Synthesis and the crystal structure of the supramolecular complex $[Cl_3InW_3S_4(H_2O)_9]^{2+}$ with cucurbituril

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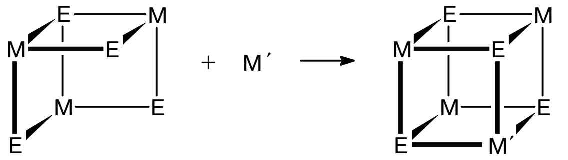
The supramolecular complex $\{[Cl_3InW_3S_4(H_2O)_9]_2(C_{36}H_{36}N_{24}O_{12})\}Cl_4 \cdot 28H_2O$ was prepared by mixing solutions of $[Cl_3InW_3S_4(H_2O)_9]^{2+}$ and cucurbituril in hydrochloric acid. The molecular and crystal structure of the resulting complex was established by X-ray diffraction analysis.

Key words: sulfide clusters, tungsten, indium, cucurbituril, crystal structure, supramolecular adduct.

The triangular chalcogenide-bridged cluster complexes $[M_3E_4(H_2O)_9]^{4+}$ (M = Mo or W; E = S or Se) are characterized by the ability to incorporate the transition and posttransition elements (M′) giving rise to heterometallic cubane-like structures $M'M_3E_4$ (Scheme 1).[1,2]

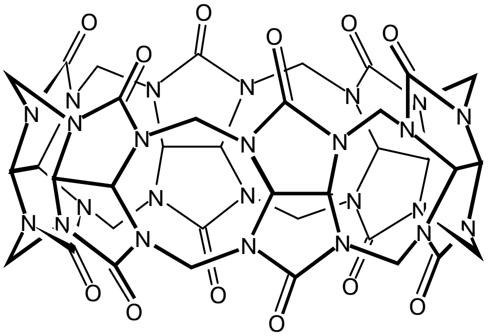
Scheme 1



The reactions involving compounds containing M = Mo and E = S have received the most study. About 20 heterometals were incorporated in this cluster.[1,2]

Previously,[3] the formation of the heterometallic cluster $[Cl_3SnW_3S_4(NCS)_9]^{6-}$ has been studied in detail and the scheme of the reaction of the triangular cluster $[W_3S_4(NCS)_9]^{5-}$ with $SnCl_3^-$ has been proposed. According to this scheme, the electron density transfer from the heterometal to $2a_1$-MO of the triangular cluster (π-acceptor) is responsible for an increase in nucleophilicity (electron density) on the coordinatively unsaturated bridging chalcogen atoms resulting in coordination of the heterometal.

In the case of M′ = Sn^{2+}, systematic studies of the crystal structures of four heterometallic clusters $[Cl_3SnM_3E_4(NCS)_9]^{6-}$ (M = Mo or W; E = S or Se) made it possible to correlate the bond lengths in the cluster core $[Cl_3SnM_3E_4]^{3+}$ with stability of the clusters.[3—6] For other heterometals, the structural data necessary for performing such comparison are lacking. In the case of In^+, which is isoelectronic to Sn^{2+}, only the crystal structure of the $[InMo_3S_4]^{5+}$ derivative was established,[7] whereas the structures of $[InW_3S_4]^{5+}$ and $[InW_3Se_4]^{5+}$ were characterized only in solutions.[8—10] In the present study, the cluster $[Cl_3InW_3S_4(H_2O)_9]^{2+}$ as a supramolecular complex with macrocyclic cavitand cucurbituril, *viz.*, $\{[Cl_3InW_3S_4(H_2O)_9]_2(C_{36}H_{36}N_{24}O_{12})\}Cl_4 \cdot 28H_2O$ (**1**), was structurally characterized by X-ray diffraction analysis.



