FULL PAPER

Octahedral Molybdenum Cluster Cyanide Complexes with Selenide and Halide Ligands in the Cluster Core

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Two new octahedral molybdenum cluster cyanide complexes with mixed selenide/halide ligands in the cluster core, $Cs_5[Mo_6Se_{3.6}Cl_{4.4}(CN)_6]$ (**1**) and $Cs_5[Mo_6Se_{3.4}Br_{4.6}(CN)_6]$ (**2**), have been synthesized by the reaction of Mo_6Cl_{12} or Mo_6Br_{12} with an aqueous solution of Cs_2Se_3, and then with an aqueous solution of KCN. Both compounds have been characterized by single-crystal X-ray diffraction methods. The com-

pounds are isostructural and crystallize in the trigonal space group $P\bar{3}c1$ with two formula units per unit cell. The unit cell dimensions at 153 K are $a = 9.8895(9)$ Å, $c = 19.395(3)$ Å, $V = 1642.7(3)$ Å^3 (**1**) and $a = 9.9805(9)$ Å, $c = 19.763(2)$ Å, $V = 1704.9(3)$ Å^3 (**2**).

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Introduction

Molybdenum(II) chloride comprising a Mo_6Cl_8 cluster core was discovered over 100 years ago. Complexes with the cluster cores Mo_6Q_8 (Q = S, Se, Te) and Mo_6Y_8 (Y = Cl, Br, I) are now well known,[1−4] and include anionic cyanide complexes.[5−8] Nevertheless, only limited number of complexes with the mixed chalcohalide core $Mo_6Q_xY_{8-x}$ are known. The first such cluster anion, $[(Mo_6SCl_7)Cl_6]^{3-}$, was obtained in 1982.[9] Since then other complexes with one or two halogen atoms substituted by chalcogen atoms have been synthesized. These include the species $[(Mo_6QY_7)Y'_6]^{3-}$ (VEC = 24) and $[(Mo_6QY_7)Y'_6]^{2-}$ (VEC = 23) (Y, Y' = Cl, Br; Q = S, Se),[10,11] $[Et_4N]_3[(Mo_6TeCl_7)Cl_6]$ (VEC = 24),[12] $[Et_4N]_3[(Mo_6Se_2Cl_6)Cl_6]$ (VEC = 23), $[Ph_4P]_2[H_3O]_2[(Mo_6Se_2Cl_6)Cl_6]$ (VEC = 24),[13] $Cs_4[(Mo_6Q_2Br_6)Br_6]$ (VEC = 24),[14] and $Cs_{0.4}K_{0.6}[Et_4N]_{11}[(Mo_6Q_2Br_6)(CN)_6]_3\cdot16H_2O$ (VEC = 24) (Q = S, Se).[14]

Herein we present the syntheses and structure determinations of two new Mo_6 cyanide complexes that possess mixed chalcohalide cluster cores.

Results

Syntheses

The Mo_6S_8 cluster unit may be synthesized from Mo_6Cl_{12} by its reaction with NaSH and NaOBu in refluxing nBuOH/pyridine.[15] This synthesis demonstrates that in

solution the μ_3-halide ligands in the cluster core may be easily substituted by chalcogen ligands. Recently we found that the reaction in water of Mo_6Br_{12} with Cs_2S_3 leads to the formation of the tetrahedral molybdenum polysulfide $Cs_6[Mo_4S_{23.6}]$.[16] However, we find that the reaction of Mo_6Y_{12} (Y = Cl, Br) with Cs_2Se_3 leads to amorphous products that are different from those from the reaction with Cs_2S_3. To discover the structure of these products, we have "excised" the cluster core by treating these solids with KCN in boiling water, and then letting the resultant solutions evaporate. In this way, crystals in the form of hexagonal plates were obtained, and their structures have been determined by X-ray diffraction methods. These reactions take place without cluster decomposition, but with partial substitution of the Y ligands by Se to form $Cs_5[Mo_6Se_{3.6}Cl_{4.4}(CN)_6]$ (**1**) and $Cs_5[Mo_6Se_{3.4}Br_{4.6}(CN)_6]$ (**2**), both of which contain the cluster core $Mo_6Se_xY_{8-x}$. Both compounds are soluble in water, but the resulting solutions are not stable in air. Partial stabilization may be achieved by the addition of KCN to the solutions. Such differences in behavior of S and Se octahedral complexes were recently observed for Mo_6 chalcocyanide complexes. Whereas Mo_6Se_8 reacts with KCN to afford the octahedral $[Mo_6Se_8(CN)_6]^{7-}$ cluster anion,[6] in a similar reaction Mo_6S_8 affords the tetrahedral $[Mo_4S_4(CN)_{12}]^{6-}$ cluster anion.[7]

