Inorg. Chem. **2004**, *43*, 219–226

Inorganic Chemistry
Article

Synthesis and Characterization of Mo_6 Chalcobromides and Cyano-Substituted Compounds Built from a Novel $[(Mo_6Br^i{}_6Y^i{}_2)L^a{}_6]^{n-}$ Discrete Cluster Unit (Y^i = S or Se and L^a = Br or CN)

Stéphane Cordier,[†] Nikolaï G. Naumov,[‡] Diala Salloum,[†] Frédéric Paul,[§] and Christiane Perrin*,[†]

Laboratoire de Chimie du Solide et Inorganique Moléculaire, UMR 6511 CNRS-Université de Rennes 1, Institut de Chimie de Rennes, Avenue du Général Leclerc, 35042 Rennes Cedex, France, Institute of Inorganic Chemistry, SB RAS, Ak. Lavrentiev prosp. 3, Novosibirsk, 630090 Russia, and Laboratoire "Organométalliques et Catalyse: Chimie et Electrochimie Moléculaire", UMR 6509 CNRS-Université de Rennes 1, Institut de Chimie de Rennes, Avenue du Général Leclerc, 35042 Rennes Cedex, France

Received April 28, 2003

The syntheses, crystal structures determined by single-crystal X-ray diffraction, and characterizations of new Mo_6 cluster chalcobromides and cyano-substituted compounds with 24 valence electrons per Mo_6 cluster (VEC = 24), are presented in this work. The structures of $Cs_4Mo_6Br_{12}S_2$ and $Cs_4Mo_6Br_{12}Se_2$ prepared by solid state routes are based on the novel $[(Mo_6Br^i{}_6Y^i{}_2)Br^a{}_6]^{4-}$ (Y = S, Se) discrete units in which two chalcogen and six bromine ligands randomly occupy the inner positions, while the six apical ones are fully occupied by bromine atoms. The interaction of these two compounds with aqueous KCN solution results in apical ligand exchange giving the two first Mo_6 cyano-chalcohalides: $Cs_{0.4}K_{0.6}(Et_4N)_{11}[(Mo_6Br_6S_2)(CN)_6]_3\cdot 16H_2O$ and $Cs_{0.4}K_{0.6}(Et_4N)_{11}[(Mo_6Br_6Se_2)(CN)_6]_3\cdot 16H_2O$. Their crystal structures, built from the original $[(Mo_6Br^i{}_6Y^i{}_2)(CN)^a{}_6]^{4-}$ discrete units, will be compared to those of the two solid state precursors and other previously reported Mo_6 cluster compounds. Their redox properties and ^{77}Se NMR characterizations will be presented. Crystal data: $Cs_4Mo_6Br_{12}S_2$, orthorhombic, *Pbca* (No. 61), $a = 11.511(5)$ Å, $b = 18.772(5)$ Å, $c = 28.381$ Å (5), $Z = 8$; $Cs_4Mo_6Br_{12}Se_2$, *Pbca* (No. 61), $a = 11.6237(1)$ Å, $b = 18.9447(1)$ Å, $c = 28.4874(1)$ Å, $Z = 8$; $Cs_{0.4}K_{0.6}(Et_4N)_{11}[(Mo_6Br_6S_2)(CN)_6]_3\cdot 16H_2O$, *Pm*-3*m* (No. 221), $a = 17.1969(4)$ Å, $Z = 1$; $Cs_{0.4}K_{0.6}(Et_4N)_{11}[(Mo_6Br_6Se_2)(CN)_6]_3\cdot 16H_2O$, *Pm*-3*m* (No. 221), $a = 17.235(5)$ Å, $Z = 1$.

