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Synthesis and structure of a new octahedral molybdenum thiocyanide cluster complex $K_7[Mo_6(\mu_3\text{-}S)_8(CN)_6] \cdot 8H_2O$

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The new octahedral molybdenum thiocyanide cluster complex $K_7[Mo_6S_8(CN)_6] \cdot 8H_2O$ was synthesized by excision of the cluster core (the reaction of $ZnMo_6S_8$ with a melt of KCN). The structure of the complex was established by X-ray diffraction analysis. The reaction of Mo_6Se_8 with a KCN—KSCN mixture afforded the mixed-ligand cluster anions $[Mo_6(Se,S)_8(CN)_6]^{7-}$. The salt of composition $K_{1.5}Cs_{5.5}[Mo_6Se_{6.8}S_{1.2}(CN)_6] \cdot 8H_2O$ was obtained. The complexes are isostructural to each other and to the selenium analog described previously. The magnetic properties and the electronic and IR spectra were measured and discussed.

Key words: molybdenum, octahedral clusters, Chevreul phases, thiocyanide complexes, excision reactions, crystal structure, X-ray diffraction analysis.

The molecular octahedral molybdenum chalcogenide cluster complexes $[Mo_6(\mu_3\text{-}Q)_8(PEt_3)_6]$ (Q = S or Se) were prepared for the first time by reductive dimerization of trinuclear thio and seleno molybdenum complexes.[1,2] More recently,[3—5] a procedure was developed for the synthesis of such complexes by the replacement of chloride ligands in the cluster core $\{Mo_6(\mu_3\text{-}Cl)_8\}$ of molybdenum dichloride by chalcogenide ligands. The properties of a series of the octahedral chalcogenide cluster complexes $Mo_6Q_8L_6$ (X = S or Se; L are organic ligands, such as PEt_3, py, *etc.*) were surveyed in reviews.[6,7]

Recently, we have demonstrated[8] that the cluster core $\{Mo_6Se_8\}$ can be excised from the polymeric phase $[Mo_6Se_8]_\infty$ in its reaction with a KCN melt giving rise to the soluble anionic molecular complex $[\{Mo_6Se_8\}(CN)_6]^{7-}$. The resulting anion was isolated as the salt $K_7[Mo_6Se_8(CN)_6] \cdot 8H_2O$ (**1**). The structure of salt **1** was established and its selected properties were studied. More recently,[9] these data were confirmed. In addition, the formation of a new polymeric phase of composition $K_6[Mo_6Se_8(CN)_5]$ with the chain structure was observed. The latter contains the cluster anions linked through the bridging CN ligands.

In the present study, we report the results of a search for approaches to the synthesis of the thiocyanide anion $[Mo_6S_8(CN)_6]^{7-}$, the preparation of the salt $K_7[Mo_6S_8(CN)_6] \cdot 8H_2O$, and investigation of the crystal structure and properties of the latter.

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Experimental

Synthesis of $ZnMo_6S_8$ and Mo_6S_8. A specimen of $ZnMo_6S_8$ was prepared by the tube synthesis on heating of a stoichiometric mixture of the elements at 1150 °C for 24 h; Mo_6S_8 was prepared by refluxing $ZnMo_6S_8$ with an HCl solution. Identification of the resulting phases by the X-ray powder diffraction method demonstrated that the experimental data are in good agreement with the data published in the literature.[10,11]

Reaction of Mo_6S_8 with KCN. The reaction of Mo_6S_8 with KCN at 650 °C was accompanied by the formation of the known thiocyanide tetrahedral complex $K_8[Mo_4S_4(CN)_{12}] \cdot 4H_2O$ in low yield. The latter complex was identified based on the characteristic UV spectrum of an aqueous solution,[12] λ/nm: 1124, 658, 500 sh, 397 sh, 315, 270, 219.

Synthesis of $K_7[Mo_6S_8(CN)_6] \cdot 8H_2O$ (2). A mixture of $ZnMo_6S_8$ (3 g, 3.35 mmol) and KCN (1.96 g, 30.15 mmol) was placed in a quartz tube. The tube was evacuated, sealed, and kept at 600 °C for 72 h. The reaction products were washed with water on a glass filter. The green-brown solution was concentrated to 10 mL and cooled. Then MeOH (20 mL) was added. The dark-brown crystals that formed were washed with MeOH (40 mL) and Et_2O (20 mL) and dried in air. Compound **2** was obtained in a yield of 0.961 g (20%). IR (KBr), ν/cm^{-1}: 2095 (C≡N); 1613, 3550 (H_2O). UV (H_2O), λ_{max}/nm: 487. The magnetic properties: $\mu_{eff} = 1.56\ \mu_B$ (300 K) and 1.22 μ_B (77 K).