Structures

The structures of the compounds $Cs_5[Mo_6Se_{3.6}Cl_{4.4}(CN)_6]$ (**1**) and $Cs_5[Mo_6Se_{3.4}Br_{4.6}(CN)_6]$ (**2**) comprise a Mo_6 octahedron residing inside an $(SeY)_8$ pseudo-cube (Figure 1). Packing of the cluster anions in the unit cell is shown in Figure 2. The anions have crystallographically imposed $\bar{3}$ symmetry. As such, Se and Y atoms are disordered over the corners of the cube in an overall ratio

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of 3.6:4.4 for Y = Cl, and 3.4:4.6 for Y = Br. Such disorder is common in $Mo_6Q_xY_{8-x}$ cluster complexes. Important distances are: Mo–Mo, 2.642(1) Å and 2.647(1) Å (**1**), 2.656(1) Å and 2.658(1) Å (**2**); Mo–(Se/Cl), 2.534(2)–2.553(1) Å (**1**); Mo–(Se/Br), 2.595(1)–2.607(1) (**2**) Å. Each Mo atom is further ligated with a terminal cyano ligand; the Mo–C distances are 2.196(9) Å (**1**) and 2.213(7) Å (**2**). The Cs atoms in both structures are surrounded by N and Se/Y atoms, as shown in Figure 3 for compound **1**.
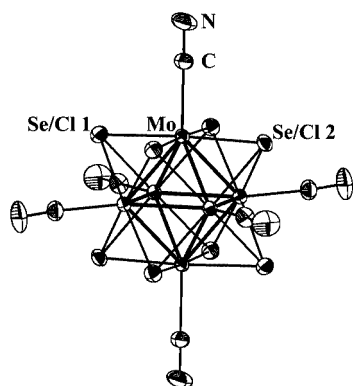

Figure 1. View of the $[Mo_6Se_{3.6}Cl_{4.4}(CN)_6]^{5-}$ anion in **1**; displacement ellipsoids are drawn at the 50% probability level
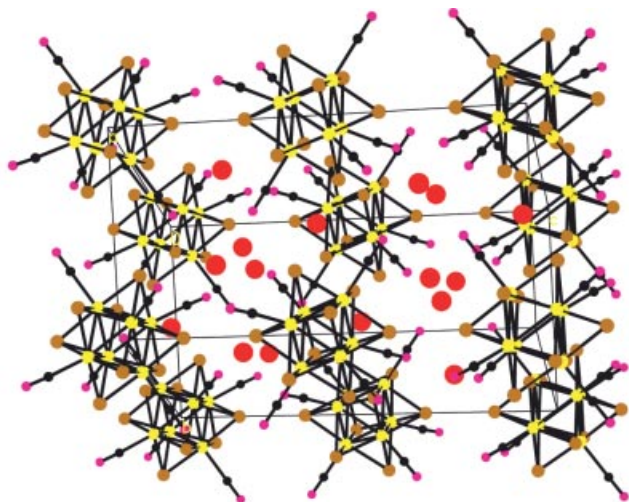

Figure 2. A view of the unit cell of $Cs_5[Mo_6Se_{3.6}Cl_{4.4}(CN)_6]$ (**1**); the yellow circles are Mo, the brown circles are Se/Cl, the black circles are C, the small red circles are N, and the large red circles are Cs atoms
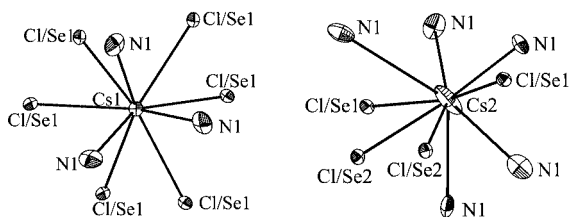