Cucurbituril ($C_{36}H_{36}N_{24}O_{12}$)

Results and Discussion

The reaction of metallic indium with a solution of $[W_3S_4(H_2O)_9]^{4+}$ in 2 *M* HCl was accompanied by a change in the color of the reaction mixture from violet to bright-blue. Since the resulting product is air-un-

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stable, the reaction was carried out under an inert atmosphere. At room temperature, the reaction was completed in several hours on slight heating. Complex **1** was isolated by cation-exchange column chromatography on a DOWEX resin. Complex **1** was eluted with 0.5 *M* HCl prior to a small amount of the unconsumed starting cluster $[W_3S_4(H_2O)_9]^{4+}$ and, apparently, bore a charge higher than +4. According to the data from the ICP analysis, the In : W molar ratio was 1 : 3. Oxidation of the resulting heterometallic cluster afforded only In^{3+} and $[W_3S_4(H_2O)_9]^{4+}$, 2 equiv. of the one-electron oxidant Fe_{aq}^{III} or Co^{III} (as a complex with 2,6-pyridinedicarboxylic acid (H_2dipic), *viz.*, $Co(dipic)_2^-$) being consumed. All the aforesaid suggest that the reaction gave rise to a heterometallic cubane cluster with the core $[InW_3S_4]^{5+}$, *i.e.*, to the product of the formal insertion of In^+. The chromatographic behavior is attributed to coordination of several chloride ions to the indium atom (in the limiting case, to $[Cl_3InW_3S_4(H_2O)_9]^{2+}$), which decreases the total charge and promotes elution. The formation of a new cluster core can be represented as follows:

$$[W_3S_4]^{4+} + In + H^+ = [InW_3S_4]^{5+} + 0.5\ H_2.$$

The involvement of the H^+ cation is a necessity because it is the only accessible oxidant in this anaerobic system. As expected, the In^+ cation, which was either generated electrochemically in a solution[11] or taken as InBr,[12] rapidly (in the course of mixing) reacted with $[W_3S_4(H_2O)_9]^{4+}$ to give the same product:

$$[W_3S_4]^{4+} + In^+ = [InW_3S_4]^{5+}.$$

Noteworthy is the fact that the behavior of indium is identical with that of the adjacent element in the Periodic system, *viz.*, of tin. Thus, the reactions with metallic tin and the Sn^{2+} cation afforded[3—6] the isoelectronic cluster with the $[SnW_3S_4]^{6+}$ core.

The first cubane cluster in the In—Mo(W)—S(Se) system was prepared by the reaction of metallic indium with $[Mo_3S_4(H_2O)_9]^{4+}$ and isolated as a crystalline salt with the *p*-toluenensulfonate (pts) anion, $[(pts)_2InMo_3S_4(H_2O)_{10}](pts)_3 \cdot 13H_2O$.[7] Curiously, the reaction of the structurally similar complex $[Mo_3S_3O(H_2O)_9]^{4+}$ performed under the same conditions gave rise to the binary cubane cluster, which was crystallized and structurally characterized as the pts salt $\{In[Mo_3S_3O(H_2O)_9]_2\}(pts)_8 \cdot 30H_2O$. This compound is a product of the formal insertion of In^0 at the nodal position between two $[Mo_3S_3O(H_2O)_9]^{4+}$ groups.[13]

It is in the form of *p*-toluenesulfonates that the heterometallic cluster aqua ions, *viz.*, the products of the above-mentioned reactions, were crystallized. Although these products are stable in hydrochloric solutions, attempts to obtain their crystals failed. We noted that both the initial triangular cluster aqua ions $[M_3E_4(H_2O)_9]^{4+}$ (M = Mo or W; E = S or Se) and the corresponding heterometallic clusters contain six H_2O molecules located approximately in a single plane (the H_2O molecules in the *trans* positions with respect to μ_2-E of the initial triangular cluster). If a macrocyclic ligand (for example, a ligand containing six oxygen atoms and a ring of an appropriate size) was accessible, it could be involved in an associate with cluster aqua ions through complementary hydrogen bonds. An analogous approach has been used previously[14] for the preparation of supramolecular compounds of amino and aqua transition metal complexes and crowns.

