Synthesis and crystal structures of supramolecular adducts of molybdenum and tungsten selenide aqua complexes with macrocyclic cavitand cucurbituril

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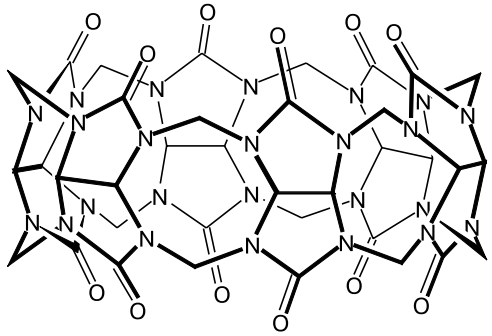
The supramolecular compounds $\{[W_3Se_4Cl_3(H_2O)_6]_2[PyH\subset C_{36}H_{36}N_{24}O_{12}]\}Cl_3 \cdot 18H_2O$ (**1**) and $\{[Cl_3SnMo_3Se_4Cl_3(H_2O)_6][Cl_3SnMo_3Se_4Cl_2(H_2O)_7](C_{36}H_{36}N_{24}O_{12})\}Cl \cdot 26H_2O$ (**2**) were isolated from solutions of the selenium-containing tungsten and molybdenum clusters $[W_3Se_4(H_2O)_9]^{4+}$ and $[Cl_3SnMo_3Se_4(H_2O)_9]^{3+}$, respectively, and organic cavitand cucurbituril. X-ray diffraction analysis demonstrated that the macrocylcic cucurbituril molecule is coordinated on both sides by the cluster cations through the formation of complementary hydrogen bonds. Compound **1** has a chain structure stabilized by Se...Se interactions between the adjacent cluster cores. In compound **2**, the bridging μ_2-selenium atoms of the cluster fragment Mo_3Se_4 are coordinated to the tin atom of the $SnCl_3^-$ ligand, thus losing the ability to be involved in Se...Se interactions.

Key words: cluster compounds, molybdenum, tungsten, cucurbituril, supramolecular adduct, crystal structure.

The construction of highly ordered supramolecular compounds with desired structures and properties starting from molecular building blocks is a fundamental problem of modern chemistry.[1—11] The use of large fragments retaining their geometry leads to an increase in the strength, directionality, and specificity of weak intermolecular nonbonded interactions. In a series of recent studies,[12—16] we have demonstrated that organic cavitand cucurbituril $C_{36}H_{36}N_{24}O_{12}$ possesses a high ability to form supramolecular compounds with triangular thio and seleno complexes of molybdenum and tungsten and their heterometallic derivatives. The macrocyclic cucurbituril molecule has a barrel-like shape with the oxygen atoms of the polarized carbonyl groups in the bottom and top planes (point symmetry group D_{6h}, the van der Waals diameter of the inner cavity is 5.5 Å, the outer diameter is 14.5 Å, the height is 9.16 Å).[17]



The presence of an extensive network of hydrogen bonds between the carbonyl groups of cucurbituril and six H_2O molecules, which are *cis*-coordinated with respect to the μ_3-chalcogen atom of the cluster cations $[M_3(\mu_3\text{-}Q)(\mu_2\text{-}Q)_3(H_2O)_9]^{4+}$ (M = Mo or W; Q = S or Se), gives rise to supramolecular ensembles in which the portals of cucurbituril are efficiently closed by one or two "lids," *viz.*, the cluster cations. The bridging μ_2-chalcogen atoms of the cluster cation are coordinatively unsaturated and exhibit a pronounced tendency both to specific nonbonded interactions with the chalcogen atoms of the adjacent cluster[18] and coordination to transition and post-transition metal atoms to form heterometallic cubane

