General and Inorganic Chemistry

Synthesis, structures, and properties of molybdenum and tungsten chalcogenide cubane complexes $(NH_4)_6[M_4Q_4(CN)_{12}] \cdot 6H_2O$ (M = Mo or W; Q = S or Se)

V. P. Fedin,[a] D. G. Samsonenko,[a] A. V. Virovets,[a] I. V. Kalinina,[a] and D. Yu. Naumov[b]*

[a] *Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, 3 prosp. Akad. Lavrent'eva, 630090 Novosibirsk, Russian Federation. Fax: +7 (383 2) 34 4489. E-mail: cluster@che.nsk.su*

[b] *Institute of Solid-State Chemistry and Mechanochemistry, Siberian Branch of the Russian Academy of Sciences, 18 ul. Kutateladze, 630128 Novosibirsk, Russian Federation. Fax: +7 (383 2) 32 2847*

Four new chalcogenide molybdenum and tungsten cubane clusters $(NH_4)_6[M_4Q_4(CN)_{12}] \cdot 6H_2O$ (M = Mo or W; Q = S or Se) were prepared by high-temperature reactions of the triangular $M_3Q_7Br_4$ complexes with KCN at 430 °C followed by crystallization from aqueous solutions of ammonium acetate. The molecular and crystal structures of $(NH_4)_6[Mo_4S_4(CN)_{12}] \cdot 6H_2O$, $(NH_4)_6[W_4S_4(CN)_{12}] \cdot 6H_2O$, and $(NH_4)_6[W_4Se_4(CN)_{12}] \cdot 6H_2O$ were established by X-ray diffraction analysis. The mixed-valence cubane clusters are diamagnetic and isostructural and have the symmetry T_d. The clusters were characterized by IR and electronic spectroscopy. The data of cyclic voltammetry demonstrated that the $[M_4Q_4(CN)_{12}]^{n-}$ clusters exist in three oxidation states from the most oxidized (n = 6; 10 cluster electrons) to the most reduced electron-precise 12-electron species (n = 8).

Key words: molybdenum, tungsten, cluster complexes, thio complexes, seleno complexes, synthesis, X-ray diffraction analysis, cyclic voltammetry.

Homo- and heterometallic chalcogenide cubane cluster complexes are known for many transition metals. These compounds belong to basis structures in the chemistry of transition metal clusters and are of great importance in bioinorganic chemistry.[1—3] Homometallic cubane molybdenum clusters Mo_4S_4 have been studied in sufficient detail.[1—5] Molecular cluster complexes containing $[Mo_4Se_4]^{4+/5+/6+}$ cubane fragments have also been described.[6,7] Unlike molybdenum complexes, tungsten chalcogenide cubane complexes are still poorly studied. The thio complex $[W_4S_8(en)_4]S$ (en = $H_2NCH_2CH_2NH_2$) containing the $[W_4S_4]^{10+}$ cubane core[8] and the β-$[W_4S_4(\mu\text{-dtp})_2(dtp)_4]$ and α-$[W_4S_4(\mu\text{-dtp})_3(dtp)_3]$ complexes (dtp = $S_2P(OEt)_2$) containing the $[W_4S_4]^{6+}$ cubane core[9] have been synthesized and structurally characterized.

As part of continuing studies of cyanide chalcogen-bridged cubane complexes of the first elements of the transition series,[10—12] in this work we developed a general procedure for the synthesis of molybdenum

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 1, pp. 18—24, January, 2000.

1066-5285/00/4901-0019 $25.00

and tungsten complexes and prepared the $(NH_4)_6[Mo_4S_4(CN)_{12}]\cdot 6H_2O$ (**1**), $(NH_4)_6[Mo_4Se_4(CN)_{12}]\cdot 6H_2O$ (**2**), $(NH_4)_6[W_4S_4(CN)_{12}]\cdot 6H_2O$ (**3**), and $(NH_4)_6[W_4Se_4(CN)_{12}]\cdot 6H_2O$ (**4**) complexes. We studied the structures, electronic spectra, and electrochemical properties of the complete series of isoelectronic mixed-valence thio-, seleno-, and telluro-bridged cyanide complexes $[M_4Q_4(CN)_{12}]^{6-}$ (M = Mo or W; Q = S, Se, or Te). The latter complexes have been synthesized by us previously.

Results and Discussion

Synthesis of cubane complexes of molybdenum and tungsten. Three procedures for the preparation of thio- and seleno-bridged molybdenum cubane complexes were reported in the literature: (a) reductive dimerization of various chalcogen-bridged Mo_2 complexes; (b) addition of mononuclear fragments to Mo_3-triangular chalcogenide complexes; and (c) self-assembly from mononuclear complexes.[3,5–7] The tungsten cubane complexes β-$[W_4S_4(\mu\text{-dtp})_2(dtp)_4]$ and α-$[W_4S_4(\mu\text{-dtp})_3(dtp)_3]$ were prepared from $W(CO)_6$ and $Na_2[WO_4]$ or $K_3[W_2Cl_9]$ in the presence of P_2S_5 in ethanol[9] in low yields. Their syntheses are poorly reproducible.

