Synthesis and crystal structure of a supramolecular adduct of the cubane cluster $[ClPdMo_3Se_4(H_2O)_7Cl_2]^+$ with macrocyclic cavitand cucurbituril

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A new heterometallic selenide-bridged 60-electron complex containing the cubane cluster fragment $[Mo_3(\mu_3\text{-}Se)_4Pd]^{4+}$ was prepared by heating a solution of $[Mo_3Se_4(H_2O)_9]Cl_4$ and palladium black in 2 *M* HCl. The cluster complex was isolated from aqueous solutions as a hydrolytically stable supramolecular adduct with macrocyclic cavitand cucurbituril. The molecular and crystal structure of $\{[ClPdMo_3Se_4(H_2O)_7Cl_2](C_{36}H_{36}N_{24}O_{12})Cl\} \cdot 7H_2O$ were established by X-ray diffraction analysis.

Key words: selenide clusters, molybdenum, palladium, cucurbituril, X-ray diffraction analysis, supramolecular adduct.

Chalcogenide homo- and heterometallic cubane complexes of many transition metals are known. These compounds belong to basic structures in the chemistry of cluster complexes and are of great importance in bioinorganic chemistry.[1—4] In heterometallic sulfide-bridged 60-electron complexes containing the cubane cluster fragments $[M_3(\mu_3\text{-}S)_4Ni]^{4+}$ (M = Mo or W) or $[Mo_3(\mu_3\text{-}S)_4Pd]^{4+}$, the nickel and palladium atoms are in the tetrahedral environment and are coordinated by three bridging sulfide ligands.[5—9] These complexes exhibit unique reactivities and react with CO, alkenes, alkynes, and isonitriles under very mild conditions. In particular, selective *trans*-addition of alcohols or carboxylic acids to alkynes and hydrodesulfurization of benzothiophene catalyzed by these heterometallic complexes are of great interest.[10—18]

In the present work, the Pd/Mo/Se complex containing a new cluster core $[PdMo_3Se_4]^{4+}$ was synthesized in high yield by the reaction of the triangular selenide-bridged molybdenum complex $[Mo_3Se_4(H_2O)_9]^{4+}$ with Pd black in a hydrochloric solution. The supramolecular approach to crystallization of aqua complexes (the construction of a system of complementary hydrogen bonds) was successfully used for the isolation of the heterometallic complex from dilute solutions in 2 *M* HCl. The structure of the supramolecular adduct with cucurbituril of composition $\{[ClPdMo_3Se_4(H_2O)_7Cl_2](C_{36}H_{36}N_{24}O_{12})Cl\} \cdot 7H_2O$ was established by X-ray diffraction analysis.

Results and Discussion

The reaction of $[Mo_3Se_4(H_2O)_9]^{4+}$ with Pd black proceeded analogously to the reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with Pd described previously.[8] Heating of Pd black with a solution of the complex $[Mo_3Se_4(H_2O)_9]Cl_4$ in 2 *M* HCl resulted in dissolution of palladium giving rise to a solution of the heterometallic selenide-bridged cubane cluster $[ClPdMo_3Se_4(H_2O)_9]Cl_3$ (**1**) in high yield. The reaction rate depends on the procedure for the preparation of palladium black. We found that reduction of a hydrochloric solution of $PdCl_2$ with formate afforded less reactive palladium than that obtained by reduction with hydrazine. The formation of the heterometallic cubane cluster complex is described by reaction (1):

$$[Mo_3Se_4(H_2O)_9]^{4+} + Pd + Cl^- = [ClPdMo_3Se_4(H_2O)_9]^{3+}. \quad (1)$$

The course of the reaction is conveniently monitored by taking into account the change in the color of the reaction solution from brown to dark-blue. The electronic absorption spectra of solutions of the starting cluster and the reaction product in 2 *M* HCl are shown in Fig. 1. Complex **1** was isolated by ion-exchange chromatography. The reaction product was eluted on a column with a cation-exchange resin prior to $[Mo_3Se_4(H_2O)_9]^{4+}$, which indicates that the charge of complex **1** is smaller than 4+ and that the chloride

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ligand is coordinated to the palladium atom. The predominant coordination of Cl^- to the heterometal atom in HCl solutions has been observed previously for $[ClM'Mo_3S_4(H_2O)_9]^{3+}$ (M′ = Fe,[19] Ni,[20] or Pd [21,22]). Cluster **1** is stable to oxidation with atmospheric oxygen. A solution of **1** in 2 *M* HCl can be stored at 5 °C for several months. Refluxing of a solution of **1** and $[Mo_3S_4(H_2O)_9]^{4+}$ in 2 *M* HCl did not lead to the transfer of Pd and the sulfide cluster $[ClPdMo_3S_4(H_2O)_9]^{3+}$ was not obtained. Concentration of a hydrochloric solution of complex **1** afforded a dark precipitate, which is insoluble in organic solvents, but is readily soluble upon addition of TsOH, HCl, or $HClO_4$. A hydrolysis product rapidly precipitated from the solution that formed upon addition of water to the solid complex. Hydrolysis was reversible and the precipitate was again dissolved upon addition of HCl.