Introduction

The molybdenum octahedral cluster chemistry is based on $[(Mo_6L^i{}_8)L^a{}_6]$ units in which the Mo_6 cluster is face-capped by eight inner ligands (L^i) and additionally bonded to six apical ones (L^a).[1] Such units are stabilized for 24 valence electrons per cluster (VEC). Crystal structures of Mo_6 compounds are built from units that are discrete or interconnected by shared inner and/or apical ligands. Up to now, in Mo_6 solid state chemistry, discrete units have been only found in ternary halides characterized by $[(Mo_6X^i{}_8)X^a{}_6]^{2-}$ anions as for instance in $A_xMo_6X_{14}$ series (A = cation, X = halogen).[2] In these halides, the anionic unit charge is always found to be −2 in relation to the 24 VEC value. The combined use of chalcogen and halogen ligands should give access to the entire series $[(Mo_6X^i{}_{8-x}Y^i{}_x)X^a{}_6]^{n-}$ (Y = chalcogen; $0 < x < 8$; $2 < n < 10$) that could be further involved in coordination chemistry for the design of molecular materials. Particularly of interest will be the $A_y[(Mo_6X_{8-x}Y_x)X_6]$ chalcohalides for which the loaded cation stoichiometry would allow control of the chalcogen/halogen ratio and consequently the anionic charges, contrary to the Mo_6 cluster chalcohalides obtained hitherto by the solution chemistry routes ($(pyH)_3(H_3O)_2[(Mo_6Cl_7S)Cl_6]\cdot 4CH_3OH$,[3] $(pyH)_3[(Mo_6$-

---

* Author to whom correspondence should be addressed. E-mail: christiane.perrin@univ-rennes1.fr.

[†] Laboratoire de Chimie du Solide et Inorganique Moléculaire, Institut de Chimie de Rennes.

[‡] Permanent address: Institute of Inorganic Chemistry, SB RAS.

[§] Laboratoire "Organométalliques et Catalyse: Chimie et Electrochimie Moléculaire", Institut de Chimie de Rennes.

(1) Schäfer, H.; von Schnering, H. G. *Angew. Chem.* **1964**, *76*, 833.

(2) (a) von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1971**, *385*, 75. (b) Healy, P. C.; Kepert, D. L.; Taylor, D.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1973**, 646. (c) Potel, M.; Perrin, C.; Perrin, A.; Sergent, M. *Mater. Res. Bull.* **1986**, *21*, 1239. (d) Böschen, S.; Keller, H.-L. *Z. Kristallogr.* **1992**, *200*, 305. (e) Peppenhorst, A.; Keller, H.-L. *Z. Anorg. Allg. Chem.* **1996**, *622*, 663. (f) Flemstroem, A.; Lidin, S. *Z. Kristallogr.* **2001**, *216*, 41.

10.1021/ic034443q CCC: \$27.50

$Cl_7S)Cl_6]\cdot3pyHCl$,[3] $Cs_3[(Mo_6Cl_7Y)Cl_6]\cdot H_2O$ (Y = S, Se),[4] $(Et_4N)_3[(Mo_6X_7Y)Cl_6]$ (X = Cl, Y = Te and X = Br, Y = S),[5,6] and $(Bu_4N)_2[(Mo_6X_7Y)Cl_6]$ (X = Cl, Y = S, Se and X = Br, Y = S)[6] with one disordered chalcogen per unit or $(Et_4N)_3[(Mo_6Cl_6Se_2)Cl_6]$ and $(Ph_4P)_2(H_3O)_2[(Mo_6Cl_6Se_2)Cl_6]\cdot4CH_3OH$, with two ordered selenium ligands[7]).

Hitherto, the high-temperature synthesis of Mo_6 chalcohalides has led only to pseudobinary compounds built from units interconnected by shared ligands, for instance $Mo_6X_{10}Y$,[8] $Mo_6X_8Y_2$,[9] $Mo_6X_2Y_6$[10] (X = halogen, Y = chalcogen), and $Mo_6Br_6S_3$.[11] In the two former compounds, halogen and chalcogen ligands are randomly distributed on the inner positions of the unit, while they are ordered in the two latter ones.

In the present work, we report the crystal structures of two new Mo_6 chalcohalides obtained by solid state synthesis and built from original $[(Mo_6Br^i_6Y^i_2)Br^a_6]^{4-}$ discrete anionic units, namely $Cs_4[(Mo_6Br_6S_2)Br_6]$ and $Cs_4[(Mo_6Br_6Se_2)Br_6]$. Their interactions with aqueous KCN solution result in apical ligand exchange and have given access to the two first cyano Mo_6 chalcohalides: $Cs_{0.4}K_{0.6}(Et_4N)_{11}[(Mo_6Br_6S_2)(CN)_6]_3\cdot16H_2O$ and $Cs_{0.4}K_{0.6}(Et_4N)_{11}[(Mo_6Br_6Se_2)(CN)_6]_3\cdot16H_2O$. Their crystal structures and properties will be compared to those of the two solid state precursors as well as $K_7[(Mo_6S_8)(CN)_6]\cdot8H_2O$,[12] $K_7[(Mo_6Se_8)(CN)_6]\cdot8H_2O$,[13] $(Me_4N)_4K_2[(Mo_6Se_8)(CN)_6]\cdot10H_2O$[13] and $(Ph_4P)_2[(Mo_6Br^i_8)(CN)_6]\cdot4H_2O$,[14] the only CN^- substituted Mo_6 compounds previously reported.

