Supramolecular Chemistry Based on $[W_3S_4(H_2O)_6Cl_3]^+$ − A Versatile Building Block

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The cluster $[W_3S_4(H_2O)_6Cl_3]^+$ (which is present in solutions of $[W_3S_4(H_2O)_9]^{4+}$ in 1–4 M HCl) reacts with the macrocyclic cavitand cucurbituril ($C_{36}H_{36}N_{24}O_{12}$) to form supramolecular adducts of 2:1 cluster/cucurbituril stoichiometry, where two portals of cucurbituril (which contains a water molecule in its cavity) are closed by two cluster cations. These aggregates are bound together in the solid by complementary hydrogen bonds between coordinated Cl^- and the cations $H_9O_4^+$ to give chains. Thus, a supramolecular architecture is achieved from three different but complementary building blocks. The packing of the chains affords a honeycomb structure (hexagonal symmetry) with channels (about 5.2 Å in diameter). The overall stoichiometry is $(H_9O_4)\{[W_3S_4(H_2O)_6Cl_3]_2(C_{36}H_{36}N_{24}O_{12})\}Cl_3\cdot16.15H_2O$ (**1**). $[W_3S_4(H_2O)_6Cl_3]^+$ reacts with $SbCl_3$ in 6 M HCl to give cuboidal $[W_3(SbCl_3)S_4(H_2O)_6Cl_3]^+$, which forms with the macrocyclic cavitand cucurbituril a 2:1 cluster/cucurbituril adduct – a discrete supramolecule consisting of five independent molecular units. In the solid it crystallizes as a salt of very rare anion $[SbCl_6]^{3-}$ with the stoichiometry $\{[W_3(SbCl_3)S_4(H_2O)_6Cl_3]_2(C_{36}H_{36}N_{24}O_{12})\}(SbCl_6)_{2/3}\cdot12H_2O$ (**2**).

Introduction

Building supramolecular aggregates relies heavily upon complementary hydrogen bond formation. Much has been done in the field of pure organic supramolecular assemblies and this new branch of organic synthesis has been aptly termed "noncovalent synthesis".[1] Though the potential of hydrogen bonds for noncovalent binding in the so-called second coordination sphere was recognized about 20 years ago and a review summarizing binding of transition metal complexes (mostly ammino complexes) to crown ethers and related macrocycles (through N−H···O bonding) appeared as early as in 1983,[2] most of the spectacular success in the field of supramolecular chemistry in the last decennium was due to the skillful use of possibilities of classical coordination chemistry.[3,4] A reason for this may well be the lesser degree of liberty with which inorganic compounds containing H-bond donors (or acceptors) can be tailored to suit the requirements of complementarity. However, if we take an aqua complex in solution of an acid whose anion is only a moderate or even a weak donor, an array of mixed complexes would form, and each individual complex will have its particular geometrical arrangement of coordinated water molecules. This can be regarded as a combinatorial library and, if the interconversion between different species within the library is rapid enough, we will have a dynamic combinatorial library.[5] By introducing an organic H-bond acceptor with a purposefully chosen geometry, we could then selectively "recognize" any single desired component, making isolation of active species in equilibrium with its chemically closely congeners simple. Our previous work suggests that triangular cluster aqua ions of the general formula $[M_3Q_4Cl_x(H_2O)_{9-x}]^{4-x}$ (M = Mo, W; Q = S, Se; $x = 1-5$) can be regarded as components of one such library.[6−10] Specific requirements of complementarity between six-coordinated water molecules in $[M_3Q_4Cl_x(H_2O)_{9-x}]^{4-x}$ (H-bond donors) and six oxygen atoms of C=O groups of a macrocyclic cavitand cucurbituril lead to the isolation of supramolecular adducts when $x = 1-3$, i.e., the specific recognition of only a part of the library components, and moreover, in each case only of one of all possible isomers.[7−11]

In the present study we show, in one case − $(H_9O_4)\{[W_3S_4(H_2O)_6Cl_3]_2(C_{36}H_{36}N_{24}O_{12})\}Cl_3\cdot16.15H_2O$ (**1**) − how the complementarity towards $[W_3S_4Cl_3(H_2O)_6]^+$ may be reinforced through introducing "guanidinium-like"