The reactivities of the triangular aqua complexes of tungsten, *viz.*, $[W_3Q_4(H_2O)_9]^{4+}$ (Q = S or Se), are substantially lower. Heterometallic clusters were not formed upon prolonged boiling of 5 *mM* solutions of these complexes in 2 *M* HCl with Pd black or upon their heating in evacuated sealed tubes at 150 °C.

The ability of the Pd center in the cluster $[ClPdMo_3S_4(H_2O)_9]^{3+}$ and its derivatives to coordinate CO, isonitriles, and alkynes (and to catalyze the reactions of the latter) has been demonstrated previously.[8] The reactivity of the selenide cluster complex synthesized by us is analogous to that of the sulfide cluster. Dilute solutions of **1** (0.1—1 mmol L^{-1}) in 2 *M* HCl rapidly reacted with CO at room temperature under atmospheric pressure; the yellow color of the product appeared in a few minutes. The reaction with acetylene proceeded more slowly. The reaction of **1** with CO is reversible (reaction (2)):

$$[ClPdMo_3Se_4(H_2O)_9]^{3+} + CO \rightleftharpoons [(CO)PdMo_3Se_4(H_2O)_9]^{4+} + Cl^- . \qquad (2)$$

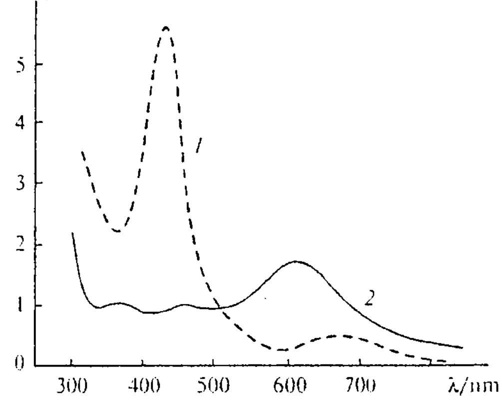
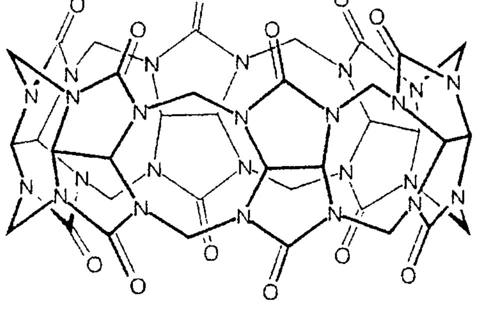


Fig. 1. Electronic absorption spectra of $[Mo_3Se_4(H_2O)_9]^{4+}$ (*1*) and $[ClPdMo_3Se_4(H_2O)_9]^{3+}$ (*2*) in 2 *M* HCl.

The complex with CO reversibly dissociated upon storage in air in a period of a few hours. When argon was passed through a solution of this complex, coordinated CO was eliminated in a few minutes giving rise to the initial complex **1** in quantitative yield (according to the data of electronic absorption spectroscopy). In the spectra of the cubane Mo/S/Pd and Mo/Se/Pd complexes with CO, the CO stretching vibrations are observed at 2085 and 2080 cm^{-1}, respectively, whereas vibrations of free CO are observed at 2143 cm^{-1}, *i.e.*, the CO stretching vibration bands in the spectra of the cubane complexes under study are substantially shifted to the long-wavelength region. It was believed[9] that this shift is associated with the fact that the heterometal atom in the cubane Mo/S/Pd complex is in the oxidation state 2+. According to the data of other studies,[23] the substantial shift observed in the case of coordination of CO to the heterometal atom in the Mo_3S_4Pd and Mo_3S_4Ni complexes is attributable to the peculiarities of the electronic structures of these complexes. The orbitals of the heterometal atom are involved not only in the heterometal—CO interaction, but also in overlapping with the orbitals of the Mo_3 triangle to form the Pd—Mo or Ni—Mo bonds. In other words, the Mo_3S_4 fragment acts as a tridentate π-acceptor and competes with CO in interacting with the orbitals of the heterometal atom.[23] We believe that the electronic structure of the selenide cluster prepared by us should be in principle similar to that of its sulfide analog.