Experimental Section

General Procedure. X-ray powder diffraction patterns were recorded with an INEL CPS 120 diffractometer using Cu $K\alpha_1$ radiation on flat plate samples. Chemical analyses of single crystals were performed at the "Centre de Microscopie Electronique à Balayage et de Microanalyse de l'Université de Rennes 1, France" for Scanning Electron Microscopy and Microanalyses of Rennes 1 University, France, by energy dispersive spectrometry (EDS) using a scanning electron microscope JEOL JSM 6400 equipped with a microprobe EDS OXFORD LINK ISIS. The IR spectra have been collected using a FTIR Bruker Equinox 55 spectrophotometer, in the 4000−400 cm^{-1} region, from a powdered sample formed as a pellet with KBr salt. UV spectra were recorded on an Ultrospec 3300 pro spectrophotometer in the range of 200−1100 nm. ^{77}Se NMR spectra were recorded at 20 °C using a Brucker 300 WB spectrometer from a solution of tetraphenylphosphonium salt in DMSO-d_6 with the effective total concentration of ~0.1 mol L^{-1}. The chemical shifts were measured relative to the external standard (solution of Ph_2Se_2) and recalculated with respect to the signal of $SeMe_2$ taken as zero. The positive shift corresponds to the downfield shift of the signal. Electrochemical measurements in CH_3CN were carried out with a PARR 263 potentiostiat. Working and counter electrodes were platinum, with SCE as reference electrode. Fc/Fc^+ couple was used as internal calibrant. The supporting electrolyte was 0.1 M Bu_4NPF_6.

Syntheses. $Cs_4Mo_6Br_{12}S_2$ (1) was prepared from a stoichiometric amount of Mo powder (Plansee), CsBr (Prolabo 99%), S (Prolabo 99.99%), and Mo_6Br_{12} previously synthesized according to the procedure described in ref 15. After grounding, the mixture (0.5 g) was formed as a pellet and placed into a silica tube (o.d. 9 mm, i.d. 7 mm, length 70 mm). Once sealed under vacuum, the tube was heated to 1100 °C. After one week of reaction, the sample was cooled to room temperature in 10 h. The red colored resulting product was stable in ambient atmosphere; the X-ray powder pattern revealed the presence of a small amount of $Mo_4S_4Br_4$[16] and MoS_2[17] secondary phases (yield: ~95%). Suitable single crystals for structural determination were obtained directly during the synthesis.

EDS analysis, atom % found: Cs, 17.29; Mo, 25.02; Br, 49.73; S, 7.96. Calcd for $Cs_4Mo_6Br_{12}S_2$: Cs, 16.66; Mo, 25; Br, 50.; S, 8.33.

$Cs_4Mo_6Br_{12}Se_2$ (2) was prepared similarly to compound **1** using Se (Fluka) as starting material and a reaction temperature of 900 °C. The red colored resulting product was stable in ambient atmosphere. The X-ray powder pattern indicated additional diffraction lines with weak intensity corresponding to a $Mo_6Br_xSe_{8-x}$ secondary phase[18] (yield: ~95%). Suitable single crystals for structural determination were obtained directly during the synthesis.

EDS analysis, atom % found: Cs, 17.88; Mo, 25.34; Br, 48.02; Se, 8.76. Calcd for $Cs_4Mo_6Br_{12}S_2$: Cs, 16.66; Mo, 25; Br, 50.; Se, 8.33.

$Cs_{0.4}K_{0.6}(Et_4N)_{11}[(Mo_6Br_6S_2)(CN)_6]_3\cdot16H_2O$ (3). Potassium cyanide (60 mg; 0.921 mmol) was dissolved in 20 mL of a 1:1 water−ethanol mixture. Compound **1** (220 mg; 0.103 mmol) was added to this solution and stirred overnight. After filtration, an orange colored crystalline powder was obtained by addition of Et_4NBr (160 mg; 0.761 mmol) and reduction of the volume of the solution under vacuum to 0.5 mL. This solid phase was collected by filtration, washed with ethanol, and dried in air. Yield: 90 mg (0.0489 mmol) (47.3%). After further evaporation, an additional amount of compound was isolated. IR, cm^{-1}: 1630, 1650 (δ_{HOH}), 2105 (ν_{CN}), 3270sh, 3390 (ν_{OH}). Bands of Et_4N^+ are omitted. UV−vis [λ/nm (ϵ/M^{-1} cm^{-1} per cluster)]: 222 (57500), 250 (23000), 380 (2870), 500 (380).