Recently, we have proposed a new approach to the synthesis of chalcogen-bridged cubane complexes,[10–12] which involves high-temperature reactions of chalcogenides or chalcohalides of the first metals of the transition series with KCN. The first complexes with the cubane cluster core M_4Te_4 (M = Mo or W), *viz.*, $K_7[Mo_4(\mu_3\text{-}Te)_4(CN)_{12}]\cdot 12H_2O$ and $K_6[W_4(\mu_3\text{-}Te)_4(CN)_{12}]\cdot 5H_2O$, were prepared in high yields by the reactions of $Mo_3Te_7I_4$ or tungsten ditelluride with KCN at 450 °C followed by crystallization from aqueous solutions.[10] Analogously, the $Cs_5K[W_4S_4(CN)_{12}]\cdot MeOH\cdot 2H_2O$ and $K_6[W_4Se_4(CN)_{12}]\cdot 6H_2O$ complexes were synthesized from $W_3Q_7Br_4$ (Q = S or Se) and KCN.[11] In the present work, this approach was used for preparing isostructural ammonium salts of composition $(NH_4)_6[M_4Q_4(CN)_{12}]\cdot 6H_2O$.

It is known that the polymeric clusters $M_3Q_7Br_4$ (M = Mo or W; Q = S or Se) react with a boiling aqueous solution of KCN to give triangular thio- and seleno-bridged cyanide complexes in high yields.[13]

$$M_3Q_7Br_4 + KCN \longrightarrow [M_3(\mu_3\text{-}Q)(\mu_2\text{-}Q)_3(CN)_9]^{5-}$$

Heating of a mixture of solid $M_3Q_7Br_4$ and KCN in evacuated sealed tubes to higher temperature (430 °C) afforded the chalcogen-bridged cubane complexes $[M_4(\mu_3\text{-}Q)_4(CN)_{12}]^{6-}$. Recrystallization from a 1 *M* aqueous solution of $AcONH_4$ yielded octahedral crystals of the isostructural salts $(NH_4)_6[M_4Q_4(CN)_{12}]\cdot 6H_2O$. Moderate yields of complexes **1**—**4** (20—40%) are attributable to the fact that stable molybdenum and tungsten dichalcogenides are simultaneously formed under the conditions of high-temperature synthesis (this fact was established by powder X-ray diffraction analysis). It was experimentally demonstrated that these compounds do not react with KCN. At temperatures higher than 450 °C, molybdenum and tungsten disulfides and diselenides were obtained instead of the cluster complexes.

Ammonium salts **1**—**4** are dark-brown crystalline compounds which are readily soluble in water and insoluble in usual organic solvents. Aqueous solutions of these compounds are air-stable at room temperature and upon boiling.

IR spectra of complexes 1—4. The IR spectra of ammonium salts **1**—**4** in Nujol mulls have characteristic ν(CN) absorption bands in the 2133—2140 cm^{-1} region. The positions of these bands are virtually independent of the nature of the metal and chalcogen atoms. In the $Cs_5K[W_4S_4(CN)_{12}]\cdot MeOH\cdot 2H_2O$ and $K_6[W_4Se_4(CN)_{12}]\cdot 6H_2O$ complexes, which we have studied previously, the ν(CN) values are substantially lower (by 15—17 cm^{-1}). In the crystals of ammonium salts **1**—**4**, each $[M_4Q_4(CN)_{12}]^{6-}$ anion is linked to twelve $[(NH_4)_3(H_2O)_3]^{3+}$ rings *via* hydrogen bonds through the cyano groups. Hydrogen bonding leads to an increase in the ν(CN) values. In the IR spectra of samples of **1**—**4** in KBr pellets, the ν(CN) stretching bands are shifted to the low-frequency region. These shifts are 5—15 cm^{-1} depending on the duration of pressing.

Procedures for the synthesis developed by us made it possible to readily prepare ammonium salts containing sulfur isotopes, *viz.*, $(NH_4)_6[Mo_4{}^{34}S_4(CN)_{12}]\cdot 6H_2O$ and $(NH_4)_6[W_4{}^{34}S_4(CN)_{12}]\cdot 6H_2O$. Their vibrational spectra were examined and the normal vibrations were calculated. The results will be published elsewhere.

Molecular and crystal structures of complexes 1—4. Compounds **1**—**4** are isostructural and crystallize in the cubic system (the space group $Pn\bar{3}m$). The structures of complexes **1**, **3**, and **4** were established by X-ray diffraction analysis. The structure of the cluster anionic complex $[Mo_4S_4(CN)_{12}]^{6-}$ is presented as an example in Fig. 1. In the crystals, the cluster anions occupy the positions *2a* with the ideal point symmetry $\bar{4}3m$ (T_d). The cluster core can be described as an ideal tetrahedron formed by the metal atoms, each face being symmetrically coordinated by the μ_3-Q ligand (Q = S or Se).