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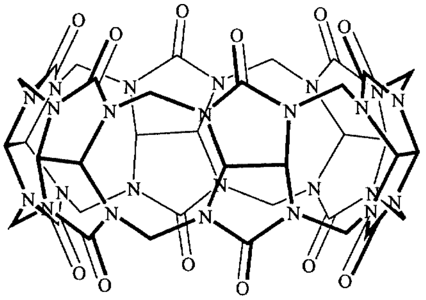
$H_9O_4^+$ which also acts as structure-directing building block making the formation of a honeycomb-like structure possible, and, in another case − $\{[W_3(SbCl_3)S_4(H_2O)_6Cl_3]_2(C_{36}H_{36}N_{24}O_{12})\}(SbCl_6)_{2/3}\cdot12H_2O$ (**2**) − how weak interactions other than hydrogen bonds may be exploited to build a nanosized supramolecular aggregate containing five units of three different building blocks, each of which is known as independent chemical species.

Results and Discussion

Although Cl^- coordination to $[M_3Q_4(H_2O)_9]^{4+}$ (M = Mo, W; Q = S, Se) in aqueous solutions is fairly weak {for the formation of $[Mo_3S_4(H_2O)_8Cl]^{3+}$ K is only 3.0 M^{-1}}, and no fully substituted species $[M_3Q_4Cl_9]^{5-}$ (or of other halides) have been isolated, some equilibration to the extent at least of $[M_3Q_4(H_2O)_4Cl_5]^-$ does take place in 1−6 M HCl.



Cucurbituril

Using cucurbituril as a second coordination sphere ligand (Cuc, $C_{36}H_{36}N_{24}O_{12}$) to promote crystallization through formation of complementary associates based on hydrogen bonds between the carbonyl groups of Cuc and water molecules *cis* to the μ_3-Q ligand of the cluster it was possible to isolate the following compounds and to determine their X-ray structures: (i) monosubstituted $\{[W_3S_4(H_2O)_8Cl](pyH\subset Cuc)\}Cl_4\cdot15.5H_2O$,[8] $\{[W_3Se_4(H_2O)_8Cl]_2(Cuc)\}Cl_6\cdot12H_2O$[11] and $\{[Mo_3Se_4(H_2O)_8Cl]_2(Cuc)\}Cl_6\cdot16H_2O$;[9] (ii) disubstituted $\{[W_3S_4(H_2O)_7Cl_2](Cuc)\}Cl_2\cdot10H_2O$;[7] (iii) trisubstituted $\{[Mo_3S_4(H_2O)_6Cl_3][Mo_3S_4(H_2O)_7Cl_2](pyH\subset Cuc)\}Cl_4\cdot17H_2O$,[7] $(H_3O)_2[Mo_3S_4(H_2O)_6Cl_3](Cuc)Cl_3\cdot9H_2O$[10] and $\{[W_3Se_4(H_2O)_6Cl_3](pyH\subset Cuc)\}_2Cl_3\cdot18H_2O$.[12] In all these structures the barrel-shaped cucurbituril molecule is effectively closed by one or two cluster "lids"; in some cases a small molecule (pyridinium cation) is included and retained inside the cucurbituril inner cavity.[7,8,12,13] The chloride substitution is always at the *trans* positions to the μ_3-chalcogen atom, other H_2O ligands are retained and used for complementary hydrogen bonding with Cuc. When more (5 Cl^-) enter into the cluster, as in $(H_3O)_2\{[Mo_3Se_4(H_2O)_4Cl_5]_2(Cuc)\}\cdot15H_2O$, the complementarity is lost.[9] In all cases the $[M_3Q_4(H_2O)_6Cl_3]^+$ species are present as the most symmetrical isomers (with a threefold axis). Comparison of the geometrical parameters of $\{W_3S_4\}$ cluster cores in the aqua complexes is given in Table 1. We can see that W−W bond lengths are only slightly affected by the environment of tungsten atoms.