EDS analysis, atom % found: K, 3.89; Cs, 2.81; Mo, 40.21; S, 13.54; Br, 39.54. Calcd for $Cs_{0.4}K_{0.6}(Et_4N)_{11}[Mo_6Br_6S_2(CN)_6]_3\cdot16H_2O$: K, 4.0; Cs, 2.66; Mo, 40.0; S, 13.33; Br, 40.0.

$Cs_{0.4}K_{0.6}(Et_4N)_{11}[(Mo_6Br_6Se_2)(CN)_6]_3\cdot16H_2O$ (4). Potassium cyanide (60 mg; 0.921 mmol) was dissolved in 20 mL of a 1:1 water−ethanol mixture. Compound **2** (220 mg; 0.103 mmol) was added to this solution and stirred overnight. After filtration, an orange colored crystalline powder was obtained by addition of Et_4NBr (160 mg; 0.761 mmol) and reduction of the volume of the

---

(3) Michel, J. B.; McCarley, R. E. *Inorg. Chem.* **1982**, *21*, 1864.
(4) Ebihara, M.; Toriumi, K.; Saito K. *Inorg. Chem.* **1988**, *27*, 13.
(5) Ebihara, M.; Imai, T.; Kawamura, T. *Acta Crystallogr.* **1995**, *C51*, 1743.
(6) Ebihara, M.; Isobe, K.; Sasaki, Y.; Saito, K. *Inorg. Chem.* **1992**, *31*, 1644.
(7) Ebihara, M.; Toriumi, K.; Sasaki, Y.; Saito, K. *Gazz. Chim. Ital.* **1995**, *125*, 87.
(8) Perrin, C.; Sergent, M.; Le Traon, F.; Le Traon, A. *J. Solid State Chem.* **1978**, *25*, 197.
(9) Perrin, C.; Sergent, M. *J. Chem. Res., Synop.* **1983**, *2*, 38.
(10) Perrin, C.; Chevrel, R.; Sergent, M.; Fischer, O. *Mater. Res. Bull.* **1979**, *14*, 1505.
(11) Perrin, C.; Potel, M.; Sergent, M. *Acta Crystallogr., Sect. C* **1983**, *39*, 415.
(12) Brylev, K. A.; Virovets, A. V.; Naumov, N. G.; Mironov, Y. V.; Fenske, D.; Fedorov V. E. *Russ. Chem. Bull. Int. Ed.* **2001**, *50*, 1140.
(13) Mironov, Y. V.; Virovets, A. V.; Naumov, N. G.; Ikorskii, V. N.; Fedorov, V. E. *Chem. Eur. J.* **2000**, *6*, 1361.
(14) Simsek, M. K.; Bublitz, D.; Preetz, D. *Z. Anorg. Allg. Chem.* **1997**, *623*, 1885.
(15) Schäfer, H.; v. Schnering, H.-G.; Tillack, J.; Kuhnen, F.; Wöhrle, H.; Baumann, H. *Z. Anorg. Allg. Chem.* **1967**, *353*, 281.
(16) Perrin, C.; Chevrel, R.; Sergent, M. *C. R. Acad. Sci.* **1976**, *281 C*, 23.
(17) Bronsema, K. D.; De Boer, J. L.; Jellinek, F. *Z. Anorg. Allg. Chem.* **1986**, *540*, 15.
(18) Perrin, C.; Sergent, M.; Prigent, J. *C. R. Acad. Sci.* **1973**, *277 C*, 465.