The solution of the structures demonstrated that the ammonium cations are disordered together with the water molecules of solvation so that the only crystallographically independent position X(1) belonging to these species is half-occupied by the nitrogen atom of the NH_4^+ cation and half-occupied by the oxygen atom of the water molecule. In the crystals, the X(1) atoms form the six-membered X_6 rings, which adopt a chair conformation with X...X distances of 2.82(1), 2.83(1), and 2.88(1) Å in complexes **1**, **3**, and **4**, respectively. The model suggested by us contains rings, which occupy the position *4c* with the point symmetry $\bar{3}m$ and in which the ammonium cations alternate with the water molecules, *i.e.*, these rings have the composition

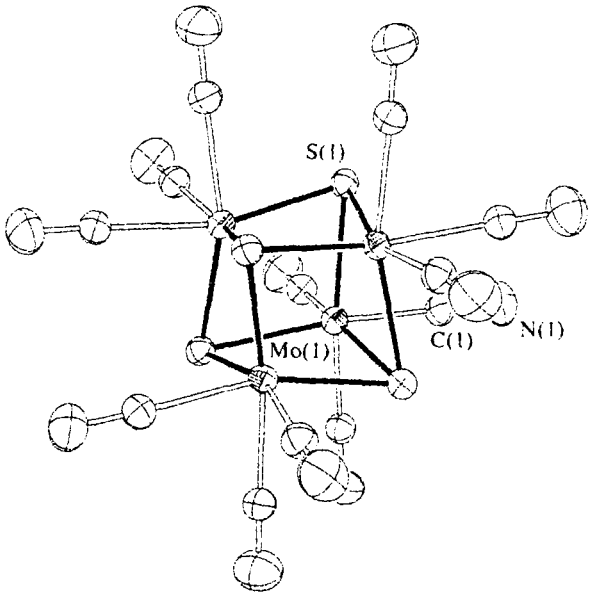

Fig. 1. Structure of the $[Mo_4S_4(CN)_{12}]^{6-}$ anion (thermal ellipsoids with 50% probability).

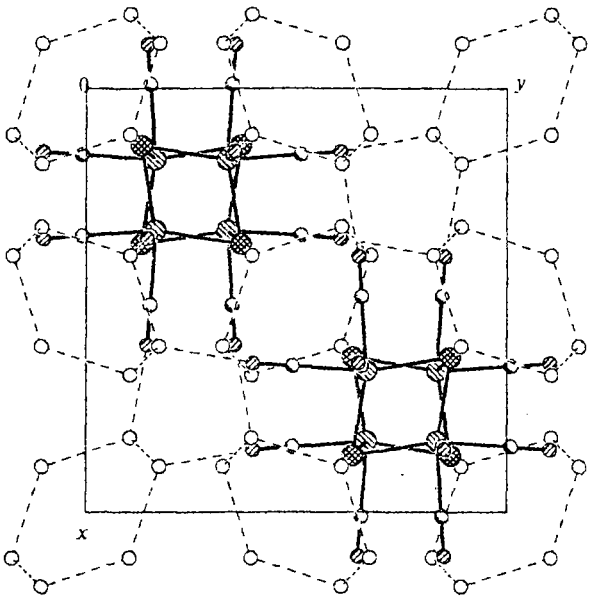

Fig. 3. Packing of the ions in the crystal of **1**.

$[(NH_4)_3(H_2O)_3]^{3+}$ (the $[(NH_4)_3(H_2O)_3]^{3+}$ cation in compound **1** is shown in Fig. 2). In this case, two modes of alternation are statistically superimposed. Therefore, the X...X distance corresponds to an N...H...O hydrogen bond. There are two rings per cluster anion. This model is consistent with the charge 6− of the cyano-containing cluster anion, which is confirmed by the spectroscopic data and does not contradict crystal-chemical considerations.

The positions of H_2O and NH_4^+ can be separated only if the symmetry of the space group is lowered. Our attempts to refine the structures in the lower-symmetry space groups were unsuccessful. Apparently, we came across the well known phenomenon that the highly symmetrical arrangement of heavy atoms governs the mode of arrangement of light atoms.

We failed to locate and refine the positions of the hydrogen atoms. Apparently, this is associated with disorder and a low relative contribution of the hydrogen atoms to the diffraction pattern.

The packing of the ions in the crystal of **1** is shown in Fig. 3. The centers of the X_6 rings are arranged according to the law of the face-centered lattice, the rings being packed in a herringbone fashion and the cluster anions occupying two tetrahedral cavities (their centers have the coordinates (1/4, 1/4, 1/4) and (3/4, 3/4, 3/4)). Each $[M_4Q_4(CN)_{12}]^{6-}$ anion is linked to twelve $[(NH_4)_3(H_2O)_3]^{3+}$ rings *via* hydrogen bonds through the cyano groups and each ring is linked to six anions to form a three-dimensional network of hydrogen bonds. The X...N distances are 2.81(1), 2.81(1), and 2.77(1) Å in complexes **1**, **3**, and **4**, respectively.

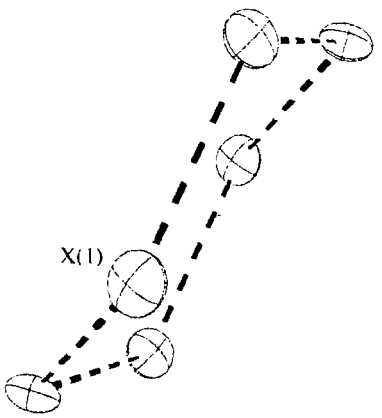

Fig. 2. Structure of the $[(NH_4)_3(H_2O)_3]^{3+}$ cation in compound **1** (the crystallographically independent X(1) position is half-occupied by the nitrogen atom of the NH_4^+ cation and half-occupied by the oxygen atom of the water molecule).