Formation and Structure of 1

The structure of the cluster cation $[W_3S_4(H_2O)_6Cl_3]^+$ in compounds **1** is shown in Figure 1. Main bond lengths of $\{W_3S_4\}$ cluster core are similar to that found in the tungsten aqua complexes (Table 1). Six water molecules in *cis* position to the core μ_3-S atom form hydrogen bonds with portal oxygen atoms of cucurbituril (O···O, 2.76−2.94 Å), and a complementary cationic associate $\{[W_3S_4(H_2O)_6Cl_3](Cuc)[W_3S_4(H_2O)_6Cl_3]\}^{2+}$ ("two lids on the barrel" type) is formed. It has a very high crystallo-

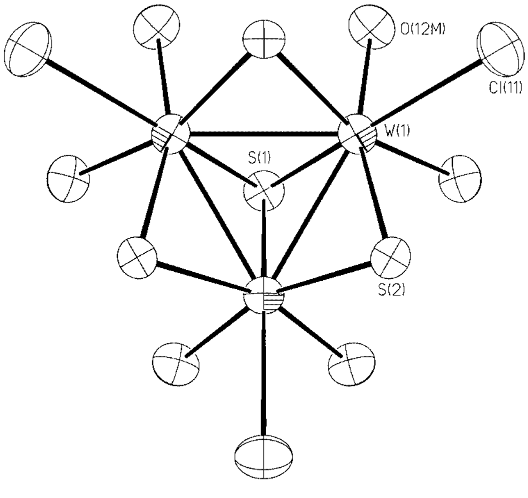


Figure 1. Cluster cation $[W_3S_4(H_2O)_6Cl_3]^+$ in the compound **1** (50% probability ellipsoids); main bond lengths [Å]: W(1)−W(1)#1 2.7360(13), W(1)−W(1)#2 2.7360(13), W(1)−S(1) 2.351(6), W(1)−S(2) 2.289(4), W(1)−S(2)#2 2.289(4), W(1)−Cl(11) 2.498(5), W(1)−O(12M) 2.175(9), W(1)−O(12M)#3 2.175(9); symmetry transformations used to generate equivalent atoms: #1: $-x + y, -x + 1, z$; #2: $-y + 1, x - y + 1, z$; #3: $-y + 1, -x + 1, z$

Table 1. Average main bond lengths in the $\{W_3S_4(H_2O)_n\}$ clusters [Å]

Formula[a]	W−W	W−μ_3-S	W−μ-S	Ref.
$\{[W_3S_4(H_2O)_7Cl_2](Cuc)\}Cl_2\cdot10H_2O$	2.714	2.340	2.285	[7]
$\{[W_3S_4(H_2O)_8Cl](pyH\subset Cuc)\}Cl_4\cdot15.5H_2O$	2.720	2.356	2.283	[8]
$[W_3S_4(H_2O)_9](pts)_4\cdot7H_2O$	2.724	2.345	2.282	[14]
$[W_3S_4(H_2O)_9](pts)_4\cdot9H_2O$	2.708	2.339	2.284	[14]
$(H_9O_4)\{[W_3S_4(H_2O)_6Cl_3]_2(Cuc)\}Cl_3\cdot16.15H_2O$	2.736	2.351	2.289	[b]

[a] pyH = pyridinium; pts = $p\text{-}CH_3C_6H_4SO_3^-$. [b] This work.

graphic symmetry, 6bar$m$2 (D_{3h}). This associate has an ellipsoidal egg-like shape of about 19.5 Å height and 14.4 Å in diameter. The associates are arranged according to the ideal hexagonal close packing (h.c.p.) motif (Figure 2). The space group of **1** is $P6_3/mmc$ − quite common for the h.c.p. structure type (e.g. Mg metal structure). It must be stressed that the associates do not contact each other in the hexagonal layer because the distances between them (16.47 Å) are longer than the van der Waals "diameter" of the associate. It means that we have not exactly close packing, but only an h.c.p.-like motif. From this point of view, the $H_9O_4^+$ cations occupy exactly one half of the tetrahedral voids. They are planar, the central oxygen atom is surrounded by three other ones at the distance of 2.59 Å which is typical for hydroxonium cations.[15] The disordered Cl^- anions and water molecules lie in the octahedral voids playing the role of a layer between the positively charged associates. The macrocyclic cavitand cucurbituril contains a water molecule in its cavity.