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complexes.[19—23] The supramolecular ensembles can be linked in chains either through nonbonded interactions between the chalcogen atoms of the adjacent trinuclear cluster molecules or due to formation of a double cube in which the chalcogen atoms of two cluster cations are linked through the heterometal atom. As an example, we refer to the $\{[W_3Se_4Cl(H_2O)_8]_2(C_{36}H_{36}N_{24}O_{12})\}Cl_6 \cdot 12H_2O$ and $\{([Mo_3Se_4Cl_2(H_2O)_7]_2Hg)(C_{36}H_{36}N_{24}O_{12})\}Cl_4 \cdot 14H_2O$ compounds.[13] Highly ordered supramolecular compounds are hydrolytically stable and can find use in separation processes and optoelectronics. Heterometallic chalcogenide cubane aqua complexes often exhibit unique reactivities and are of interest in heterogeneous catalysis.[24—28]

In the present study, we synthesized new cucurbituril-based supramolecular compounds and established their structures. The $\{[W_3Se_4Cl_3(H_2O)_6]_2[PyH\subset C_{36}H_{36}N_{24}O_{12}]\}Cl_3 \cdot 18H_2O$ compound (**1**) has a chain structure formed through the Se...Se interactions between the adjacent triangular cluster complexes. In the $\{[Cl_3SnMo_3Se_4Cl_3(H_2O)_6][Cl_3SnMo_3Se_4Cl_2(H_2O)_7](C_{36}H_{36}N_{24}O_{12})\}Cl \cdot 26H_2O$ structure (**2**), the selenium atoms of the cluster complex are coordinated to the $SnCl_3^-$ fragment with the result that chains are not formed.

Results and Discussion

Green crystals of compound **1** were prepared in 60% yield by the addition of pyridine to the reaction mixture of cucurbituril and $[W_3Se_4(H_2O)_9]^{4+}$ in 3 *M* HCl. The structure of $[W_3Se_4Cl_3(H_2O)_6]^+$ is shown in Fig. 1, *a*. Each W atom of the trinuclear cluster is coordinated by the Cl atom in the *trans* position with respect to the μ_3-Se ligand and by two H_2O molecules in *cis* positions. These six H_2O molecules are involved in hydrogen bonds with six O atoms of the cucurbituril molecule (O...O, 2.68—3.01 Å) (Fig. 2, *a*). As a result, the portals of cucurbituril encapsulating the protonated pyridine molecule are efficiently closed on both sides by the "lids." In spite of the fact that the van der Waals radius of the pyridine molecule (5.9 Å) is larger than the inner diameter of the inlet hole of cucurbituril (4.2 Å), the oxygen molecules forming the portals deviate, apparently, from their positions under the reaction conditions. The inclusion of PyH^+ into the cucurbituril molecule leads to distortions of both the cucurbituril and guest molecules. Thus, the differences between the largest and smallest diameters for the cavity of cucurbituril and pyridine are 0.60 and 0.18 Å, respectively. We failed to reveal the position of the N atom in the pyridinium cation because none of the atoms of the aromatic ring forms hydrogen bonds and the scattering ability of the C atom is very close to that of the N atom. Since the pyridinium cation is located on an inversion center, it must be disordered over at least two (conceivably, even over six) positions. The bridging μ_2-selenium atoms of the adjacent cluster cores are linked through short (compared to the sum of the van der Waals radii of 3.9 Å) nonbonded contacts (Se...Se, 3.59—3.72 Å) to form the $\{W_3Se_4\}_2$ dimers. Earlier, this phenomenon has been observed[18] in a number of crystal structures of the molyb-