Table 1. Crystallographic Data and Details of the Structural Determinations

	1	2	3	4
empirical formula	*a*	*b*	*c*	*d*
fw	2130.4	2224.1	5623.47	5908.59
space group	*Pbca* (No. 61)	*Pbca* (No. 61)	*Pm*−3*m* (No. 221)	*Pm*−3*m* (No. 221)
a (Å)	11.511(5)	11.6237(1)	17.1969(4)	17.235(5)
b (Å)	18.772(5)	18.9447(1)		
c (Å)	28.381(5)	28.4874(1)		
V (Å^3)	6133(3)	6273(3)	5085.7(2)	5120(3)
Z	8	8	1	1
D_{calc}, g cm^{-3}	4.61	4.71	1.84	1.92
cryst dimens (mm^3)	0.03 × 0.02 × 0.02	0.05 × 0.05 × 0.05	0.11 × 0.10 × 0.10	0.14 × 0.11 × 0.11
total reflns collect.	101237	76947	54672	69564
unique reflns	7040	9188	1102	1228
R_{int} [all]	0.234	0.114	0.062	0.059
R_{int} [$I > 2\sigma(I)$]	0.038	0.037	0.043	0.030
μ (mm^{-1})	22.83	24.50	4.9	5.99
T (°C)	18	18	18	18
λ (Å)	0.71073	0.71073	0.71073	0.71073
obsd reflns [$I > 2\sigma(I)$]	3230	4961	1102	1228
refined params	225	272	88	95
R_1,[e] [$I > 2\sigma(I)$]	0.056	0.050	0.047	0.036
wR$_2$,[e] all data	0.153	0.130	0.145	0.097
$\Delta\rho_{min}/\Delta\rho_{max}$ (e Å^{-3})	−2.01/2.19	−2.07/2.80	−0.51/0.87	−0.69/0.80

[a] $Cs_4[(Mo_6Br_{6.1(3)}S_{1.9(3)})Br_6]$. [b] $Cs_{3.9(5)}[(Mo_6Br_6Se_2)Br_6]$. [c] $Cs_{0.40(1)}K_{0.60(1)}(Et_4N)_{11}[(Mo_6Br_{5.81(3)}S_{2.19(3)})(CN)_6]_3\cdot16H_2O$. [d] $Cs_{0.44(1)}K_{0.56(1)}(Et_4N)_{11}[(Mo_6Br_6Se_2)(CN)_6]_3\cdot16H_2O$. [e] $R_1 = \sum_{hkl}|F_o - F_c|/\sum_{hkl}|F_o|$; $wR_2 = [\sum_{hkl}[w(F_o^2 - F_c^2)^2]/\sum_{hkl}[w(F_o^2)^2]]^{1/2}$.

solution under vacuum to 0.5 mL. This solid phase was collected by filtration, washed with ethanol and dried in air. Yield: 110 mg (0.0572 mmol) (63.6%). After further evaporation, an additional amount of compound was isolated. IR, cm^{-1}: 1625, 1647 (δ_{HOH}), 2104 (ν_{CN}), 3250sh, 3390 (ν_{OH}). Bands of Et_4N^+ are omitted. UV−vis [λ/nm (ϵ/M^{-1} cm^{-1} per cluster)]: 220 (67800), 245 (25600), 380 (3740), 510 (445).

EDS analysis, atom % found: K, 4.05; Cs, 2.66; Mo, 39.89; Se, 13.30; Br, 40.09. Calcd for $Cs_{0.4}K_{0.6}(Et_4N)_{11}[Mo_6Br_6Se_2(CN)_6]_3\cdot16H_2O$: K, 4.0; Cs, 2.66; Mo, 40.0; Se, 13.33; Br, 40.0.

X-ray Crystallography. Single-crystal X-ray diffraction data were collected at room temperature on a Nonius KappaCCD X-ray area-detector diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å) (Centre de Diffractométrie de l'Université de Rennes 1, France). Details of data collections are reported in Table 1. Once the data processing was performed by the Kappa CCD analysis software[19] the structure determinations were carried out by direct methods using the SIR97[20] program for **1** and **2** and the SHELXS-97[21] program for **3** and **4**. Structural refinements by least-squares techniques, combined with Fourier difference syntheses, were performed using the SHELXL-97[22] program for **1**, **2**, **3**, and **4**.

Structure Determination of $Cs_4Mo_6Br_{12}S_2$ (1). Direct methods yielded to a first partial structural solution in the *Pbca* space group including molybdenum cluster units and cesium atoms. Subsequently combined least-squares refinements and Fourier difference syntheses evidenced that apical bromine, molybdenum, and the four cesium sites were fully occupied and that the inner ligand sites were randomly occupied by sulfur and bromine atoms. Indeed, sulfur and bromine were introduced with the same positional and thermal parameters on the inner ligand sites, but for each crystallographic site, the sum of the occupancies was restricted to the value corresponding to a fully occupied position. The final refinement led to the $Cs_4Mo_6Br_{12.1(3)}S_{1.9(3)}$ formula that will be rounded to $Cs_4Mo_6Br_{12}S_2$ in the following for clarity.