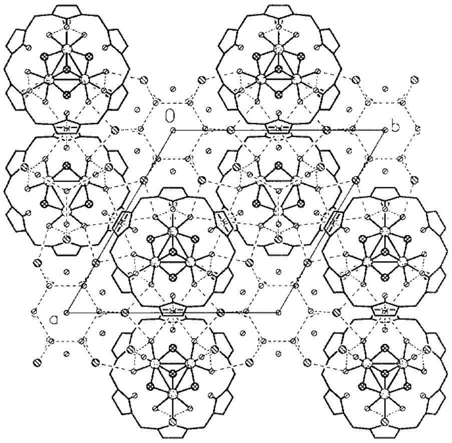


Figure 2. Crystal packing in compound **1** (projection on *a*,*b* plane); hydrogen bonds are shown as dashed lines

Once the discrete "lid-on-the-barrel" complexes between Cuc and $[M_3Q_4Cl_x(H_2O)_{9-x}]^{4-x}$ ($x = 1-3$) are formed, their further aggregation in the solid state can take place. First, through noncovalent Q···Q interactions between bridging μ_2-Q atoms (which seem to be more important when Q = Se) polymeric chains may form. This is the case for $\{[W_3Se_4(H_2O)_8Cl]_2(Cuc)\}Cl_6\cdot12H_2O$,[11] $\{[Mo_3Se_4(H_2O)_8Cl]_2(Cuc)\}Cl_6\cdot16H_2O$,[9] $\{[Mo_3S_4(H_2O)_6Cl_3][Mo_3S_4(H_2O)_7Cl_2](pyH\subset Cuc)\}Cl_4\cdot17H_2O$,[7] $\{[W_3Se_4(H_2O)_6Cl_3](pyH\subset Cuc)\}_2Cl_3\cdot18H_2O$.[12] The reluctance of the $\{W_3S_4\}$ unit to dimerise through S···S interactions is apparent here. Instead of this kind of association, in the structure of **1** the $H_9O_4^+$ cations lie between cluster−cucurbituril associates. They form hydrogen bonds with three terminal chlorine ligands of two cluster cations, Cl···O being of 3.11 Å. The guanidinium-like structure of $H_9O_4^+$ makes it suitable for complementary O−H···Cl hydrogen bonding with $[W_3S_4(H_2O)_6Cl_3]^+$. The resulting chains run along the *c* axis (Figure 3). They are shifted in such a way that each $H_9O_4^+$ cation is surrounded by four associates.

In structure **1** there are also channels along the *c* axis filled with disordered Cl^- anions and water molecules. The diameter of the channels is 5.2 Å, taking the values 1.70, 1.15, 1.40 and 1.36 Å as van der Waals radii of C, H, N and O, respectively.[16] These channels, from the h.c.p.'s point of view, are nothing else than the columns of octahedral voids. The porous frameworks built on relatively strong noncovalent interactions, like H-bonds, are of certain interest since they can be more easily disassembled than ones based on stronger covalent bonding. Kim and co-workers recently reported another cucurbituril-based honeycomb structure in $\{[Rb_2(OH)_2(CH_3OH)_2(H_2O)_2](Cuc)\}\cdot17H_2O$ where the channels have a mean diameter of about 8.9 Å.[17]

Formation and Structure of 2

The complementarity for hydrogen bonding with cucurbituril is not lost when cuboidal chalcogen-bridged aqua complexes are dealt with since they retain the unit $\{M_3Q_4(H_2O)_6\}$. One of the most interesting properties of the triangular clusters with $\{M_3Q_4\}$ cores is their ability to incorporate a low-valent metal M′ with the formation of a cuboidal cluster $\{M_3M'Q_4\}$. In the case of $Mo_3S_4^{4+}$, some 20 transition and post-transition metals have been incorporated. It seems that all metals having $d^{10}s^2$ configuration [e.g. those of group 12 (Cd^0, Hg^0), 13 (Ga^I, In^I, Tl^I), 14 (Ge^{II}, Sn^{II}, Pb^{II}), 15 (As^{III}, Sb^{III}, Bi^{III}), and possibly group 16] can react in this way. Reactions are generally fast but in some cases (Tl^I, Pb^{II}, As^{III}, Bi^{III}) reaction does not take place in aqueous solution and/or with aqua ions, but proceed smoothly in organic solvents and with different coordination environment.[18] Antimony seems to be a border case. We observed characteristic color changes on addition of $SbCl_3$ to solutions of $[M_3Q_4(H_2O)_9]^{4+}$ in HCl, but it turned out to be difficult to characterize the reaction products.