Figure 3. The coordination environments of atoms Cs1 and Cs2 in $Cs_5[Mo_6Se_{3.4}Cl_{4.4}(CN)_6]$ (**1**); displacement ellipsoids are drawn at the 50% probability level

It is useful to compare metrical data as a function of VEC numbers for these complexes. For example, the average Mo–Mo distance is equal to 2.651(1) Å for $Cs_{0.4}K_{0.6}[Et_4N]_{11}[(Mo_6Se_2Br_6)(CN)_6]_3\cdot16H_2O$ (VEC = 24),[14] 2.657(1) Å for compound **2** (VEC = 23.5), 2.700(3) Å for $K_7[(Mo_6Se_8)(CN)_6]\cdot H_2O$ (VEC = 21),[6] and 2.711(2) Å for $(Me_4N)_4K_2[(Mo_6Se_8)(CN)_6]\cdot10H_2O$ (VEC = 20).[6] Although the differences are small, it is clear that the average Mo–Mo distance increases as the VEC value decreases.

Magnetism

Figure 4 displays the temperature dependence of the inverse magnetic susceptibilities of $Cs_5[Mo_6Se_{3.6}Cl_{4.4}(CN)_6]$ (**1**) and $Cs_5[Mo_6Se_{3.4}Br_{4.6}(CN)_6]$ (**2**). Both compounds are paramagnetic. Over the temperature range 78–300 K, the magnetic susceptibility data are well described by the Curie–Weiss law together with a temperature-independent term $N\alpha$ [Equation (1)] where $C = N\beta^2\mu_B^2/3k$.
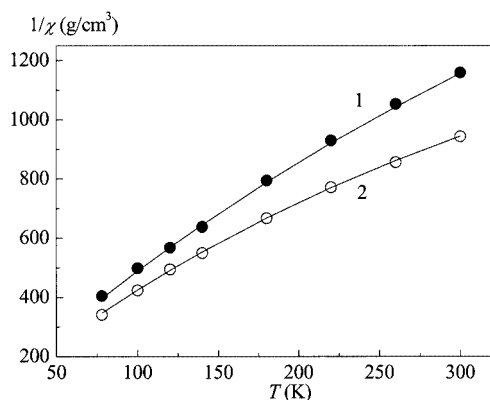
$$\chi = C*(T-\theta)^{-1} + N\alpha \tag{1}$$

Figure 4. The temperature dependence of the inverse magnetic susceptibility of $Cs_5Mo_6Se_{3.6}Cl_{4.4}(CN)_6$ (**1**) and $Cs_5Mo_6Se_{3.4}Br_{4.6}(CN)_6$ (**2**); the solid curves were calculated from Equation (1)

Table 1 presents the parameters derived from the magnetic data. The effective magnetic moments of these complexes of 1.24 μ_B (**1**) and 1.27 μ_B (**2**) are less than the spin-only value of 1.73 μ_B. Hence, only part of the cluster complexes contains unpaired electrons. To estimate the number of clusters, n (Table 1), containing one unpaired electron (% per mol) we used the ratio $n = \mu_{eff}^2/[4S(S+1)]\cdot100\% = \mu_{eff}^2/3\cdot100\%$, where $[4S(S+1)]^{1/2}$ is the electron spin magnetic moment.

Discussion

As we noted previously,[17] crystal-structure determinations provide limited insight into the true nature of the cluster core in compounds such as the present ones in which Q/Y disorder at the cube corners of the $Mo_6Q_xY_{8-x}$ core

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Table 1. Magnetic data

	C [cm³·K/mol]	$-\theta$ [K]	$N\alpha$ [cm³/mol]	μ_{eff} [μ_B]	$n^{[a]}$ (%)
Cs₅Mo₆Se₃.₆Cl₄.₄(CN)₆ (**1**)	0.191	6	0.24·10⁻³	1.24	51
Cs₅Mo₆Se₃.₄Br₄.₆(CN)₆ (**2**)	0.203	3	0.39·10⁻³	1.27	54

[a] Contents of paramagnetic components in **1** and **2**.

can arise in diverse ways. These include cocrystallization of different compounds, geometric disorder, orientational disorder, or a combination of these. Given the magnetic measurements, the simplest, but by no means unique interpretation, is that the compounds Cs₅[Mo₆Se₃.₆Cl₄.₄(CN)₆] (**1**) and Cs₅[Mo₆Se₃.₄Br₄.₆(CN)₆] (**2**) comprise solid solutions of Cs₅[Mo₆Se₃Y₅(CN)₆] and Cs₅[Mo₆Se₄Y₄(CN)₆] (Y = Cl or Br) in an approximate 1:1 ratio.