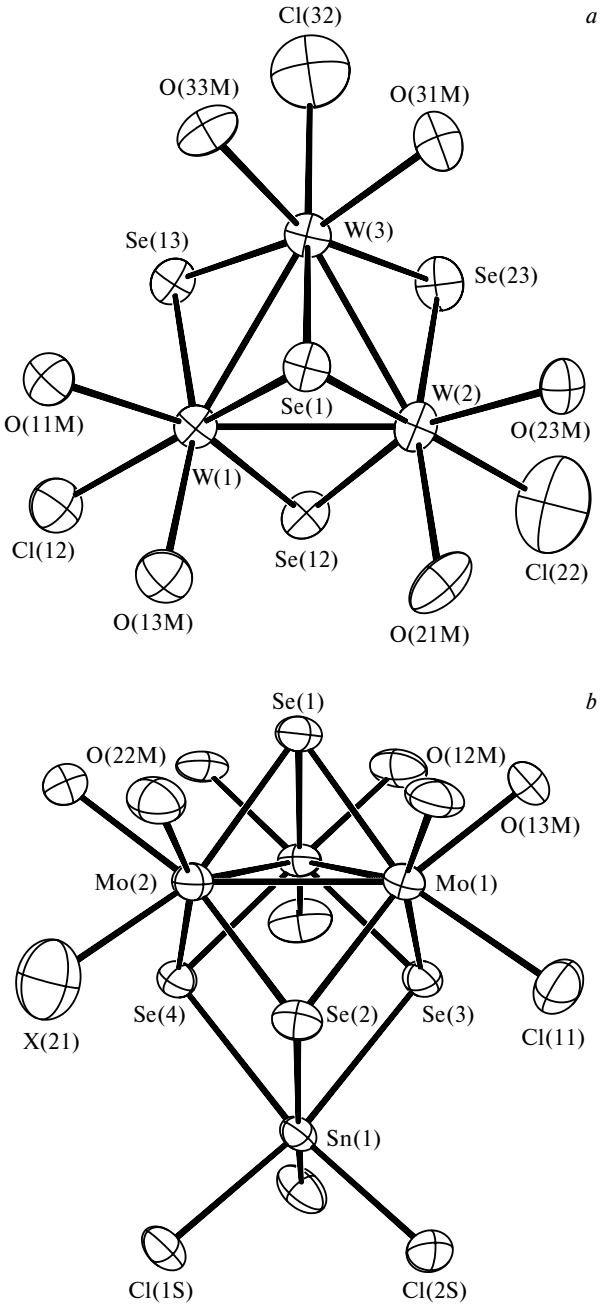

Fig. 1. Structures of the cluster cations in compounds **1** (*a*) and **2** (*b*). In compound **2**, the X(21) position in half of the complexes is occupied by the Cl atoms and in another half of the complexes is occupied by the H_2O molecules.