Cucurbituril ($C_{36}H_{36}N_{24}O_{12}$) is another suitable macrocyclic ligand. This compound has the symmetry D_{6h} and contains a large cavity bounded by two identical "portals" due to which it can be assigned to cavitands.[15] Each "portal" contains six carbonyl groups. As we have demonstrated by preliminary modeling, these carbonyl groups are geometrically suitable for hydrogen bonding with the above-mentioned six H_2O molecules of the cluster aqua complex $[Cl_3InW_3S_4(H_2O)_9]^{2+}$. Isolation of this cluster and its X-ray diffraction study confirmed the validity of our choice.

The structure of the supramolecular cluster—cucurbituril complex $\{[Cl_3InW_3S_4(H_2O)_9]_2(C_{36}H_{36}N_{24}O_{12})\}Cl_4 \cdot 28H_2O$ (**1**) is shown in Fig. 1. According to the stoichiometry of the product, each portal of cucurbituril is closed by the cluster cation $[Cl_3InW_3S_4(H_2O)_9]^{2+}$ (Fig. 2). The latter is linked only through hydrogen bonds. All six H_2O molecules of the complex cation are involved in hydrogen bonding. The O...O distances are in the range of 2.586—2.895 Å. As a result, a large closed cavity (a "molecular container") is formed. In the case under consideration, this cavity is empty. Noteworthy is selective coordination of the Cl^- ion to the In atom, which provides an example of differentiation of the metal atoms of the heterometallic cluster with respect to different ligands. According to the available data, the Mo and W atoms exhibit low affinity for the Cl^- ion. For the first stage of replacement of $[Mo_3S_4(H_2O)_9]^{4+}$ by Cl^- ions, $K = 3.24$ L mol^{-1}.[16]

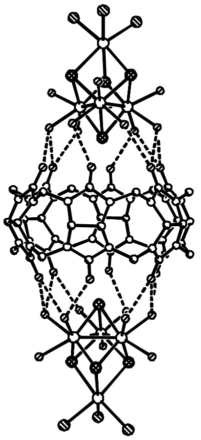

Fig. 1. Structure of the supramolecular adduct in complex **1**. Hydrogen bonds are indicated by dashed lines.

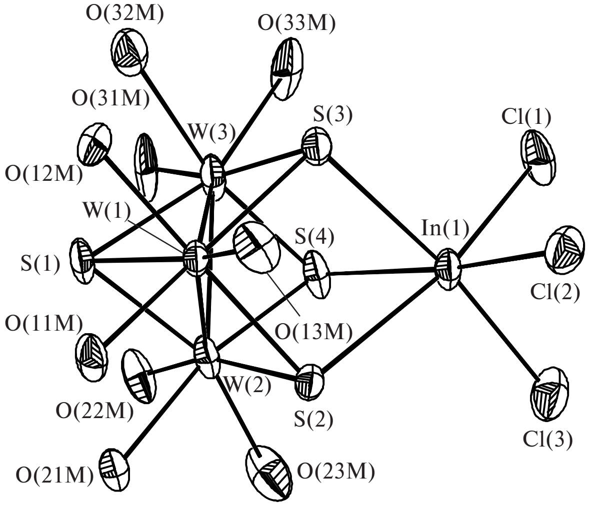

Fig. 2. Structure of the heterometallic cluster in complex **1**.

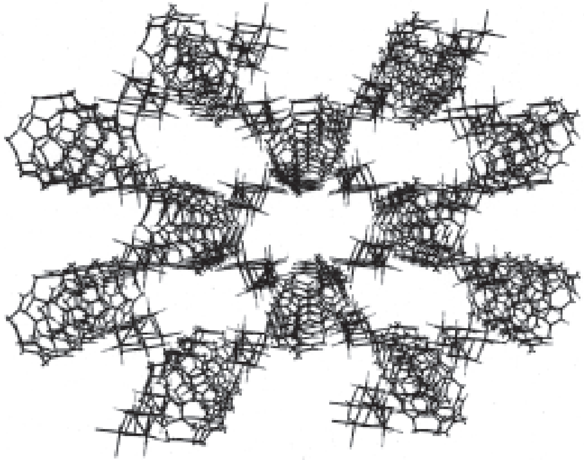

Fig. 3. Crystal packing of molecules **1** projected along the axis *a* (water molecules of solvation and chloride ions are omitted).