The substitution of inner halogen ligands by chalcogens in Mo₆ cluster complexes drastically decreases oxidation potentials [for example, +1.38 V for (Mo₆Br₈), +0.55 V for (Mo₆SBr₇), −0.056 V for (Mo₆S₂Br₆)].[14] For clusters that have VEC = 24, additional substitution of inner halogen atoms must lead to a similar cathodic shift because stabilization of species with a lower number of valence electrons occurs. Examples include the present [Mo₆Se₄Y₄(CN)₆]⁵⁻ cluster anions (VEC = 23) and complexes with Mo₆Q₈ cores (VEC = 21, 20).[6,7]

Experimental Section

General: All reagents were used as purchased. Mo₆Br₁₂ was synthesized by the reaction of Mo with Br₂ at 750 °C.[18] Mo₆Cl₁₂ was synthesized by the reaction of Mo with MoCl₅ at 650 °C.[19] Cs₂Se₃ was synthesized by the reaction of Cs with Se in liquid ammonia. FT-IR data were collected with a Bio-Rad Digilab FTS-60 instrument. Microanalyses for C, H, and N were performed by Oneida Research Services, Whitesboro, NY, USA.

Synthesis of Cs₅[Mo₆Se₃.₆Cl₄.₄(CN)₆] (1): Mo₆Cl₁₂ (0.2 g, 0.2 mmol) and Cs₂Se₃ (0.8 g, 1.6 mmol) were placed in degassed boiling water (20 mL) for 1 h. KCN (0.5 g, 7.7 mmol) was then added to the mixture, which was boiled for another hour before filtering. The dark

red-brown filtrate was evaporated to a volume of 5 mL and then cooled to room temperature. The dark crystalline product was filtered off, and was washed twice with cold water (2 mL) until the solution turned violet. The crystals were then washed twice with ethanol (10 mL) and then dried. Yield: 0.25 g (68% based on Mo). Semi-quantitative analysis of the crystals with an EDX-equipped Hitachi S-3500 SEM gave Cs:Mo:Se:Cl = 4.7:6:3.8:4.3. C₆Cl₄.₄Cs₅Mo₆N₆Se₃.₆ (derived from X-ray data) calcd. C 3.9, N 4.6; found C 4.1, N 4.8. IR (KBr): ṽ = 2085 s (ν_{CN}) cm⁻¹.

Synthesis of Cs₅Mo₆Se₃.₄Br₄.₆(CN)₆ (2): The synthesis above was followed with Mo₆Br₁₂ substituted for Mo₆Cl₁₂. Yield: 0.28 g (69%). Examination of the crystals with an EDX-equipped Hitachi S-3500 SEM gave the ratio Cs:Mo:Se:Br = 5.2:6:3.5:4.7. C₆Br₄.₆Cs₅N₆Mo₆Se₃.₄ calcd. C 3.5, N 4.1; found C 3.5, N 4.5. IR (KBr): ṽ = 2092 s (ν_{CN}) (cm⁻¹).

X-ray Crystallography: Single-crystal X-ray diffraction data were collected on Cs₅[Mo₆Se₃.₆Cl₄.₄(CN)₆] (**1**) and Cs₅[Mo₆Se₃.₄Br₄.₆(CN)₆] (**2**) with the use of graphite-monochromotized MoK$_\alpha$ radiation (λ = 0.71073 Å) at 153 K with a Bruker Smart-1000 CCD diffractometer with the operating program SMART.[20] The crystal-to-detector distance was 5.023 cm. Crystal decay was monitored by recollecting 50 initial frames at the end of the data collection. Data were collected in groups of 606 frames, with a scan step of 0.3° in ω and with φ settings of 0°, 90°, 180°, and 270°. The exposure time was 15 s/frame. Cell refinement and data reduction were carried out with the program SAINT.[20] A face-indexed absorption correction was performed numerically with the use of XPREP.[21] The program SADABS[20] was then employed to make incident beam and decay corrections. Both structures were solved by direct methods, by means of SHELXS of the SHELXL[21] suite of programs, and were refined by full-matrix least-squares techniques.[21] Both structures were standardized through the use of the program TIDY.[22] Cs₅[Mo₆Se₃.₆Cl₄.₄(CN)₆] (**1**) displays Se:Cl disorder. The Se:Cl occupancy values at each of the two crystallo-