$$[M_3Q_4(H_2O)_9]^{4+} + SbCl_3 \rightarrow [M_3(SbCl_3)Q_4(H_2O)_9]^{4+}$$

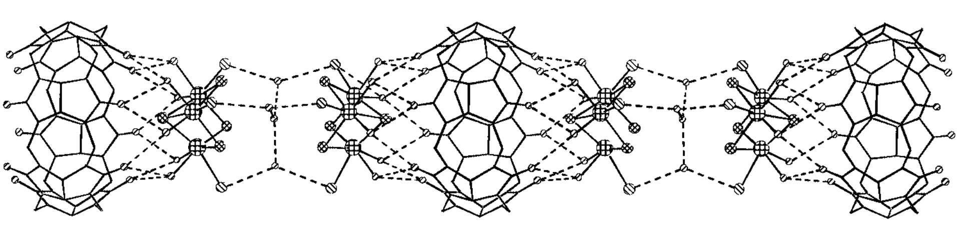


Figure 3. Fragment of the supramolecular chain in compound **1**; hydrogen bonds are shown as dashed lines

Column purification, which is a standard procedure in this kind of chemistry, cannot be applied since (i) this equilibrium is shifted very much to the left, (ii) lowering $[H^+]$ destroys $SbCl_3$ to give oxochlorides or eventually $Sb(OH)_3$. Solutions of such cuboidal clusters in HCl are notoriously difficult to crystallize, and using Hpts (*p*-toluenesulfonic acid) for crystallization is excluded by the absence of soluble Sb^{III} cationic species in this media for the range of concentration involved (1−4 M Hpts). Therefore crystallization with cucurbituril was attempted and allowed us to isolate a cuboidal cluster $[W_3(SbCl_3)S_4(H_2O)_6Cl_3]^+$ as $\{[W_3(SbCl_3)S_4(H_2O)_6Cl_3]_2(C_{36}H_{36}N_{24}O_{12})\}(SbCl_6)_{2/3}\cdot 12H_2O$ (**2**).

The structure of the cluster cation $[W_3(SbCl_3)S_4(H_2O)_6Cl_3]^+$ in **2** is shown in Figure 4. The only other known cuboidal cluster with the $W_3SbS_4{}^{7+}$ core is found in $[W_3(SbI_3)S_4(OAc)(dtp)_3(DMF)]$ (dtp = diethyl dithiophosphate).[19] Also several derivatives of the $Mo_3SbS_4{}^{7+}$ core have been reported; they all contain dtp ligands at Mo and 3 X (X = Cl, Br, I) at Sb (Table 2).[20−22] We can see that in the case of tungsten complexes the Sb−S bond lengths are notably longer than in Mo_3SbS_4 clusters. At the same time the M−M and M−S bonds are not affected by the nature of M.

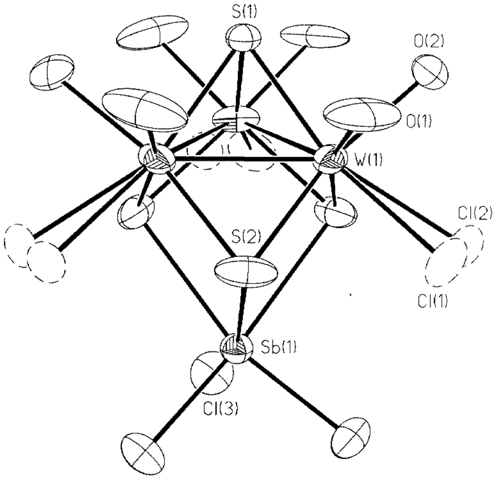


Figure 4. Cluster cation $[W_3(SbCl_3)S_4(H_2O)_6Cl_3]^+$ in the compound **2** (50% probability ellipsoids); disordered terminal chlorine ligands are shown by dashed ellipsoids, site occupancies being equal to 0.5; main bond lengths [Å]: W(1)−W(1)#1 2.7100(12), W(1)−W(1)#2 2.7100(12), W(1)−S(1) 2.349(5), W(1)−S(2) 2.300(5), W(1)···Sb(1) 3.8660(12), W(1)−Cl(1) 2.502(10), W(1)−Cl(2) 2.503(10), W(1)−O(1) 2.133(13), W(1)−O(2) 2.143(13), Sb(1)−S(2)#2 2.845(4), Sb(1)−Cl(3) 2.404(4); symmetry transformations used to generate equivalent atoms: #1: $-z+1$, $x-1/2$, $-y+1/2$; #2: $y+1/2$, $-z+1/2$, $-x+1$