Structure Determination of $Cs_4Mo_6Br_{12}Se_2$ (2). The structure was solved by direct methods in the *Pbca* space group. Although it appeared that $Cs_4Mo_6Br_{12}Se_2$ is isostructural with $Cs_4Mo_6Br_{12}S_2$, combined least-squares refinements and Fourier difference syntheses could not evidence a random distribution of bromine and selenium atoms on inner positions in relation to their close scattering factors and ionic radii. However, for the reasons discussed in the following section, the distribution of two Se atoms and six bromine atoms on the eight inner positions noted L (L = Se/Br) is an obvious matter of fact. The cesium atoms were initially placed on four 8*c* Wyckoff positions, but significant residual electronic peaks remained close to these positions. Lower reliability factors and small residual electronic peaks were obtained using a split model for the cesium atoms. Indeed Cs1, Cs2, and Cs3 were split on two crystallographic positions while Cs4 was split on three crystallographic positions. All the atoms were refined anisotropically, and the final structural results led to the $Cs_{3.9(5)}Mo_6Br_{12}Se_2$ refined formula that will be rounded in the following to $Cs_4Mo_6Br_{12}Se_2$ for clarity.

Structure Determination of $Cs_{0.4}K_{0.6}(Et_4N)_{11}[(Mo_6Br_6S_2)(CN)_6]_3\cdot16H_2O$ (3). The structure was solved and refined in the *Pm*-3*m* space group using the same strategy as for **1**. Sulfur and bromine inner ligands occupy one crystallographic site with the S:Br ratio equal to 0.273(4):0.727(4), whereas the apical ligands consist of CN groups. Cesium and potassium cations are randomly distributed on the same crystallographic positions with a Cs:K ratio equal to 0.40(1):0.60(1). Nitrogen atoms of the two Et_4N^+ groups fully occupy two crystallographic sites while the carbon atoms of the ethyl groups are orientationally disordered. The water molecules statistically occupy six crystallographic sites. The structural results led to the $Cs_{0.40(1)}K_{0.60(1)}(Et_4N)_{11}[Mo_6Br_{5.81(3)}S_{2.19(3)}(CN)_6]_3\cdot16H_2O$ refined stoichiometry that will be rounded to $Cs_{0.4}K_{0.6}(Et_4N)_{11}[Mo_6Br_6S_2(CN)_6]_3\cdot16H_2O$ in the following.

Structure Determination of $Cs_{0.4}K_{0.6}(Et_4N)_{11}[(Mo_6Br_6Se_2)(CN)_6]_3\cdot16H_2O$ (4). The structure was solved and refined in the *Pm*-3*m* space group using the same strategy as for **3**. Although it

---

(19) Nonius. *COLLECT, DENZO, SCALEPACK, SORTAV: KappaCCD Program Package*; Nonius B.V.: Delft, The Netherlands, 1999.

(20) Cascarano, G.; Altomare, A.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Siliqi, D.; Burla, M. C.; Polidori, G.; Camalli, M. *Acta Crystallogr.* **1996**, *A52*, C-79.

(21) Sheldrick, G. M. *SHELXS-97: Program for Crystal structure Solution*; University of Göttingen: Göttingen, 1990.

(22) Sheldrick, G. M. *SHELXL-97: Program for the Refinement of Crystal Structure*; University of Göttingen: Göttingen, 1997.