Comparison of the properties of thio-, seleno-, and telluro-bridged cyanide cubane complexes of molybdenum and tungsten

We performed quantum-chemical calculations for molybdenum and tungsten cyanide chalcogen-bridged cubane complexes by the extended Hückel method using the CACAO program.[14] The results of our calculations for the thio, seleno, and telluro complexes $[M_4Q_4(CN)_{12}]$ agree qualitatively with the results of calculations performed previously[15] for cubane M_4S_4 complexes. On the whole, the contribution of the chalcogen atoms to HOMO and LUMO is insignificant. In complexes possessing the symmetry T_d, there is a block of six bonding

molecular orbitals M—M (a_1 + e + t_2) (Fig. 4). The lowering of the symmetry of the cubane fragment to D_{2d} causes splitting of the t_2 level into b_2 + e. For the symmetry D_2, the t_2 level is split into b_1 + b_2 + b_3. The mixed-valence $[M_4Q_4]^{6+}$ complexes (the average formal degree of oxidation of metal is +3.5) have 10 cluster valence electrons and these cluster complexes may be diamagnetic or paramagnetic depending on their symmetry and the environment temperature. The $[M_4Q_4]^{6+}$ cluster fragments in ammonium salts **1—4** prepared in the present work have the symmetry T_d. According to the X-ray diffraction data, the $Cs_5K[W_4S_4(CN)_{12}] \cdot MeOH \cdot 2H_2O$, $K_6[W_4Se_4(CN)_{12}] \cdot 6H_2O$, $Cs_6[Mo_4Te_4(CN)_{12}] \cdot 2H_2O$, and $K_6[W_4Te_4(CN)_{12}] \cdot 5H_2O$ complexes described previously contain distorted $[M_4Q_4]^{6+}$ cluster fragments (see below). Nevertheless, all cyanide cubane complexes are diamagnetic at room temperature or at the temperature of liquid nitrogen. This fact is in good agreement with the known tendency of the atoms of the 4d- and 5d-transition metals to form low-spin compounds and, consequently, compounds with an even number of electrons very often exhibit diamagnetic properties.

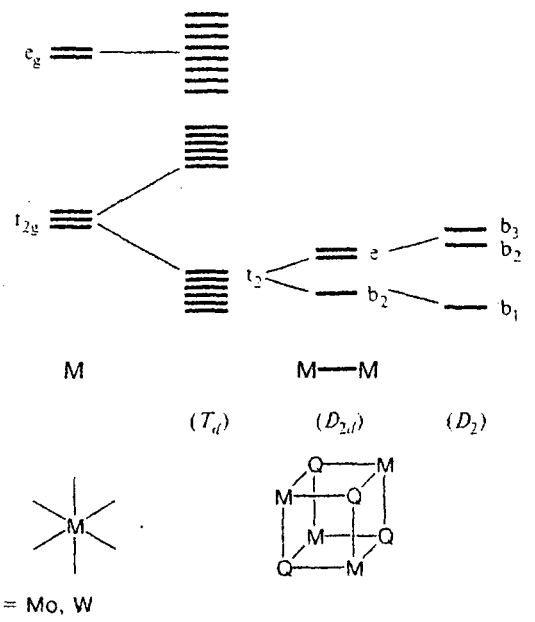

Fig. 4. Scheme of MOs for chalcogen-bridged cubane complexes of molybdenum and tungsten.

The most important geometric parameters of the structurally studied $[M_4Q_4(CN)_{12}]^{6-}$ cluster complexes are given in Table 1. The distinguishing feature of the ammonium salts $(NH_4)_6[M_4Q_4(CN)_{12}] \cdot 6H_2O$ prepared in the present work is the symmetry T_d of the M_4Q_4 cluster core. The symmetry of the M_4Q_4 core in all other salts is lower, the M_4 tetrahedra being distorted to a larger extent than the M_3Q tetrahedra. The degree of deviation of the geometry of the M_4 cluster core from the ideal tetrahedron varies with the nature of M and Q. Thus, this distortion is insignificant in the case of W_4Se_4, is noticeably larger in the case of W_4S_4, and is pronounced in M_4Te_4. The dependence of the distortion of the tetrahedron on the symmetry of the crystallographic position of the cluster anion is not evident. Thus, the degree of distortion of the W_4Se_4 core in the potassium salt is small although the symmetry of the position is low. Interestingly, the volumes of the W_4 tetrahedra and the average W—W and W—S bond lengths in the complexes $Cs_5K[W_4S_4(CN)_{12}] \cdot MeOH \cdot 2H_2O$ [11] (in which the W—W bond lengths vary within 0.104(1) Å) and $(NH_4)_6[W_4S_4(CN)_{12}] \cdot 6H_2O$ (which has the crystallographic symmetry T_d) are identical. On going from M = Mo to M = W, the M—M bond length changes only slightly, whereas the M—M bond lengths and the volumes of the M_4 tetrahedra in the series of the complexes with thio, seleno, and telluro bridges increase substantially.