In the cluster cation $[W_3(SbCl_3)S_4(H_2O)_6Cl_3]^+$ main bond lengths of $\{W_3S_4\}$ cluster core are similar to that found in the tungsten aqua complexes (Table 1). Along with the large distances W···Sb (3.87 Å) and Sb−S (2.85 Å) it makes a strong case for regarding the $[W_3(SbCl_3)S_4(H_2O)_6Cl_3]^+$ in **2** as a rather weakly bound associate of $[W_3S_4(H_2O)_6Cl_3]^+$ and $SbCl_3$. There are also a few complexes of $SbCl_3$ with thioethers [1,4,7-trithiacyclononane, 1,4,7,10,13,16-hexathiacyclooctadecane, 1,2-bis(methylthio)ethane]. A general feature is that all of them have very long Sb−S distances, no shorter than 2.97 Å.[23,24] That in our case as well as in the other $M_3SbS_4{}^{7+}$ clusters the Sb−S bonds are shorter may be regarded as the result of a partial charge transfer from Sb onto M_3S_4 unit, diminishing the electron density on Sb and increasing it on S − a synergetic effect, as has been put forward to explain similar structural features of $W_3SnS_4{}^{6+}$.[25]

In the case of compound **2** the complementary associate cluster−cucurbituril−cluster ("two lids on the barrel" type) is also formed (Figure 5), O···O being of 2.77−2.83 Å. Thus, a nanosized supramolecular aggregate containing five units of three different building blocks, each of which is known as independent chemical species ($[W_3S_4(H_2O)_6Cl_3]^+$, $SbCl_3$ and Cuc), is formed. The largest distance between outermost chlorine atoms in this aggregate is 26.7 Å. In structure **2** associates are located on the non-intersecting

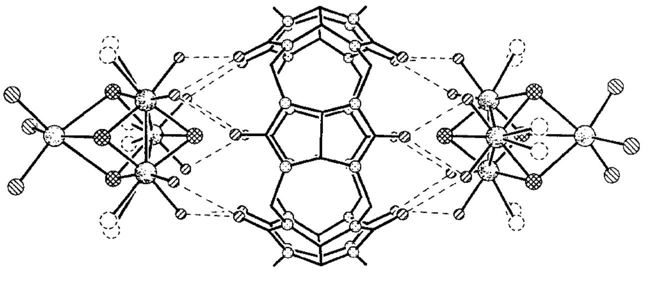


Figure 5. Complementary associate in the crystal structure of compound **2**; hydrogen bonds are shown as dashed lines

Table 2. Average main bond lengths in the $\{M_3SbS_4\}$ (M = Mo, W) clusters [Å]

Formula[a]	M−M	M···Sb	Sb−S	Ref.
$[W_3(SbI_3)S_4(\mu\text{-}MeCOO)(Etdtp)_3(DMF)]\cdot H_2O$	2.719	3.902	2.846	[18]
$[Mo_3(Sb.I_3)S_4(\mu\text{-}MeCOO)(Etdtp)_3(py)]\cdot MeCOOH$	2.721	3.855	2.797	[18]
$[Mo_3(SbBr_3)S_4(\mu\text{-}MeCOO)(Etdtp)_3(py)]\cdot MeCOOEt$	2.703	3.850	2.793	[18]
$[Mo_3(SbI_3)S_4(\mu\text{-}MeCOO)(Etdtp)_3(py)]\cdot MeCOOEt$	2.723	3.865	2.796	[18]
$[Mo_3(SbI_3)S_4(\mu\text{-}S_2CNC_4H_8)(S_2CNC_4H_8)_3(py)]\cdot 2H_2O$	2.730	3.797	2.741	[19]
$[Mo_3(Sb.I_3)S_4(\mu\text{-}Etdtp)(Etdtp)_3(EtOH)]\cdot EtOH$	2.735	3.818	2.775	[20]
$[Mo_3(Sb.I_3)S_4(\mu\text{-}Etdtp)(Etdtp)_3(H_2O)]\cdot 2H_2O$	2.717	3.807	2.779	[20]
$[Mo_6SbS_8(H_2O)_{18}](pts)_8\cdot 24H_2O$	2.717	3.680	2.609	[21]
$\{[W_3(SbCl_3)S_4(H_2O)_6Cl_3]_2(Cuc)\}(SbCl_6)_{2/3}\cdot 12H_2O$	2.710	3.866	2.845	[b]