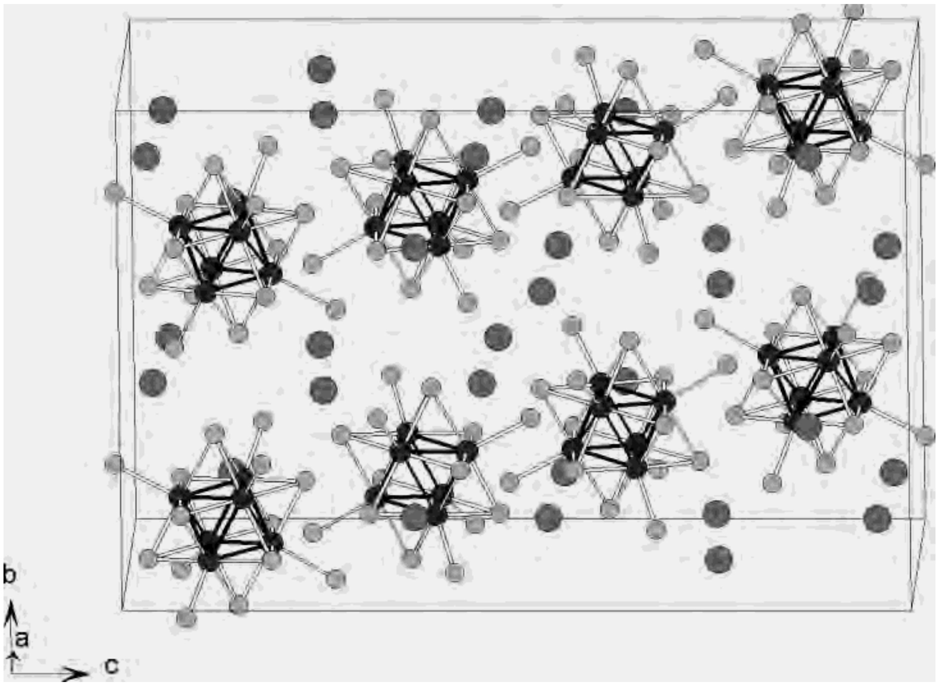


Figure 1. Structural representation of $Cs_4[(Mo_6Br_6S_2)Br_6]$. Isolated atoms represent cesium cations.

appeared that compound **4** is isostructural with $Cs_{0.4}K_{0.6}(Et_4N)_{11}[(Mo_6Br_6S_2)(CN)_6]_3 \cdot 16H_2O$, as stressed above for $Cs_4Mo_6Br_{12}Se_2$, the structural refinement did not provided evidence of a random distribution of bromine and selenium atoms on inner positions. However, as it will be discussed in the following section, the distribution of two Se atoms and six bromine atoms on the eight inner positions noted L (L = Se/Br) is an obvious matter of fact. Thus, the value of the Br/Se ratio was fixed at 0.75:0.25 during refinement according to chemical analysis. Cesium and potassium countercations are randomly distributed on the same crystallographic position with a Cs:K ratio equal to 0.44(1):0.56(1). Nitrogen atoms of the two Et_4N^+ groups fully occupy two crystallographic sites while the carbon atoms of the ethyl groups are orientationally disordered. The water molecules are located in six crystallographic sites with partial occupancies. The refinement led to the $Cs_{0.44(1)}K_{0.56}(Et_4N)_{11}[(Mo_6Br_6Se_2)(CN)_6]_3 \cdot 16H_2O$ formula, which will be rounded to the $Cs_{0.4}K_{0.6}(Et_4N)_{11}[(Mo_6Br_6Se_2)(CN)_6]_3 \cdot 16H_2O$ formula.

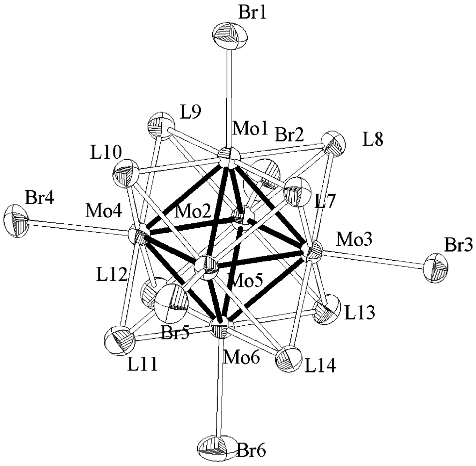


Figure 2. Representation of the $[(Mo_6L^i{}_8)Br^a{}_6]^{4-}$ cluster anion in the structure of $Cs_4[(Mo_6Br_6S_2)Br_6]$. Displacement ellipsoids are shown at the 50% probability level.

Results and Discussion

Crystal Structures: Description of the Mo_6L_{14} Units. The structure of the two chalcobromides, $Cs_4Mo_6Br_{12}S_2$ and $Cs_4Mo_6Br_{12}Se_2$, represented in Figure 1 are built from discrete $[(Mo_6Br^i{}_6Y^i{}_2)Br^a{}_6]^{4-}$ (Y = S or Se) anionic units (Figure 2) in which the cluster is randomly face-capped by six bromine and two chalcogen ligands while the six apical positions are fully occupied by bromine. In the $Cs_4Mo_6Br_{12}Se_2$ compound, the presence of both bromine and selenium elements could not be evidenced by X-ray diffraction analyses but has been clearly observed and quantified by EDS analyses.