Electrochemical properties. Chalcogenide cubane complexes of molybdenum and tungsten are characterized by stepwise redox conversions.[1,3] According to the data of cyclic voltammetry, two-step reversible reduction of the $[M_4Q_4(CN)_{12}]^{6-}$ complexes yielding the $[M_4Q_4(CN)_{12}]^{7-}$ and $[M_4Q_4(CN)_{12}]^{8-}$ anions occurs in aqueous solutions:

$$[M_4Q_4(CN)_{12}]^{6-} + e^- \rightleftharpoons [M_4Q_4(CN)_{12}]^{7-},$$

$$[M_4Q_4(CN)_{12}]^{7-} + e^- \rightleftharpoons [M_4Q_4(CN)_{12}]^{8-}.$$

In the most reduced $[M_4Q_4(CN)_{12}]^{8-}$ complexes, 12 cluster valence electrons account for the M—M bonds in

Table 1. Selected geometric parameters of the M_4Q_4 cluster cores

Cluster	Symmetry	M_4 volume /Å^3	M—M (aver.)	Δ(M—M)	M—Q (aver.)	Δ(M—Q)
			Å			
$(NH_4)_6[Mo_4S_4(CN)_{12}] \cdot 6H_2O$ (**1**)	T_d	2673	2.831	0	2.377	0
$(NH_4)_6[W_4S_4(CN)_{12}] \cdot 6H_2O$ (**3**)	T_d	2711	2.845	0	2.395	0
$Cs_5K[W_4S_4(CN)_{12}] \cdot MeOH \cdot 2H_2O$	C_1	2710	2.845	0.104(1)	2.394	0.006(1)
$K_6[W_4Se_4(CN)_{12}] \cdot 6H_2O$	C_{2v}	2828	2.884	0.013(1)	2.506	0.006(3)
$(NH_4)_6[W_4Se_4(CN)_{12}] \cdot 6H_2O$ (**4**)	T_d	2849	2.891	0	2.507	0
$Cs_6[Mo_4Te_4(CN)_{12}] \cdot 2H_2O$	C_1	3067	2.966	0.195(6)	2.678	0.045(6)
$K_6[W_4Te_4(CN)_{12}] \cdot 5H_2O$	C_1	3055	2.962	0.215(2)	2.686	0.030(2)

Table 2. Voltammetric characteristics ($E_{1/2}$) of the molybdenum and tungsten cubane complexes

Complex	$E_{1/2}$/V	
	$[M_4Q_4]^{6+/5+}$	$[M_4Q_4]^{5+/4+}$
$[Mo_4S_4(CN)_{12}]^{6-}$	1.18	0.23
$[Mo_4Se_4(CN)_{12}]^{6-}$	1.03	0.18
$[Mo_4Te_4(CN)_{12}]^{6-}$	0.81	−0.03
$[W_4S_4(CN)_{12}]^{6-}$	0.77	−0.30
$[W_4Se_4(CN)_{12}]^{6-}$	0.69	−0.34
$[W_4Te_4(CN)_{12}]^{6-}$	0.56	−0.40

Note. All potentials are given relative to the standard hydrogen potential; 10^{-3} mol L^{-1} solutions of the complex in 0.1 *M* Na_2SO_4; the scan rate was 100 mV s^{-1}.

Table 3. Electronic absorption spectra of the complexes in water

Complex	λ_{max}/nm (ε/L mol^{-1} cm^{-1})
$[Mo_4S_4(CN)_{12}]^{6-}$	315 (12500), 400* (2950), 490* (1060), 660 (590)
$[Mo_4Se_4(CN)_{12}]^{6-}$	340 (9680), 460* (1950), 530,* 690 (310)
$[Mo_4Te_4(CN)_{12}]^{6-}$	390* (4500), 520* (1780), 950 (200)
$[W_4S_4(CN)_{12}]^{6-}$	300, 365.* 460* (1490), 790 (390)
$[W_4Se_4(CN)_{12}]^{6-}$	314 (15500), 385* (4790), 490* (1250), 850 (375)
$[W_4Te_4(CN)_{12}]^{6-}$	357 (8000), 382,* 474* (3140), 869 (440)

* Shoulder.

the M_4 tetrahedra. This corresponds to complete filling of the six highest bonding molecular orbitals (the so-called electron-precise clusters). The data of cyclic voltammetry for the molybdenum and tungsten cyanide cubane complexes are given in Table 2. The potentials of the redox reactions depend strongly on the nature of the metal and chalcogen atoms. Thus, the potentials of the redox conversions for both the molybdenum and tungsten complexes decrease substantially on going from the thio to the seleno and telluro complexes. Therefore in the S—Se—Te series, the electron-deficient $[M_4Q_4(CN)_{12}]^{6-}$ complexes are more stable than the electron-precise anionic cluster complexes $[M_4Q_4(CN)_{12}]^{8-}$. All potentials for the tungsten cyanide cubane complexes under study are substantially lower than the corresponding values found for the molybdenum complexes, which agrees with the known higher stability of the high-valence tungsten compounds compared to the corresponding molybdenum compounds. Analogously, in the case of the heterometallic cubane complexes containing simultaneously molybdenum and tungsten, *viz.*, $[W_3MoQ_4(H_2O)_9]^{4+/5+/6+}$ (Q = S or Se), the $E_{1/2}$ values for both the $[W_3MoQ_4(H_2O)_9]^{6+}/[W_3MoQ_4(H_2O)_9]^{5+}$ and $[W_3MoQ_4(H_2O)_9]^{5+}/[W_3MoQ_4(H_2O)_9]^{4+}$ pairs are 500—600 mV lower than the corresponding potentials for the molybdenum complexes $[Mo_4Q_4(H_2O)_9]^{4+/5+/6+}$ (Q = S or Se).[16] In the case of the octahedral complexes $[M_6S_8(PEt_3)_6]^{-1/0/+1}$ (M = Mo or W), these potentials are also 200—300 mV lower for the tungsten complexes.[17]