[a] Etdtp = $(C_2H_5O)_2PS_2{}^-$; pts = $p\text{-}CH_3C_6H_4SO_3{}^-$; DMF = $OC(H)N(CH_3)_2$. [b] This work.

threefold axes of $Pa\bar{3}$ space group, forming crystal packing similar to solid CO_2.

An interesting feature of this structure is the occurrence of the rare octahedron $[SbCl_6]^{3-}$ as counterion. The Sb−Cl distance is 2.678 Å, which is in agreement with the range 2.675−2.765 Å, reported for hexachloroantimonate(3−).[26,27] On the contrary, in $SbCl_6^-$ the Sb−Cl bonds are much shorter − about 2.37 Å.[28] To the best of our knowledge, there are only two other reports on $[SbCl_6]^{3-}$: in $[Co(NH_3)_6][SbCl_6]$[26] and in 2-aminoguanidinium 2-ammonioguanidinium hexachloroantimonate(III) $(CH_8N_4)(CHN_4)[SbCl_6]$.[27] In all three structures the lone pair in $[SbCl_6]^{3-}$ does not occupy a coordination site, but rather is a spherically symmetric *s* orbital.

Experimental Section

General: All reactions were carried out in air. Stock solutions of $[W_3S_4(H_2O)_9]^{4+}$ in 2 M HCl were prepared by a published procedure[29] and made up to the required $[H^+]$ concentration with 12 M HCl. Cucurbituril was synthesized by a published procedure.[30] $SbCl_3$ was of commercial quality (Aldrich). Elemental analyses were carried out in the Laboratory of Microanalysis, Institute of Organic Chemistry, Novosibirsk.

$(H_9O_4)\{[W_3S_4(H_2O)_6Cl_3]_2(C_{36}H_{36}N_{24}O_{12})\}Cl_3\cdot 16.15H_2O$ (1): A cucurbituril solution (0.3 mL, 20 mM) in 4 M HCl was added to a $[W_3S_4(H_2O)_9]^{4+}$ solution (1.5 mL, 10 mM) in 10 M HCl. The reaction mixture was stirred and left in a closed vial at room temperature for 5 d. Dark violet hexagonal crystals of **1** were collected by filtration and dried in air. Yield: 7 mg (20%). $C_{36}H_{101.3}Cl_9N_{24}O_{44.15}S_8W_6$ (3255.74): calcd. C 13.29, H 3.13, Cl 9.81, N 10.33, S 7.89; found C 13.98, H 2.59, Cl 9.00, N 10.74, S 7.94.

$\{[W_3(SbCl_3)S_4(H_2O)_6Cl_3]_2(C_{36}H_{36}N_{24}O_{12})\}(SbCl_6)_{2/3}\cdot 12H_2O$ (2): A cucurbituril solution (0.3 mL, 20 mM) in 6 M HCl was added to a mixture of a $[W_3S_4(H_2O)_9]^{4+}$ solution (1.5 mL, 10 mM) in 6 M HCl, containing 10 mg of $SbCl_3$. The reaction mixture was stirred and left in a closed vial at room temperature for 2 d. Red crystals of **2** were collected by filtration and dried in air. Yield: 8 mg (32%). $C_{36}H_{84}Cl_{16}N_{24}O_{36}S_8Sb_{2.67}W_6$ (3680.52): calcd. C 11.62, H 2.28, N 9.03; found C 11.79, H. 2.91, N 9.15.