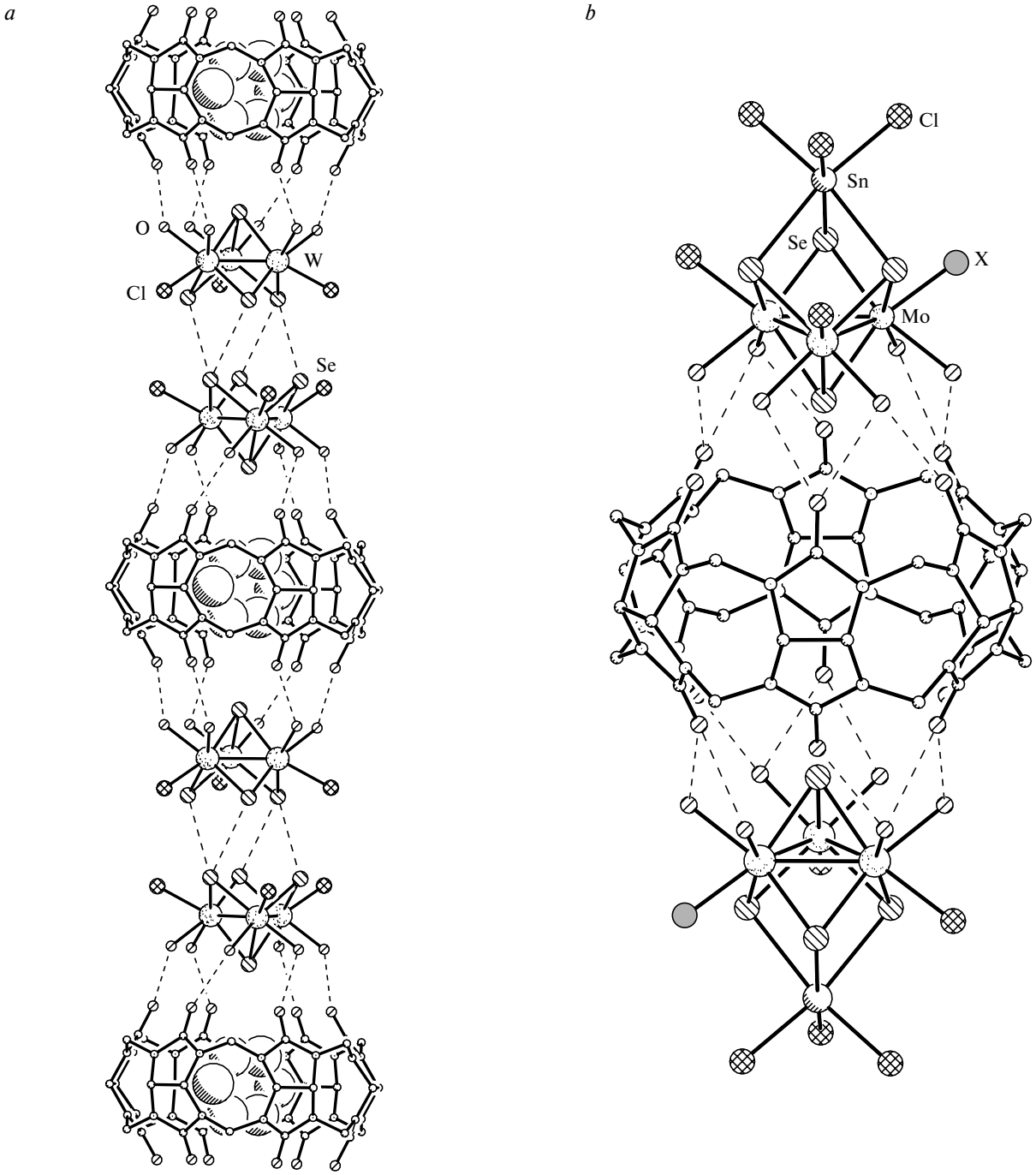

Fig. 2. Structures of the supramolecular adducts in **1** (*a*) and **2** (*b*). Hydrogen bonds and Se...Se contacts are indicated by dashed lines. In compound **2**, the positions X = 0.5 Cl + 0.5 H_2O.

denum and tungsten clusters M_3Q_4. The cucurbituril molecules linked by these dimers are located one above the other to form supramolecular chains (see Fig. 2, *a*). We believe that the chalcogen—chalcogen interactions play an important role (probably, their role is equal to that of hydrogen bonds) in the structure formation of supramolecular compounds in systems composed of cucurbituril and a triangular molybdenum or tungsten aqua complex. In the crystal structure of **1**, the Cl^- anions and H_2O molecules are located between the chains, whereas the pyridine molecules were not revealed between the chains.

Complex **1** is structurally analogous to the chain selenium-containing tungsten complex with cucurbituril $\{[W_3Se_4Cl(H_2O)_8]_2(C_{36}H_{36}N_{24}O_{12})\}Cl_6)\cdot 12H_2O$, which has been prepared earlier[13] under the same experimental conditions but without the addition of pyridine. The only

difference is the mode of packing of the chains in the crystal structures. The principal geometric parameters of the cluster cores W_3Se_4 in these complexes are identical. The encapsulation of PyH^+ in the cavity of cucurbituril leads to an increase in the (μ_3-Se)...(μ_3-Se) distances between two W_3Se_4 clusters by 0.1 Å. Hence, in the case of the W_3Se_4 complexes, the inclusion of the PyH^+ guest into the cavity of cucurbituril has no effect on the formation of one-dimensional supramolecular chains in the crystal structure. In the case of the W_3S_4 complexes, nonbonded S...S interactions are weaker and encapsulation of the pyridinium cation in the cucurbituril molecule leads to destruction of the chains structure.[15] This fact confirms once again that the Se...Se interaction is stronger than the S...S interaction, which is also typical of chalcogenide-bridged trinuclear molybdenum complexes. Hence, Se...Se interactions are more favorable for the construction of supramolecular structures.