Electronic absorption spectra. The intense absorption bands in the UV region of the electronic spectra of complexes **1**—**4** and of the telluride complexes $[M_4Te_4(CN)_{12}]^{6-}$ (Table 3) are identical in positions and intensities with those in the spectra of mononuclear octacyanomolybdates and tungstates. These bands are assigned to charge transfer from the ligand (CN) to the metal atoms.[18] The low-energy low-intensity absorption bands in the visible region of the spectra are predominantly associated with transitions in the M_4Q_4 chromophores. The positions of these bands depend on the nature of the metal and chalcogen atoms. In the visible regions of the spectra of the molybdenum and tungsten cubane complexes of the S—Se—Te series, a characteristic red shift is observed for the lowest-energy absorption band. The red shift is also observed for this band on going from Mo to W in the case of the thio and seleno complexes, unlike the telluro complexes. The red shift in the electronic absorption spectra has also been observed in the case of the molybdenum cubane aqua complexes and the triangular molybdenum and tungsten cyanide complexes $[M_3Q_4(CN)_9]^{5-}$ on going from S to Se.[13]

The preparation of the $K_8[Mo_4S_4(CN)_{12}] \cdot 4H_2O$ salt containing the $[Mo_4S_4]^{4+}$ cluster fragment was reported.[19] However, the electronic absorption spectra of this compound coincide with our data for the $(NH_4)_6[Mo_4S_4(CN)_{12}] \cdot 6H_2O$ complex and are characteristic of $[Mo_4S_4]^{6+}$ clusters. It is often difficult to unambiguously determine the composition of cyanide cluster anions in potassium salts due to disorder of the cationic positions.[10—12] Besides, data of elemental analysis for potassium were not reported in Ref. 19. We believe that there is a need to refine the crystal structure of the above-mentioned potassium salt.

Experimental

Reagents of analytical grade were used. The polymeric compounds $M_3Q_7Br_4$ (M = Mo or W; Q = S or Se) were prepared by heating stoichiometric amounts of the metal, chalcogen, and bromine.[20,21] Elemental analysis was performed at the Laboratory of Microanalysis of the 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 and in Nujol mulls. The electronic absorption spectra in the 300—1100 nm region were recorded on a Shimadzu UV-1202 spectrophotometer. The magnetic susceptibility was measured at ~20 °C and at the temperature of liquid nitrogen using the Faraday method. The suitability of the single crystals was proved by comparing the theoretically calculated diffraction patterns with those obtained experimentally (Philips APD 1700 diffractometer, Cu-Kα radiation, 2θ = 5—60°). The cyclic

Table 4. Crystallographic characteristics and details of X-ray diffraction studies for compounds **1**, **3**, and **4**

Parameter	**1**	**3**	**4**
Molecular formula	$C_{12}H_{36}Mo_4N_{18}O_6S_4$	$C_{12}H_{36}N_{18}O_6S_4W_4$	$C_{12}H_{36}N_{18}O_6Se_4W_4$
Molecular weight	1040.59	1392.23	1579.83
System	Cubic	Cubic	Cubic
Space group*; Z	$Pn\bar{3}m$; 2	$Pn\bar{3}m$; 2	$Pn\bar{3}m$; 2
a/Å	12.159(1)	12.1800(9)	12.219(1)
V/Å^3	1797.6(3)	1806.9(2)	1824.3(3)
d_{calc}/g cm^{-3}	1.922	2.559	2.876
μ/mm^{-1}	1.651	12.976	16.614
Crystal dimensions/mm	0.15×0.15×0.15	0.16×0.16×0.16	0.16×0.15×0.12
Diffractometer	CAD4 Enraf-Nonius	STOE STADI4	CAD4 Enraf-Nonius
Radiation (λ/Å)	Mo-Kα (0.7107)	Mo-Kα (0.7107)	Mo-Kα (0.7107)
Number of measured/ independent reflections	1194/315	1706/350	1227/314
R_{int}	0.0497	0.0331	0.0436
R_1; wR_2 for $F > 4\sigma(F)$	0.0382; 0.1082	0.0281; 0.0651	0.0233; 0.0438
R_1; wR_2 for all reflections	0.0850; 0.1122	0.0371; 0.0683	0.0588; 0.0457
GOOF for all reflections	0.967	1.311	0.726

* The origin of coordinates is located in the inversion center ($\bar{3}m$) at a (1/4, 1/4, 1/4) distance from the point with the highest symmetry $\bar{4}3m$.