X-ray Crystal Structure Determinations: Structures of both **1** and **2** were determined by X-ray analysis on single crystals in essentially a routine manner. **1:** $C_{36}H_{101.3}Cl_9N_{24}O_{44.15}S_8W_6$, formula mass 3255.74, hexagonal, space group $P6_3/mmc$, $Z = 2$, $a = 16.474(3)$, $c = 21.307(3)$ Å, $\gamma = 120°$, $V = 5008.0(12)$ Å^3, $D_{calcd.} = 2.159$ g·cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 7.362$ mm^{-1}. Experimental data were measured at $T = 203$ K from a dark-violet crystal of 0.20 × 0.18 × 0.16 mm size by the standard technique with a STOE STADI4 four-cycle diffractometer using Mo-K_α radiation ($\lambda = 0.7107$ Å). A total of 6236 reflections was measured up to $2\theta_{max} = 50°$, of which 1701 are unique, $R_{int} = 0.1134$. Absorption correction was applied by measuring 3 azimuthal scans, transmission factors were from 0.7094 to 0.9965. The structure was solved by direct methods and refined by full-matrix methods for all non-hydrogen atoms using SHELX-97 program set.[31] Solvent water molecules and chlorine anions were seriously disordered. Their site occupancy factors were refined taking into account the chemical analysis data, electroneutrality and refined values of atomic thermal parameters, leading to the resulting formula that is in a good agreement with other data. $R_1 = 0.0512$ for 1089 $F \geq 4\sigma(F)$, $wR_2 = 0.1339$, $GooF = 1.142$ for all unique data. **2:** $C_{36}H_{84}Cl_{16}N_{24}O_{36}S_8Sb_{2.67}W_6$, formula mass 3680.52, cubic, space group $Pa\bar{3}$, $Z = 8$, $a = 21.788(3)$ Å, $V = 10344(2)$ Å^3, $D_{calcd.} = 2.363$ g·cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 7.984$ mm^{-1}. Experimental data were measured at $T = 293$ K from a red crystal of 0.1 × 0.08 × 0.08 mm size by the standard technique with a Bruker SMART CCD diffractometer using Mo-K_α radiation ($\lambda = 0.7107$ Å). A total of 48756 reflections was measured up to $2\theta_{max} = 46.5°$, of which 2491 were unique, $R_{int} = 0.1968$. Absorption correction was applied empirically using the SADABS program, the ratio between minimum and maximum transmission factors was 0.8622. The structure was solved by direct methods and refined by full-matrix methods for all non-hydrogen atoms using the SHELXTL program set.[32] All non-hydrogen atoms were refined anisotropically. The Sb(1) atom was found in a special position (on a threefold axis) coordinated to three symmetry-related equivalent chlorine atoms Cl(3) and to three symmetry-related sulfur atoms S(2) (Figure 4). The hexachloroantimonate(3−) anion was found in a special position and refined as partially occupied in order to balance the overall charge of the cluster. Attempts to refine the $[SbCl_6]^{3-}$ anion with full occupancy resulted in high equivalent isotropic displacement parameters for both antimony (120 Å^2) and chlorine (240 Å^2) and a electron density hole of -3 e$^-$Å^{-3} near the antimony position. The equivalent isotropic displacement parameters in our partially occupied model were 70 Å^2 for antimony and 150 Å^2 for chlorine while the electron density hole near antimony decreased to 1.56 e$^-$Å^{-3} (highest peak is 1.30 e$^-$Å^{-3}). Based on this we decided to balance our cluster charge refining the antimony anion with partial occupancy instead of assuming the protonation of one of the crystallization water molecules. One tungsten atom per asymmetric unit was found in a general position and was coordinated to two O atoms from water molecules *cis* to μ_3-S−(W_3) [O(1) and O(2)] and to one Cl atom. The anisotropic thermal parameters of this Cl atom suggested a splitting of the electron density in two positions Cl(1) and Cl(2). The positions of all cucurbituril hydrogen atoms were generated geometrically, assigned isotropic thermal parameters and allowed to ride on the respective parent carbon atoms. Water hydrogen atoms were not refined. The five highest peaks left on the electron density map were assigned to partially occupied crystallization water molecules and refined isotropically. Convergence was reached at residuals of $R_1 = 0.0551$ and $wR_2 = 0.1348$ with a goodness-of-fit parameter of 1.041. CCDC-201934 and -201935 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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