The heterometallic cubane aqua complex $[Cl_3SnMo_3Se_4(H_2O)_9]^{3+}$ was prepared according to a known procedure[29] by the addition of tin(II) chloride to a solution of $[Mo_3Se_4(H_2O)_9]^{4+}$ in 3 *M* HCl. The addition of a solution of cucurbituril to a yellow-green solution of the aqua complex taken in a ratio of 2 : 1 afforded green octahedral crystals of the $\{[Cl_3SnMo_3Se_4Cl_3(H_2O)_6][Cl_3SnMo_3Se_4Cl_2(H_2O)_7](C_{36}H_{36}N_{24}O_{12})\}Cl \cdot 26H_2O$ complex (**2**). The tin-containing cubane cluster $SnMo_3Se_4$ has been prepared previously and structurally characterized[29] as the isothiocyanate complex $(NH_2Me_2)_6[Cl_3SnMo_3Se_4(NCS)_9] \cdot 0.5H_2O$. Crystallization with cucurbituril allowed us for the first time to isolate and structurally characterize the mixed chloro aqua complexes $[Cl_3SnMo_3Se_4Cl_3(H_2O)_6]$ and $[Cl_3SnMo_3Se_4Cl_2(H_2O)_7]^+$ (Fig. 1, *b*).

The structure of the $\{[Cl_3SnMo_3Se_4Cl_3(H_2O)_6][Cl_3SnMo_3Se_4Cl_2(H_2O)_7](C_{36}H_{36}N_{24}O_{12})\}^+$ complex is shown in Fig. 2, *b*. The cucurbituril molecule in this complex, like that in complex **1**, is closed on both sides by the cluster complexes as the lids through a system of hydrogen bonds between the H_2O molecules of the cluster and the carbonyl O atoms of cucurbituril (O...O, 2.785(2)—2.965(2) Å). One position of the terminal ligands, *viz.*, X(21), is statistically occupied by the Cl (50%) + O (50%) atoms, *i.e.*, the same position in the crystal is occupied by the $[Cl_3SnMo_3Se_4Cl_2(H_2O)_7]^+$ cation and neutral $[Cl_3SnMo_3Se_4Cl_3(H_2O)_6]$ complex with equal occupancies. This is reflected in the Mo—X bond length (X = 0.5 Cl + 0.5 O), which is intermediate between the typical Mo—Cl and Mo—O bond lengths. The cluster fragment as a whole is located on the mirror plane perpendicular to the *z* axis and has the symmetry C_s. This fragment is linked to the cucurbituril molecule through hydrogen bonds. The second cluster fragment is located on the opposite side of the cucurbituril molecule. These two cluster fragments are related by a twofold axis parallel to the *z* axis. As a result, the supramolecular adduct as a whole has the charge +1 and occupies the crystallographic position with the point symmetry $2/m$ (C_{2h}).

The bridging μ_2-selenium atoms of the cluster Mo_3Se_4 fragment are coordinated to the tin atom of the $SnCl_3^-$ ligand (Se—Sn, 2.804(2)—2.824(2) Å), thus losing the ability to be involved in Se...Se interactions. The principal geometric parameters of the heterometallic cubane cluster fragment $SnMo_3Se_4$ are close to the corresponding parameters in the isothiocyanate complex $(NH_2Me_2)_6[Cl_3SnMo_3Se_4(NCS)_9] \cdot 0.5H_2O$ (Mo—Mo, 2.7774(6)—2.8056(7) Å; Mo—μ_3-Se, 2.4552(6)—2.4643(7) Å; Mo—μ_2-Se, 2.4450(7)—2.4656(7) Å; Sn—Se, 2.7341(7)—2.8052(7) Å);[29] only a slight elongation of the Sn—Se distances is observed.

In the crystal structures of **1** and **2**, the molecules are linked through branched networks of hydrogen bonds involving water molecules of solvation. Complexes **1** and **2** are hydrolytically stable and are insoluble in water or 3 *M* HCl even upon refluxing.

Experimental

The starting solutions of $[W_3Se_4(H_2O)_9]^{4+}$ and $[Mo_3Se_4(H_2O)_9]^{4+}$ in 3 *M* HCl were prepared according to known procedures.[30,31] Commercially available cucurbituril decahydrate (Merck) was used without additional purification. Elemental analysis was carried out at the N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry of the Siberian Branch of the Russian Academy of Sciences. The IR spectra were recorded on a Bruker IFS-85 Fourier spectrometer in KBr pellets.