Table 2. Crystal data and structure refinement details for Cs₅[Mo₆Se₃.₆Cl₄.₄(CN)₆] (**1**) and Cs₅Mo₆Se₃.₄Br₄.₆(CN)₆ (**2**)

	1	**2**
Empirical formula	C₆Cl₄.₄Cs₅Mo₆N₆Se₃.₆	C₆Br₄.₆Cs₅N₆Mo₆Se₃.₄
Formula mass [g/mol]	1837.42	2032.36
a [Å]	9.8895(9)	9.9805(9)
c [Å]	19.395(3)	19.763(3)
V [Å³]	1642.7(3)	1704.9(3)
$\rho_{calcd.}$ [g/cm³]	3.715	3.959
Space group	$P\bar{3}c1$	$P\bar{3}c1$
Z	2	2
μ [cm⁻¹]	120.57	164.31
T [K]	153	153
$R_1(F)$ [$F_o^2 > 2\sigma(F_o^2)$][a]	0.0466	0.0467
$R_w(F^2)$[b]	0.1114	0.106

[a] $R_1(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $Rw(F_o^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (0.04F_o^2)^2$ for $F_o^2 > 0$; $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 \leq 0$.

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graphically independent sites were refined. The results were: Se(1):Cl(1) = 0.472(8):0.528(8); Se(2):Cl(2) = 0.393(14):0.607(14). The position of the Cs2 atom in **2** is disordered over two symmetry-equivalent positions, the refinement of the occupancy value converged to 0.456(4). These occupancy values lead to the composition $Cs_{4.74(9)}[Mo_6Se_{3.62(3)}Cl_{4.38(3)}(CN)_6]$. The occupancy of atom Cs2 was set to 0.5 in subsequent refinements; this had no significant effect on the final metrical data. Given the hazards of establishing compositions through the refinement of X-ray data[23] we adopt the formula $Cs_5[Mo_6Se_{3.6}Cl_{4.4}(CN)_6]$ for compound **1**. $Cs_5[Mo_6Se_{3.4}Br_{4.6}(CN)_6]$ (**2**) displays Se/Br disorder, but owing to the very similar X-ray scattering powers of Se and Br, no site occupancy refinement was possible. Rather, each site was assumed to contain Se:Br in the ratio 0.425:0.575, as determined from the EDX results. The final results are essentially independent of this ratio. The positions of the Cs1 atoms are well defined in both structures. The disorder of the Cs2 position in compound **2** has been modeled in a somewhat unsatisfactory way by the introduction of atoms Cs2 and "Cs3". Their combined occupancy values converged to 0.49(1) and were set at 0.5. Despite the differences in the Cs occupancy values, we consider the two compounds to be isostructural. Additional experimental details are given in Table 2, and in the crystallographic data files, which have been deposited with FIZ Karlsruhe.[24]

Magnetic Measurements: The magnetic susceptibility measurements on $Cs_5[Mo_6Se_{3.6}Cl_{4.4}(CN)_6]$ (**1**) and $Cs_5[Mo_6Se_{3.4}Br_{4.6}(CN)_6]$ (**2**) were carried out by the Faraday method at 10 kOe over the temperature range 78−300 K. Data were corrected for the diamagnetic contributions of -696×10^{-6} and -737×10^{-6} cm^3/mol for **1** and **2**, respectively.

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[24] Crystallographic data in CIF format for $Cs_5[Mo_6Se_{3.6}Cl_{4.4}(CN)_6]$ (**1**) and $Cs_5[Mo_6Se_{3.4}Br_{4.6}(CN)_6]$ (**2**) have been deposited with FIZ Karlsruhe. Further details of the crystal-structure investigation(s) may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: + 49-7247-808-666; E-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-414112 (**1**) and -414113 (**2**).