Since the structure of the aqua ion $[W_3S_4(H_2O)_9]^{4+}$ was also established for the salts $[W_3S_4(H_2O)_9](pts)_4 \cdot nH_2O$ (n = 7 or 9),[17] we analyzed the changes in the geometric parameters of the cluster caused by insertion of the $InCl_3^{2-}$ fragment. The general tendency for the change in the geometric parameters of the cluster $[W_3S_4(H_2O)_9]^{4+}$ upon formation of the heterometallic complex $[Cl_3InW_3S_4(H_2O)_9]^{2+}$ agrees with the data obtained earlier[3] and with the theoretical concepts developed recently[18] for such heterometallic clusters. First, the In—W distances are nonbonded (3.774—3.816 Å). Second, the W—W bond lengths in **1** are substantially smaller (2.6483(7)—2.6599(7) Å) than the average values of 2.723 Å (heptahydrate) and 2.696 Å (nonhydrate) in the initial triangular cluster. Shortening of the W—W distances is more pronounced than that of the Mo—Mo distances (compared to the bond length of 2.732(7) Å observed[17] in $[Mo_3S_4(H_2O)_9](pts)_4 \cdot 9H_2O$) found in the isoelectronic clusters $[(pts)_2InMo_3S_4(H_2O)_{10}](pts)_3 \cdot 13H_2O$ (2.675(2)—2.691(2) Å) and $[GaMo_3S_4(H_2O)_{12}](pts)_5 \cdot 13H_2O$) 2.708(2)—2.718(3) Å).[19] The bonds between the W atoms and the μ_2-S ligands (which become μ_3-bridging on coordination to the heterometal) are elongated to 2.325(3)—2.345(3) Å (compared to the average value of 2.283(5) Å). The In—Cl distances in complex **1** are in the range of 2.525(3)—2.589(3) Å and are substantially larger than the corresponding distances in the edge isomer $[InCl_3(H_2O)_3]$ (2.42—2.47 Å).[20] According to the data available in the Cambridge Structural Database,[21] of 373 In^{III}—Cl bond lengths only 24 values fall within the range of 2.52—2.60 Å, with the average bond length being 2.430 Å. A comparison directly with the In^I—Cl^- system cannot be performed because complex formation, at least in solutions, proceeds no further than to the $InCl_2^-$ form.[22]

The In—S distances in complex **1** (2.680(3)—2.715(3) Å) are larger than the corresponding distances in $[(pts)_2InMo_3S_4(H_2O)_{10}](pts)_3 \cdot 13H_2O$ (the average value is 2.645 Å)[7] and are substantially larger than those in the cubane cluster $In_4S_4[C(SiMe_3)_3]_4$ with the In_4S_4 core (the average value is 2.549 Å).[23] The observed elongation of the In—S bonds in complex **1** correlates well with the reaction of the formal transfer of In^+, which we have observed previously[10] in 2 *M* HCl. For indium, the molybdenum derivative appeared to be more stable than the corresponding tungsten derivative.

$$[Cl_3InW_3S_4(H_2O)_9]^{2+} + [Mo_3S_4(H_2O)_9]^{4+} \longrightarrow$$

$$\longrightarrow [Cl_3InMo_3S_4(H_2O)_9]^{2+} + [W_3S_4(H_2O)_9]^{4+}$$

In the transfer reactions of heterometals, the Sn^{II} complexes behave analogously.[10]

The crystal of compound **1** contains channels along the axis *a* (Fig. 3). These channels are filled with water molecules of solvation, which accounts for the large hydration number. In the structure of **1**, an extensive network of hydrogen bonds exists.

Experimental

The synthesis, chromatographic purification, and crystallization of the cluster were carried out under nitrogen. Oxygen was removed from solutions of hydrochloric acid under a stream of nitrogen for at least 1 h. Metallic indium was used as a wire. Cucurbituril (Merck) was used as a commercial decahydrate. A solution of the cluster $[Cl_3InW_3S_4(H_2O)_9]^{4+}$ in 2 *M* HCl was prepared according to a procedure reported previously.[8] Chromatographic isolation and purification of the clusters in solutions were carried out using a DOWEX 50W-X2 cation-exchange resin.