Table 5. Principal bond lengths (d) and bond angles (ω) in the structures of compounds **1**, **3**, and **4**

Complex **1**		Complex **3**		Complex **4**	
Bond	d/Å	Bond	d/Å	Bond	d/Å
Mo(1)—Mo(1)^a	2.831(3)	W(1)—W(1)^a	2.845(1)	W(1)—W(1)^a	2.891(2)
Mo(1)—S(1)	2.377(4)	W(1)—S(1)	2.395(3)	W(1)—Se(1)	2.508(2)
Mo(1)—C(1)	2.13(1)	W(1)—C(1)	2.17(1)	W(1)—C(1)	2.17(1)
C(1)—N(1)	1.18(2)	C(1)—N(1)	1.14(1)	C(1)—N(1)	1.16(2)
Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
S(1)—Mo(1)—Mo(1)^b	53.46(8)	S(1)—W(1)—W(1)^b	53.56(5)	Se(1)—W(1)—W(1)^b	54.79(3)
S(1)—Mo(1)—Mo(1)^c	101.3(1)	S(1)—W(1)—W(1)^c	101.44(7)	Se(1)—W(1)—W(1)^c	102.99(4)
S(1)^b—Mo(1)—S(1)	104.6(1)	S(1)^b—W(1)—S(1)	104.78(8)	Se(1)^b—W(1)—Se(1)	106.53(4)
C(1)—Mo(1)—Mo(1)^a	139.2(2)	C(1)—W(1)—W(1)^a	139.1(2)	C(1)—W(1)—W(1)^a	138.7(2)
C(1)—Mo(1)—Mo(1)^b	96.2(3)	C(1)—W(1)—W(1)^b	96.1(2)	C(1)—W(1)—W(1)^b	95.4(4)
C(1)—Mo(1)—S(1)^b	85.8(2)	C(1)—W(1)—S(1)^b	85.6(2)	C(1)—W(1)—Se(1)^b	84.0(2)
C(1)—Mo(1)—S(1)^a	162.5(4)	C(1)—W(1)—S(1)^a	162.5(3)	C(1)—W(1)—Se(1)^a	161.6(4)
C(1)—Mo(1)—C(1)^d	81.0(5)	C(1)—W(1)—C(1)^d	81.1(4)	C(1)—W(1)—C(1)^d	82.2(5)
Mo(1)—S(1)—Mo(1)^a	73.1(2)	W(1)—S(1)—W(1)^a	72.9(1)	W(1)—Se(1)—W(1)^a	70.42(6)
N(1)—C(1)—Mo(1)	178(1)	N(1)—C(1)—W(1)	178.5(9)	N(1)—C(1)—W(1)	179(1)

$^{a-d}$ The coordinates of the atoms are generated from those of the basis atoms by the symmetry operations: ^{a} $-x+1/2$, $-y+1/2$, z; ^{b} $-x+1$, y, $-z+1/2$; ^{c} x, $-y+1/2$, $-z+1/2$; ^{d} y, $-z+1/2$, $-x+1/2$.

voltammetric measurements were carried out on a CV-50W instrument at ~20 °C in aqueous solutions containing Na_2SO_4 (0.1 mol L^{-1}) with a scan rate of 100 mV s^{-1}. The solutions (the concentrations were 10^{-3} mol L^{-1}) were degassed with a stream of N_2. The reference electrode (Ag/AgCl) was calibrated against the ferrocyanide/ferricyanide pair. All potentials are given relative to the standard hydrogen electrode.

Synthesis of the $(NH_4)_6[M_4(\mu_3\text{-}Q)_4(CN)_{12}]\cdot 6H_2O$ salts (M = Mo or W; Q = S or Se) (general procedure). A mixture of powders of $M_3Q_7Br_4$ (1.00 g) and KCN (1.00 g) was heated in an evacuated sealed glass tube at 430 °C for 48 h. The reaction product was refluxed with water (40 mL). The resulting dark-brown solution was filtered and slowly concentrated to 10 mL at 80 °C. Then MeOH was added until the formation of the precipitate ceased and the solution decolorized. The precipitate was washed with a 60% aqueous MeOH solution and diethyl ether. Dark octahedral crystals of ammonium salts were obtained by slow concentration (5—7 days) of the solution of the resulting precipitate in a 1 *M* $AcONH_4$ solution (10 mL).

Hexaammonium dodecacyanotetrathiotetramolybdate(*Mo—Mo*) hexahydrate, $(NH_4)_6[Mo_4S_4(CN)_{12}]\cdot 6H_2O$ (1). The yield was 20%. Found (%): C, 13.65; H, 3.33; N, 24.21; S, 12.45.

$C_{12}H_{36}Mo_4N_{18}O_6S_4$. Calculated (%): C, 13.85; H, 3.49; N, 24.23; S, 12.32. IR, ν/cm^{-1}: 2139 (CN).

Hexaammonium dodecacyanotetraselenotetramolybdate-(*Mo—Mo*) hexahydrate, $(NH_4)_6[Mo_4Se_4(CN)_{12}] \cdot 6H_2O$ (2). The yield was 18%. Found (%): C, 11.54; H, 3.05; N, 19.88. $C_{12}H_{36}Mo_4N_{18}O_6Se_4$. Calculated (%): C, 11.74; H, 2.95; N, 20.53. IR, ν/cm^{-1}: 2133 (CN).

Hexaammonium dodecacyanotetrathiotetratungstate(*W—W*) hexahydrate, $(NH_4)_6[W_4S_4(CN)_{12}] \cdot 6H_2O$ (3). The yield was 41%. Found (%): C, 10.21; H, 2.59; N, 18.02; S, 9.20. $C_{12}H_{36}N_{18}O_6S_4W_4$. Calculated (%): C, 10.35; H, 2.61; N, 18.11; S, 9.21. IR, ν/cm^{-1}: 2140 (CN).

Hexaammonium dodecacyanotetraselenotetratungstate(*W—W*) hexahydrate, $(NH_4)_6[W_4Se_4(CN)_{12}] \cdot 6H_2O$ (4). The yield was 25%. Found (%): C, 9.10; H, 2.41; N, 15.63. $C_{12}H_{36}N_{18}O_6Se_4W_4$. Calculated (%): C, 9.12; H, 2.30; N, 15.96. IR, ν/cm^{-1}: 2133 (CN).