Cucurbituril(pyridinium)bis{hexaaquatrichloro(μ_3-selenido)tris(μ_2-selenido)tritungsten(W-W)} trichloride octadecahydrate (1). Complex **1** was prepared by the addition of a 5 *mM* cucurbituril solution (1.3 mL) in 3 *M* HCl (0.0065 mmol) and a 1% pyridine solution (1.0 mL) in 3 *M* HCl to a 13 *mM* $[W_3Se_4(H_2O)_9]^{4+}$ solution (1.0 mL) in 3 *M* HCl (0.013 mmol). The reaction mixture was stirred and kept for 12 h. The resulting green crystalline compound was filtered off and dried in air for one day. The yield was 14 mg (60%). IR, ν/cm^{-1}: 3186 s, 1726 s, 1623 m, 1539 m, 1477 s, 1414 s, 1373 s, 1324 s, 1282 s, 1234 s, 1189 s, 1144 m, 984 m, 960 s, 801 s, 757 s, 678 m, 632 w, 451 s. Found (%): C, 13.64; H, 2.83; N, 9.34. $C_{41}H_{102}Cl_9N_{25}O_{42}Se_8W_6$. Calculated (%): C, 13.41; H, 2.80; N, 9.54.

Cucurbituril{trichlorotinhexaaquatrichlorotetra(μ_3-selenido)trimolybdenum(Mo-Mo)trichlorotinheptaaquadichlorotetra(μ_3-selenido)trimolybdenum(Mo-Mo)} chloride 26-hydrate (2). Complex **2** was prepared by the dropwise addition of a 0.5 *M* $SnCl_2$ solution in HCl to a 33 *mM* $[Mo_3Se_4(H_2O)_9]^{4+}$ solution (1.0 mL) in 3 *M* HCl (0.033 mmol) until the color of the solution changed from yellow-brown to yellow-green (3—5 drops). Then a 5 *mM* cucurbituril solution (3 mL) in 3 *M* HCl (0.015 mmol) was added and the reaction mixture was kept for 12 h. The resulting green crystalline compound was filtered off and dried in air for one day. The yield was 30 mg (56%). IR, ν/cm^{-1}: 3179 s, 1726 s, 1604 m, 1474 s, 1412 m, 1370 s, 1323 s, 1236 s, 1191 s, 1144 m, 958 s, 757 m, 677 m, 633 w, 492 w,

Table 1. Crystallographic characteristics and details of X-ray diffraction study

Parameter	Compound **1**	Compound **2**
Molecular formula	$C_{41}H_{102}Cl_9N_{25}O_{42}Se_8W_6$	$C_{36}H_{114}Cl_{12}Mo_6N_{24}O_{51}Se_8Sn_2$
Molecular weight	3671.31	3569.61
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	*Pnnm*
Z 1	2	
a/Å	12.6978(13)	22.048(5)
b/Å	13.0426(13)	14.2079(15)
c/Å	16.0457(16)	16.5688(12)
α/deg	96.643(2)	—
β/deg	105.572(2)	—
γ/deg	108.847(2)	—
V/Å^3	2362.1(4)	5190.3(14)
d_{calc}/g cm^{-1}	2.581	2.284
T/K	296(2)	203(1)
$2\theta_{max}$/deg	60	50
Number of measured (independent) reflections	34707 (13683)	4724 (4724)
Number of observed reflections ($F_{hkl} \geq 4\sigma(F)$)	5579	2735
R_{int}	0.1033	—
λ/Å	0.71073	0.71073
μ/mm^{-1}	10.710	4.387
R_1 for observed reflections	0.0476	0.0748
wR_2 for all reflections	0.1022	0.2089
GOOF for all reflections	0.747	1.100

455 w. Found (%): C, 12.30; H, 3.17; Cl, 12.15; N, 9.45. $C_{36}H_{114}Cl_{12}Mo_6N_{24}O_{51}Se_8Sn_2$. Calculated (%): C, 12.11; H, 3.22; Cl, 11.92; N, 9.42.