The investigation of the heterogeneous catalytic reactions involving heterometallic chalcogenide cubane complexes calls for the development of procedures for the preparation of their solid hydrolytically stable aqua complexes. The only approach to the isolation of such cubane complexes as aqua ions requires crystallization of *para*-toluenesulfonates.[5—9] However, this procedure relates the structural data to the behavior of the aqua ions only in one medium, generally, in 4 *M* TsOH.

Recently,[24—26] we have developed a new supramolecular approach to the isolation of chalcogenide cluster aqua complexes from dilute hydrochloric solutions as their adducts with cucurbituril ($C_{36}H_{36}N_{24}O_{12}$).



Cucurbituril

Cucurbituril is a macrocyclic ligand, which has the symmetry D_{6h} and a large cavity bounded by two identi-

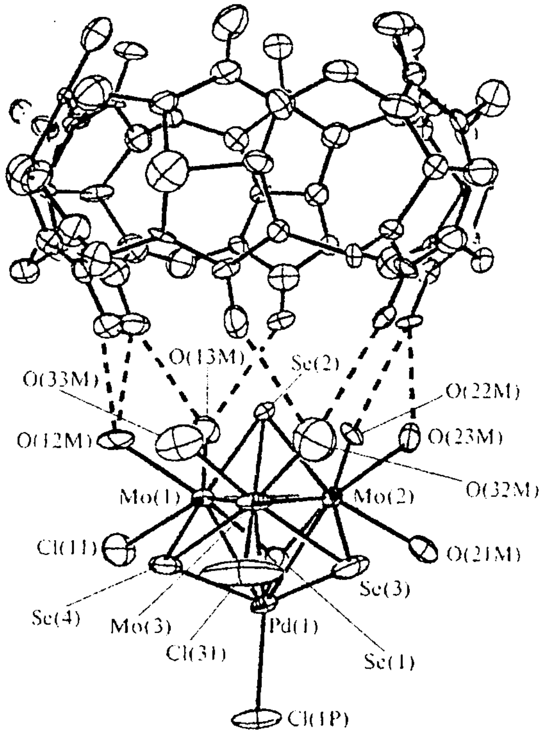


Fig. 2. Structure of the cluster—cucurbituril supramolecular adduct $\{[ClPdMo_3Se_4(H_2O)_7Cl_2](C_{36}H_{36}N_{24}O_{12})\}^+$. Hydrogen bonds shorter than 3 Å are indicated by dashed lines.

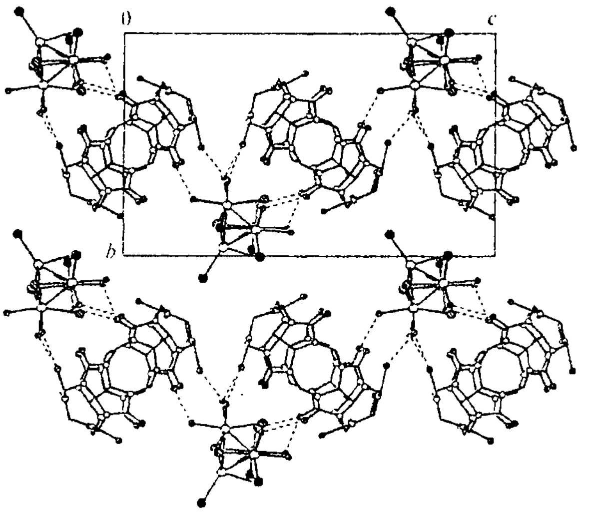


Fig. 3. Packing of the supramolecular adducts in the crystal of **2** (only one layer is shown). The water molecule of solvation and the Cl^- anions are omitted. Hydrogen bonds shorter than 3 Å are indicated by dashed lines.

cal "portals," due to which it can be assigned to the class of cavitands.[27,28] Each "portal" contains six carbonyl groups whose oxygen atoms (as we have demonstrated previously) can form a system of complementary hydrogen bonds with coordinated water molecules of the triangular aqua complexes $[M_3Q_4(H_2O)_9]^{4+}$ and the heterometallic biscubane mercury complexes $\{[M_3Q_4(H_2O)_9]_2Hg\}^{8+}$ (M = Mo or W; Q = S or Se).[25,26]

The addition of cucurbituril to solutions of $[ClPdMo_3Se_4(H_2O)_9]^{3+}$ in 2 *M* HCl afforded a supramolecular adduct of composition $\{[ClPdMo_3Se_4(H_2O)_7Cl_2](C_{36}H_{36}N_{24}O_{12})Cl\} \cdot 7H_2O$ (**2**) in low yield (4—8%). The addition of glycerol to the reaction mixture resulted in crystallization of complex **2** in high yield. In the presence of an excess of cubane cluster complex **1**, a supramolecular adduct of composition cluster/cucurbituril = 2/1 was not obtained.