X-ray diffraction study. The crystallographic characteristics and details of X-ray diffraction studies for **1**, **3**, and **4** are given in Table 4. The black single crystals have the shape of almost regular octahedra. The intensities of reflections were measured using the standard $\theta/2\theta$ scanning technique in the range of indices $0 \le h \le 14$, $0 \le k \le 14$, $0 \le l \le 14$ to $2\theta_{max} = 50°$ (**1** and **4**) and to $2\theta_{max} = 51°$ (**3**). The absorption corrections were applied using azimuth scanning curves (**1** and **4**) and with the use of integration based on the dimensions and habitus of the crystal (**3**). The structures were solved by the direct method and refined anisotropically by the full-matrix least-squares method using the SHELX97 program package.[22] We failed to locate the hydrogen atoms. The symmetrically independent bond lengths and bond angles are given in Table 5. The atomic coordinates, the thermal parameters, and the complete list of the bond lengths and bond angles were deposited with the Cambridge Structural Database.

We thank M. N. Sokolov for performing cyclic voltammetric measurements.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 99-03-32788) and INTAS (Grant 96-1256).

References

1. R. H. Holm, *Adv. Inorg. Chem.*, 1992, **38**, 1.
2. I. Dance and K. Fisher, *Prog. Inorg. Chem.*, 1994, **41**, 637.
3. T. Saito, *Adv. Inorg. Chem.*, 1996, **44**, 45.
4. T. Shibahara, *Adv. Inorg. Chem.*, 1991, **37**, 143.
5. T. Shibahara, *Coord. Chem. Rev.*, 1993, **123**, 73.
6. M. Nasreldin, G. Henkel, G. Kampmann, B. Krebs, G. J. Lamprecht, C. A. Routledge, and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1993, 737.
7. W. McFarlane, M. Nasreldin, D. M. Saysell, Z.-S. Jia, W. Clegg, M. R. J. Elsegood, K. S. Murray, B. Moubaraki, and A. G. Sykes, *J. Chem. Soc., Dalton. Trans.*, 1996, 363.
8. P. T. Wood, W. T. Pennington, J. W. Kolis, B. Wu, and C. J. O'Connor, *Inorg. Chem.*, 1993, **32**, 129.
9. S.-F. Lu, J.-Q. Huang, H.-H. Zhuang, J.-Q. Li, D.-M. Wu, Z.-X. Huang, C.-Z. Lu, J.-L. Huang, and J.-X. Lu, *Polyhedron*, 1991, **10**, 2203.
10. V. P. Fedin, I. V. Kalinina, A. V. Virovets, N. V. Podberezskaya, and A. G. Sykes, *J. Chem. Soc., Chem. Comm.*, 1998, 237.
11. V. P. Fedin, I. V. Kalinina, D. G. Samsonenko, Y. V. Mironov, M. N. Sokolov, S. V. Tkachev, A. V. Virovets, N. V. Podberezskaya, M. R. J. Elsegood, W. Clegg, and A. G. Sykes, *Inorg. Chem.*, 1999, **38**, 1956.
12. V. P. Fedin, I. V. Kalinina, A. V. Virovets, N. V. Podberezskaya, I. S. Neretin, and Yu. L. Slovokhotov, *J. Chem. Soc., Chem.Comm.*, 1998, 2579.
13. V. P. Fedin, G. J. Lamprecht, T. Kohzuma, W. Clegg, M. R. J. Elsegood, and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1997, 1747.
14. C. Mealli and D. M. Proserpio, *J. Chem. Educ.*, 1990, **67**, 399.
15. S. Harris, *Polyhedron*, 1989, **8**, 2843.
16. I. J. McLean, R. Hernandez-Molina, M. N. Sokolov, M.-S. Seo, A. V. Virovets, M. R. J. Elsegood, W. Clegg, and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1998, 2557.
17. T. Saito, A. Yoshikawa, T. Yamagata, H. Imoto, and K. Unoura, *Inorg. Chem.*, 1989, **28**, 3588.
18. A. Golebiewski and H. Kowalski, *Theor. Chim. Acta*, 1968, **12**, 293.
19. A. Müller, R. Jostes, W. Eltzner, C.-S. Nie, E. Diemann, H. Bögge, M. Zimmermann, M. Dartmann, U. Reinsch-Vogell, S. Che, S. J. Cyvin, and B. N. Cyvin, *Inorg. Chem.*, 1985, **24**, 2872.
20. V. P. Fedin, M. N. Sokolov, O. A. Gerasko, B. A. Kolesov, V. Ye. Fedorov, A. V. Mironov, D. S. Yufit, Yu. L. Slovokhotov, and Yu. T. Struchkov, *Inorg. Chim. Acta*, 1990, **175**, 217.
21. V. P. Fedin, M. N. Sokolov, K. G. Myakishev, O. A. Gerasko, V. Ye. Fedorov, and J. Macicek, *Polyhedron*, 1991, **10**, 1311.
22. G. M. Sheldrick, *SHELX97. Release 97-2*, Göttingen University, Göttingen (Germany), 1997.

Received April 16, 1999;
in revised form July 14, 1999