X-ray diffraction study. The structures of compounds **1** and **2** were established by X-ray diffraction analysis. The crystallographic characteristics and details of X-ray diffraction studies are given in Table 1. The X-ray diffraction data for compound **1** were collected according to a standard procedure on a three-circle automated Bruker SMART CCD diffractometer (ω scanning of narrow frames) at 296(2) K. The X-ray diffraction data for compound **2** were collected on a four-circle automated STOE STADI4 diffractometer (θ/2θ scan technique with a variable rate) at 203(1) K. The absorption corrections were applied using the intensities of equivalent reflections for **1** and with the use of the azimuth scanning curves for **2**. The structures were solved by direct methods and refined by the full-matrix least-squares method using the SHELX-97 program package.[32] The X-ray data were processed with the use of the standard SAINT and X-RED programs available for the software of the Bruker SMART CCD and Stoe STADI4 diffractometers. In compound **2**, one position of the terminal ligands, *viz.*, X(21), is statistically occupied by the Cl and O atoms with equal occupancies (50%). The latter fact is confirmed by the thermal pa-

Table 2. Bond lengths (d) in the cluster cation in the structure of **1**

Bond	d/Å	Bond	d/Å
W(1)—W(2)	2.7761(7)	W(2)—Se(23)	2.4158(13)
W(1)—W(3)	2.7960(7)	W(2)—O(21M)	2.181(8)
W(1)—Se(1)	2.4809(12)	W(2)—Cl(22)	2.417(5)
W(1)—Se(12)	2.4077(13)	W(2)—O(23M)	2.172(7)
W(1)—Se(13)	2.4156(12)	W(3)—Se(1)	2.4747(12)
W(1)—O(11M)	2.189(7)	W(3)—Se(13)	2.4082(13)
W(1)—Cl(12)	2.497(3)	W(3)—Se(23)	2.4110(13)
W(1)—O(13M)	2.158(7)	W(3)—O(31M)	2.236(7)
W(2)—W(3)	2.7700(7)	W(3)—Cl(32)	2.459(5)
W(2)—Se(1)	2.4684(12)	W(3)—O(33M)	2.143(7)
W(2)—Se(12)	2.4096(13)		

Table 3. Bond lengths (d) in the cluster complex in the structure of **2**

Bond	d/Å	Bond	d/Å
Sn(1)—Se(2)*	2.804(2)	Mo(1)—Cl(11)	2.511(5)
Sn(1)—Se(2)	2.804(2)	Mo(1)—O(12M)	2.229(11)
Sn(1)—Se(3)	2.824(3)	Mo(1)—O(13M)	2.183(11)
Sn(1)—Cl(1S)	2.450(6)	Mo(2)—Mo(1)*	2.760(2)
Sn(1)—Cl(2S)	2.443(4)	Mo(2)—Se(1)	2.459(3)
Sn(1)—Cl(2S)*	2.443(4)	Mo(2)—Se(2)	2.433(2)
Mo(1)—Mo(1)*	2.778(3)	Mo(2)—Se(2)*	2.433(2)
Mo(1)—Mo(2)	2.760(2)	Mo(2)—X(21)**	2.335(16)
Mo(1)—Se(1)	2.461(2)	Mo(2)—O(22M)*	2.195(11)
Mo(1)—Se(2)	2.434(2)	Mo(2)—O(22M)	2.195(11)
Mo(1)—Se(3)	2.436(2)		

* The atom is generated from the basis atom by the symmetry operation x, y, $1 - z$.

** This position contains 50% of Cl atoms + 50% of O atoms.

rameter and the Mo—X distance, which is intermediate between the standard Mo—Cl and Mo—OH_2 bond lengths. The positions of the hydrogen atoms of the cucurbituril molecules and the pyridinium cations were refined from geometric considerations. The positions of the hydrogen atoms of the water molecules were not revealed. The atomic coordinates were deposited with the Cambridge Structural Database. The bond lengths in the cluster complexes are given in Tables 2 and 3.

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