The structure of the supramolecular cluster—cucurbituril adduct of composition $\{[ClPdMo_3Se_4(H_2O)_7Cl_2](C_{36}H_{36}N_{24}O_{12})\}^+$ is shown in Fig. 2. According to the stoichiometry of the product, only one portal of cucurbituril is closed by the cluster cation $[ClPdMo_3Se_4(H_2O)_7Cl_2]^+$. The latter is linked only through hydrogen bonds. Six water molecules of the cation in the *cis* positions with respect to Se(2) are involved in hydrogen bonding. The O...O distances are in the range of 2.76—3.04 Å. The Se(2) atom, which is involved in bonds only with the molybdenum atoms, is located within the cavity formed by the oxygen atoms of the carbonyl groups of cucurbituril. The cationic cluster, which closes the portal, exists as the $[ClPdMo_3Se_4(H_2O)_7Cl_2]^+$ ion. The principal bond lengths and bond angles in the cluster cation are given in Table 1. Without considering the M—M bonds, the coordination environments about the molybdenum atoms are distorted octahedra, the chlorine atoms being coordinated only to the Mo(1) and Mo(3) atoms. To the contrary, the palladium atom is in a tetrahedral environment and is coordinated by three bridging selenium atoms and one terminal chlorine atom. The Mo—Mo and Mo—Pd distances in the Mo_3Pd cluster core correspond to metal—metal bonds.

Table 1. Principal bond lengths (*d*) in the structure of **2**

Bond	*d*/Å	Bond	*d*/Å
Pd(1)—Mo(1)	2.790(5)	Mo(1)—O(13M)	2.29(3)
Pd(1)—Mo(2)	2.802(6)	Mo(2)—Mo(3)	2.808(7)
Pd(1)—Mo(3)	2.787(6)	Mo(2)—Se(1)	2.422(7)
Pd(1)—Se(1)	2.402(7)	Mo(2)—Se(2)	2.439(6)
Pd(1)—Se(3)	2.460(8)	Mo(2)—Se(3)	2.486(8)
Pd(1)—Se(4)	2.438(7)	Mo(2)—O(21M)	2.27(3)
Pd(1)—Cl(1P)	2.45(2)	Mo(2)—O(22M)	2.25(3)
Mo(1)—Mo(2)	2.780(6)	Mo(2)—O(23M)	2.16(3)
Mo(1)—Mo(3)	2.820(7)	Mo(3)—Se(2)	2.440(7)
Mo(1)—Se(1)	2.440(7)	Mo(3)—Se(3)	2.467(7)
Mo(1)—Se(2)	2.480(7)	Mo(3)—Se(4)	2.405(9)
Mo(1)—Se(4)	2.470(8)	Mo(3)—Cl(31)	2.52(2)
Mo(1)—Cl(11)	2.46(2)	Mo(3)—O(32M)	2.30(5)
Mo(1)—O(12M)	2.18(3)	Mo(3)—O(33M)	2.17(4)

In the crystal, the supramolecular adducts are linked in chains through strong hydrogen bonds between the hydrogen atom of the H_2O ligand located in the *trans* position with respect to the Se(2) atom and the oxygen atom of the cucurbituril moiety of the adjacent adduct (O...O is 2.55 Å) (Fig. 3). The zigzag chains, in turn, form layers perpendicular to the *a* axis.

Experimental

The starting solution of $[Mo_3Se_4(H_2O)_9]Cl_4$ in HCl was prepared according to a procedure reported previously.[29] Palladium black was prepared by reduction of a hydrochloric solution of $PdCl_2$ with hydrazine.[30] Cucurbituril (Merck) was used as a decahydrate without additional purification. The electronic absorption spectra were recorded on a Specord M40 instrument. The IR spectra were measured on a Bruker IFS-85 Fourier spectrometer.