The elemental compositions were determined by atomic absorption spectroscopy (ICP).

Complex $\{[Cl_3InW_3S_4(H_2O)_9]_2(C_{36}H_{36}N_{24}O_{12})\}Cl_4 \cdot 28H_2O$ (1). Single crystals of **1** were prepared by mixing a solution of the aqua complex $[Cl_3InW_3S_4(H_2O)_9]^{2+}$ (10 mL) in 2 *M* HCl (3 mmol) with a solution of cucurbituril (5 mmol) in 3 *M* HCl

Table 1. Principal bond lengths (*d*) in the cluster anion of **1**

Bond	*d*/Å	Bond	*d*/Å
W(1)—W(2)	2.6549(7)	W(2)—O(23M)	2.177(10)
W(1)—W(3)	2.6483(7)	W(3)—S(1)	2.352(3)
W(1)—S(1)	2.344(3)	W(3)—S(3)	2.325(3)
W(1)—S(2)	2.338(3)	W(3)—S(4)	2.345(4)
W(1)—S(3)	2.342(3)	W(3)—O(31M)	2.182(9)
W(1)—O(11M)	2.160(7)	W(3)—O(32M)	2.217(9)
W(1)—O(12M)	2.177(8)	W(3)—O(33M)	2.284(9)
W(1)—O(13M)	2.188(8)	In(1)—S(2)	2.715(3)
W(2)—W(3)	2.6599(8)	In(1)—S(3)	2.680(3)
W(2)—S(1)	2.349(3)	In(1)—S(4)	2.681(3)
W(2)—S(2)	2.335(3)	In(1)—Cl(1)	2.525(3)
W(2)—S(4)	2.332(3)	In(1)—Cl(2)	2.589(3)
W(2)—O(21M)	2.161(8)	In(1)—Cl(3)	2.536(4)
W(2)—O(22M)	2.182(9)		

(4 mL) in a sealed flask under an atmosphere of nitrogen. After 2 days, dark-blue crystal that formed were filtered off and dried under a stream of nitrogen. The yield of compound **1** was 35%.

X-ray diffraction study was performed on a Bruker SMART CCD diffractometer at 160(2) K (graphite monochromator, Mo-Kα radiation, standard procedure, the scan step was 0.3°, frames were exposed for 40 s). A total of 34778 reflections were measured of which 13536 reflections were independent (R_{int} = 0.0642) in the scan range $1.38° \le \theta \le 28.54°$. The crystals belong to the monoclinic system, a = 12.6779(11) Å, b = 18.0282(15) Å, c = 25.902(2) Å, β = 100.116(2)°, V = 5828.1(9) Å^3, space group $P2_1/c$, Z = 4, d_{calc} = 2.148 g cm^{-3}, μ = 6.752 cm^{-1}. The final reliability factors were as follows: R_1 = 0.0576, wR_2 = 0.1412 for 7611 $F_{hkl} \ge 4\sigma(F)$. The absorption correction was applied based on intensities of equivalent reflections using the SADABS program.[24]

The structure was solved by a combination of direct methods and subsequent calculations of electron density syntheses (the SHELXTL program package[25]). The hydrogen atoms of the cucurbituril molecules were placed in geometrically calculated positions. We failed to locate the hydrogen atoms of the water molecules. The structure was refined by the full-matrix least-squares method with anisotropic thermal parameters for all nonhydrogen atoms using all independent reflections and taking into account corrections for absorption and extinction. The refinement was carried out with the use of the weighting scheme $w = 1/[\sigma^2(F_0{}^2) + (0.0709P)^2 + 0.0000P)]$, where $P = (F_0{}^2 + 2F_c{}^2)/3$. The atomic coordinates were deposited with the Cambridge Structural Database. The principal bond lengths in the cluster anion are given in Table 1.

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