 Å) by performing ϕ and ω scans of narrow (0.5°) frames at 90–100 K. The crystal structures of **2**–**4** and **6** were solved by direct methods and refined by full-matrix least-squares treatment against $|F^2|$ in an anisotropic approximation with SHELXTL.[24] Absorption corrections were applied empirically by using the SADABS program.[25] All non-hydrogen atoms were refined anisotropically, except for the light atoms, the occupancy factors of which were lower than 0.5. Some restraints mainly concerning the atomic displacement parameter (a.d.p.) refinement had to be applied for oxygen atoms of the POMs because of nonpositive values arising from the difficulties in applying absorption corrections properly. Hydrogen atoms of both coordinated and disordered solvent water molecules were not located from electron density maps. The cationic compositions were deduced mainly from analysis of the distances between the cations and their oxygen environment. For each cation and for the oxygen atoms of solvate water molecules s.o.f. refinement was applied with constrained a.d.p. parameters, and the a.d.p. parameters were then refined with s.o.f. fixed to the refined magnitude.

Bond lengths and angles are summarized in Tables 1 and 2. The anion packing motif and specific contacts were analyzed with the TOPOS 4.0 Professional program suite for crystal chemical analysis (Table 3).[26]

Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-421719 to -421722 (for **2**–**4** and **6**, respectively).

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