Synthesis of tetrakis(μ_3-selenido)tris(triaquamolybdenum)chloropalladium trichloride (1). Palladium black (100 mg) was added to a 20 *mM* solution of $[Mo_3Se_4(H_2O)_9]Cl_4$ (10 mL) in 2 *M* HCl. The reaction mixture was heated with intense stirring under argon at 90—100 °C for 6 h. In the course of the reaction, the color of the solution changed from brown to dark-blue. The resulting solution was filtered, diluted fivefold with water, and applied to a column (8×2 cm) with a Dowex 50W×2 (H^+) cation-exchange resin. The column was washed with 0.25 *M* HCl (100 mL) and the product was eluted with 1 *M* HCl. The yield was ~80%. The typical concentrations of $[ClPdMo_3Se_4(H_2O)_9]Cl_3$ were 1—5 mmol L^{-1}. (The yields and the concentrations were determined by electronic spectroscopy. The ε value was calculated from the absorption of the solution with the known concentration, which was determined by analyzing the solution for the Mo, Pd, and Se contents.) The electronic absorption spectrum in 1 *M* HCl, λ/nm (ε/L mol^{-1} cm^{-1}): 390 (1010), 475 (1000), 611 (1820). According to the data of inductively-coupled plasma mass spectrometry, the Mo : Se : Pd ratio in the solution was 3.00 : 4.02 : 1.01.

Reaction of $[ClPdMo_3Se_4(H_2O)_9]^{3+}$ with CO. Carbon monoxide was passed through a 1 *mM* solution of $[ClPdMo_3Se_4(H_2O)_9]^{3+}$ (3 mL) in 1 *M* HCl for 5 min. The color of the solution gradually changed to yellow. The electronic absorption spectrum (1 *M* HCl), λ/nm: 441, 483 sh. IR (an emulsion of a hydrochloric solution in Nujol mulls): ν/cm^{-1}: 2080 (CO).

Reaction of $[ClPdMo_3Se_4(H_2O)_9]^{3+}$ with C_2H_2 was carried out as described above (the reaction time was 3 h). After completion of the reaction, the solution turned red. The electronic absorption spectrum (1 *M* HCl), λ/nm: 452, 488 sh.

Synthesis of cucurbituril(chloropalladium)tetra-μ_3-selenoheptaaquadichlorotrimolybdenum chloride heptahydrate (2). A 3 *mM* solution of cucurbituril (1 mL) in 2 *M* HCl (0.03 mmol) and glycerol (0.5 mL) was added to a 5 *mM* solution of $[ClPdMo_3Se_4(H_2O)_9]^{3+}$ (2 mL) in 2 *M* HCl (0.01 mmol). The reaction mixture was stirred and then kept at -20 °C for 2 days. The crystals that precipitated were filtered off and dried in air. The yield was 69%. The composition of supramolecular compound **2** was established by X-ray diffraction analysis.

X-ray diffraction study. The structure of compound **2** was established by X-ray diffraction analysis. The X-ray data were collected on an automated Enraf-Nonius CAD 4 diffractometer from a single crystal of dimensions of 0.29×0.21×0.06 mm at -20 °C. The crystallographic data and details of X-ray diffraction study are given in Table 2. The absorption correction was applied using three azimuth scanning curves. The crystal gave a weak diffraction pattern due, apparently, to its small dimensions. The structure was solved by direct methods and refined anisotropically by the full-matrix least-squares method using the SHELX-97 program package.[31] 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 atomic coordinates were deposited with the Cambridge Structural Database and can be obtained from the authors.

Table 2. Crystallographic data and details of X-ray siffraction study of supramolecular adduct **2**

Parameter	**2**
Molecular formula	$C_{36}H_{64}Cl_4Mo_3N_{24}O_{26}PdSe_4$
Molecular weight	2100.97
Space group	*Cc*
System	Monoclinic
a/Å	20.496(6)
b/Å	14.589(4)
c/Å	24.539(6)
β/deg	102.30(2)
V/Å^3	7169(3)
d_{calc}/g cm^{-3}	1.947
Z	4
μ(Mo-Kα)/mm^{-1}	3.029
$2\theta_{max}$/deg	50.0
Number of measured reflections	4576
Number of reflections with $F_{hkl} \geq 4\sigma(F)$	1661
Weighting scheme	$w^{-1} = \sigma^2(F_o^2) + (0.1050P)^2 + 0.0000P$, where $P = (F_o^2 + 2F_c^2)/3$
R_1, wR_2 for $F_{hkl} \geq 4\sigma(F)$	0.0794, 0.1889
R_1, wR_2 for all independent reflections F_{hkl}	0.1617, 0.2126
GOOF for all independent reflections F_{hkl}	0.793

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