Reaction of Mo_6Se_8 with a KCN—KSCN mixture. The reaction of Mo_6Se_8 with a KCN—KSCN mixture (the Mo_6Se_8 : KSCN ratio was 1 : 2, 650 °C, 12 h) afforded the mixed-ligand cluster anion $[Mo_6(Se,S)_8(CN)_6]^{7-}$, which was isolated as the salt $K_{1.5}Cs_{5.5}[Mo_6Se_{6.8}S_{1.2}(CN)_6] \cdot 8H_2O$ (**3**) in 50% yield. IR (KBr), ν/cm^{-1}: 2081, 2109 (C≡N). UV (H_2O), λ_{max}/nm: 550.

X-ray diffraction study of $K_7[Mo_6S_8(CN)_6] \cdot 8H_2O$ (2). Single crystals of complex **2** were prepared from an aqueous solution by diffusion of MeOH at 5 °C. X-ray diffraction data were collected on a STOE Stadi4 diffractometer (graphite monochromator, λ(Mo-Kα) = 0.71073 Å, 213 K, $\theta/2\theta$ scanning technique). The crystallographic data and the principal characteristics of the refinement are as follows: molecular formula $C_6H_{16}K_7Mo_6N_6O_8S_8$, molecular weight was 1406.07, cubic system, $a = 15.358(3)$ Å, $V = 3622.3(10)$ Å^3, space group $Fm\bar{3}m$, $Z = 4$, $D_x = 2.578$ g cm^{-3}, $\mu = 3.320$ mm^{-1}; orthogonal-prismatic crystals of dimensions 0.36×0.25×0.22 mm. The absorption correction was applied using three azimuthal scan curves, $T = 0.7883$—0.9984. To check the true symmetry and the Bravais lattice, all reflections were measured ignoring systematic absences in the region $-19 \le h \le 19$, $0 \le k \le 19$, $0 \le l \le 20$ ($2\theta_{max} = 55°$). The intensities of 8936 reflections were measured of which 2247 reflections satisfied observations in the F lattice. Analysis of the systematic absences demonstrated that only 10 reflections violated the F-centering law. Averaging of the intensities in the high-symmetry Laue class $m\bar{3}m$ gave 258 independent reflections with $R_{int} = 0.0280$. The structure was solved by the direct method in the space group $Fm\bar{3}m$ and refined anisotropically by the full-matrix least-squares method using the SHELX-97 program package. The positions of the hydrogen atoms were not revealed. The final reliability factors were as follows: $R_1 = 0.0201$, $wR_2 = 0.0540$ for 246 reflections with $F_{hkl} \ge 4\sigma(F)$, $R_1 = 0.0215$, $wR_2 = 0.0546$, GOOF = 1.279 for all independent reflections.

X-ray powder diffraction study. The compounds synthesized were characterized by the X-ray powder diffraction method. The X-ray patterns were measured on a Philips APD 1700 diffractometer (Cu-Kα radiation, graphite monochromator, $2\theta = 5$—60°, the scan step was 0.02°, accumulation for 1 s) at ~20 °C. The X-ray powder patterns of the compounds synthesized are in good agreement with the data calculated based on the results of the single-crystal study.

Results and Discussion

Recent studies in the field of solid state chemistry demonstrated that excision of the cluster core from polymeric cluster compounds accompanied by the involvement of the former into molecular complexes is a fruitful reaction. We applied this procedure to the synthesis of a series of new molecular chalcocyanide octahedral rhenium(III) complexes $[Re_6Q_8(CN)_6]^{4-}$ (Q = S, Se, or Te), which can be used as building blocks in the synthesis of complex polymeric chalcocyanides of different dimensions. The design of such structures was discussed in the review.[13]

Recently, we have demonstrated[8] that an analogous reaction can be performed with the lowest molybdenum selenide Mo_6Se_8, which is a parent compound of the family of the Chevreul phases and whose polymeric structure is characterized by the presence of numerous intercluster Mo—Se and Mo—Mo bonds. The reaction of Mo_6Se_8 with a melt of KCN afforded the molecular complex $[Mo_6Se_8(CN)_6]^{7-}$. It was of interest to prepare the sulfur-containing analog.

By analogy with the above-mentioned reaction, the most evident procedure for the synthesis of the thio complex could involve the reaction of the molybdenum sulfide cluster Mo_6S_8 with potassium cyanide. However, it is known that Mo_6S_8 is thermodynamically unstable and decomposes at rather low temperatures (~470 °C).[11] Hence, Mo_6S_8 is generally synthesized by the low-temperature reactions of the ternary phases MMo_6S_8 (M = Zn, Ni, or other metals) with hydrochloric acid according to the following scheme

$$MMo_6S_8 + 2\ HCl = Mo_6S_8 + H_2 + MCl_2.$$

Therefore, the low thermal stability of the starting phase Mo_6S_8 may be an unfavorable factor in the reaction with a melt of KCN, which requires higher temperature. The experimental test confirmed our concerns. Thus this reaction did not give rise to the octahedral anion $[Mo_6S_8(CN)_6]^{7-}$ in a noticeable amount; instead, the known[12] compound $K_8[Mo_4S_4(CN)_{12}] \cdot 4H_2O$ was obtained in low yield.

Taking into account the experimental results, we chose thermodynamically stable ternary sulfide $ZnMo_6S_8$ for the synthesis of $[Mo_6S_8(CN)_6]^{7-}$. The reaction of this sulfide with KCN afforded the compound $K_7[Mo_6S_8(CN)_6] \cdot 8H_2O$ in moderate yield. The latter appeared to be isostructural to the selenium analog prepared previously. The formation of the anion $[Mo_6S_8(CN)_6]^{7-}$ from $ZnMo_6S_8$ was accompanied by formal oxidation of the cluster core according to the reaction $\{Mo_6S_8\}^{2-} - e^- \rightarrow \{Mo_6S_8\}^{1-}$ as a result of which compound **2** acquired the paramagnetic properties (21 e$^-$ per Mo_6 cluster, $\mu_{eff} = 1.56\ \mu_B$ at 300 K).

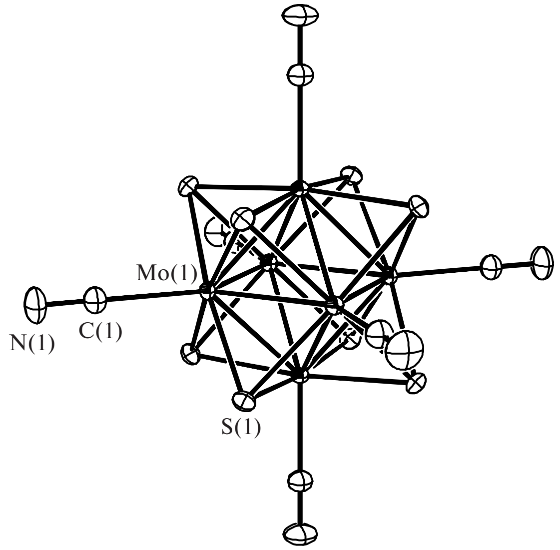

Fig. 1. The cluster anion in the structure of $K_7[Mo_6S_8(CN)_6] \cdot 8H_2O$ (**2**) (the thermal ellipsoids are drawn at the 50% probability level).

Crystal structure. The structure of the cluster anion of compound **2** (Fig. 1) is analogous to that of the selenium-containing analog and is typical of other octahedral complexes of the $\{M_6Q_8L_6\}$ type. The Mo_6 octahedron is surrounded by eight μ_3-S ligands forming the S_8 cube. Each Mo atom is coordinated by the linear CN ligand through the C atom. The anion occupies the position with the highest crystallographic symmetry O_h. The Mo—Mo distances in molecule **2** (2.6656(9) Å) are somewhat shorter than those in molecule **1** (2.700(3) Å).

It is of interest to compare the Mo—Mo bond lengths in molecule **2** with those found in other compounds containing the cluster core $\{Mo_6S_8\}$. In the structure of the Chevreul phase Mo_6S_8, the Mo_6 octahedron is substantially distorted and possesses two types of Mo—Mo bond lengths (2.698 and 2.862 Å.).[11] These values are substantially larger than the corresponding bond lengths in molecule **2**. Comparison of molecule **1** with Mo_6Se_8 revealed the same regularity.[8] The presence of the second metal in Chevreul phases can lead to shortening of the Mo—Mo bonds, as was observed, for example, in $Cu_{2.94}Mo_6S_8$ (2.659—2.681 Å).[11] However, the Mo—Mo bonds in the latter structure are also, on the average, longer, than those in molecule **2**.

The neutral complexes $[Mo_6S_8(PR_3)_6]$[7] provide another example of compounds based on $\{Mo_6S_8\}$. The Mo_6 octahedron in the latter complexes is virtually nondistorted and the metal—metal bond length varies depending on the nature of the hydrocarbon radical R: 2.635—2.637 Å for $R_3 = Me_3$, 2.662—2.664 Å for $R_3 = Et_3$ (close to the value found in molecule **2**), and 2.678—2.694 Å for $R_3 = Me_2(C_6H_5)$.

In the crystal of **2** (Fig. 2), like in isostructural selenium-containing analog **1**, the cluster anions form the cubic close packing, whereas the K^+ cations and water molecules are disordered. In the crystal structure, the cations occupy two positions denoted as K(1) and K(2). The positions of the first type, *viz.*, K(1), are located in the octahedral cavities of the close packing, whereas the positions of the K(2) type form tetrahedra inside the tetrahedral cavities. Both cationic positions are occupied only partially. The O atoms of the H_2O molecules occupy two types of positions denoted as O(1) and O(2). The O(1) position is located at the center of the K_4 tetrahedron and the O(2) position is disordered over two sites about the position with the coordinates 1/2, 3/4, 3/4.

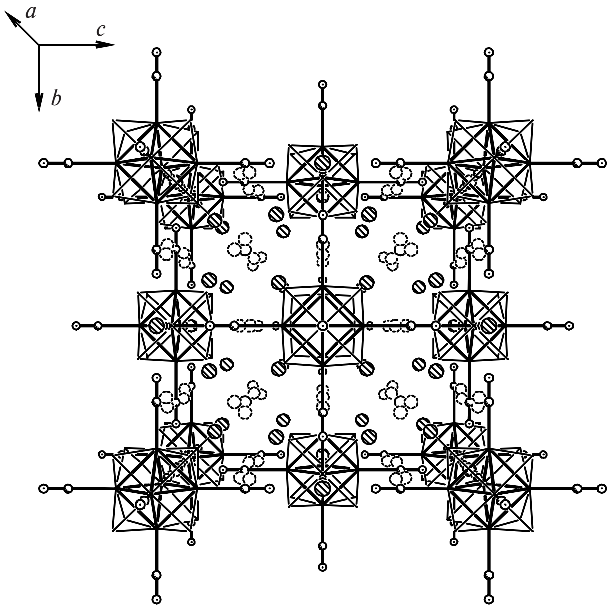

Fig. 2. Crystal packing of $K_7[Mo_6S_8(CN)_6] \cdot 8H_2O$ (**2**). The disordered positions of the O atoms of the H_2O molecules are indicated by dashed lines.

Since the thio- and selenium-containing analogs $K_7[Mo_6Q_8(CN)_6] \cdot 8H_2O$ (Q = S or Se) are isostructural, compounds of this type with mixed (S, Se) ligands can exist. We tested this assumption experimentally. It was found that the reaction of Mo_6Se_8 with a KCN—KSCN mixture afforded the mixed-ligand cluster anions $[Mo_6(Se,S)_8(CN)_6]^{7-}$. The salt of composition $K_{1.5}Cs_{5.5}[Mo_6Se_{6.8}S_{1.2}(CN)_6] \cdot 8H_2O$ (**3**) was obtained and its structure was established. Salt **3** appeared to be analogous to those of the sulfur- and selenium-containing analogs (Table 1). An increase in the unit cell parameter compared to that for the selenium-containing analog is attributed to the presence of the bulky cesium ions.

A knowledge of the electronic structure of the complex is useful in discussing the observed magnetic and electronic properties. Since the electronic structure of complex **3** is unknown, the data obtained for its analogs can be invoked. Such calculations were carried out for the neutral molecular complexes $[Mo_6Q_8(PH_3)_6]$ (Q = S or Se) containing 20 electrons per Mo_6 cluster.[14] These studies demonstrated that the frontier molecular orbitals

Table 1. Crystallographic data for $K_7[Mo_6Se_8(CN)_6] \cdot 8H_2O$ (**1**), $K_7[Mo_6S_8(CN)_6] \cdot 8H_2O$ (**2**), and $K_{1.5}Cs_{5.5}[Mo_6Se_{6.8}S_{1.2}(CN)_6] \cdot 8H_2O$ (**3**)

Parameter	**1**	**2**	**3**
Empirical formula	$C_6H_{16}K_7Mo_6N_6O_8Se_8$	$C_6H_{16}K_7Mo_6N_6O_8S_8$	$C_6H_{16}Cs_{4.5}K_{1.5}Mo_6N_6O_8S_{1.2}Se_{6.8}$
Molecular weight	1781.27	1406.07	2240.90
Color of the crystal	Dark-blue	Brown	Dark-blue
Crystal habitus	Cube	Prism	Octahedron
Crystal system	Cubic	Cubic	Cubic
Space group	$Fm\bar{3}m$	$Fm\bar{3}m$	$Fm\bar{3}m$
a/Å	15.552(2)	15.358(3)	16.092(4)
V/Å^3	3762	3622	4167

Table 2. Atomic coordinates ($\times 10^4$), occupancies (f), and equivalent thermal parameters (U_{eq}) in the structure of **2**

Atom	Coordinates			f (%)	$U_{eq} \cdot 10^3$ /Å^2
	x	y	z		
Mo(1)	1227(1)	0	0	100	12(1)
S(1)	1129(1)	1129(1)	−1129(1)	100	17(1)
K(1)	5000	0	0	69.1	27(2)
K(2)	6452(1)	6452(1)	6452(1)	78.8	84(1)
C(1)	2663(5)	0	0	100	23(2)
N(1)	3401(5)	0	0	100	37(2)
O(1)	2500	2500	−2500	100	43(3)
O(2)	5000	7340(6)	7340(6)	50	47(5)

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

Bond	d/Å	Bond	d/Å
Mo(1)—Mo(1)$^{\#1}$	2.6656(9)	K(1)—N(1)	2.456(7)
Mo(1)—S(1)	2.4565(12)	C(1)—N(1)	1.133(11)
Mo(1)—C(1)	2.204(8)	O(1)—K(2)$^{\#2}$	2.788(3)

Note. The atoms generated from the basis atoms by the symmetry operations: $^{\#1}$ z, x, y; $^{\#2}$ $-x + 1, -y + 1, z - 1$.

(HOMO and LUMO) have a pronounced mixed Mo(d)/Q(p) character, the S(3p) or Se(4p) orbitals making the major contibutions to HOMO. This mixing of MO is attributed to the fact that the energy levels of the atomic orbitals of molybdenum are close to those of chalcogens.

Based on the assumption that the complexes $[Mo_6Q_8(CN)_6]^{7-/6-}$ (Q = S or Se) have analogous electronic structures, the electronic levels in the 20 electronic complexes $Mo_6Q_8(CN)_6]^{6-}$ should be similar to those found in the isovalent complexes $[Mo_6Q_8(PH_3)_6]$. In the reduced complex $[Mo_6S_8(CN)_6]^{7-}$ containing 21 e^- per cluster, an additional unpaired electron is localized on the $17e_g$ orbital. This assumption does not contradict the experimental data. Thus, the electronic spectrum of $K_7[Mo_6S_8(CN)_6] \cdot 8H_2O$ has an intense band at 487 nm, which is similar to an analogous band in the spectrum of $[Mo_6S_8(PH_3)_6]$ assigned to the $26t_{1u} \rightarrow 17e_g$ transition.

Previously,[8] it has been found that the anion $[Mo_6Se_8(CN)_6]^{7-}$ can undergo one-electron oxidation to form the anion $[Mo_6Se_8(CN)_6]^{6-}$. The thio complex $[Mo_6S_8(CN)_6]^{7-}$ can also be oxidized. Thus the addition of bromine water led to a substantial change in the UV spectrum (the band at 487 nm in the electronic spectrum disappeared). In the future, we plan to perform crystallization of compounds containing the oxidized anion $[Mo_6S_8(CN)_6]^{6-}$.

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