Our assumption that the two Se ligands are randomly distributed on the eight inner positions is supported by similar localization of sulfur in compound **1** and by the presence of selenium atoms randomly distributed on inner positions in a number of M_6 selenohalides reported in the literature, for instance in $Mo_6Cl_{10}Se$[8] or $Re_6Cl_{10}Se_4$.[23] Let us note that previous studies evidenced that, in M_6 chalcohalides, chalcogens occupy preferentially inner positions and that halogens occupy either inner or apical positions.[24] The random sulfur/bromine distribution on inner positions deduced from X-ray analysis of **1** does not give any information about the number of isomeric $[(Mo_6Br^i{}_6S^i{}_2)Br^a{}_6]^{4-}$ units that could occur in this compound, in relation to an orientational disorder of the units in the structure.

In the structures of the two cyano-substituted isostructural compounds **3** and **4** represented in Figure 3, the apical positions of the discrete units are occupied by CN^- ligands

---

(23) Leduc, L.; Perrin, A.; Sergent, M.; Le Traon, F.; Pilet, J.-C.; Le Traon, A. *Mater. Lett.* **1985**, *3*, 209.

(24) Perrin, A.; Perrin, C.; Sergent, M. *J. Less-Common Met.* **1988**, *137*, 241.

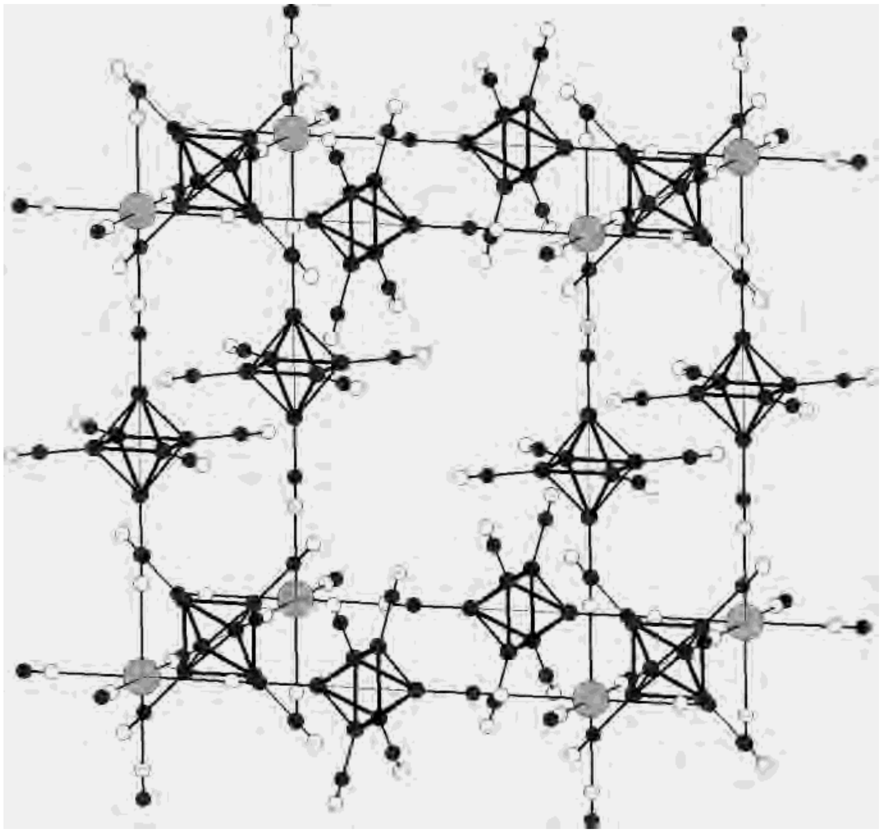


Figure 3. Structural representation of $Cs_{0.4}K_{0.6}(Et_4N)_{11}[(Mo_6Br_6S_2)(CN)_6]_3{\cdot}16H_2O$. The inner ligands, water molecules, and (Et_4N) molecules have not been represented for clarity. The gray circles correspond to (Cs,K) cations.

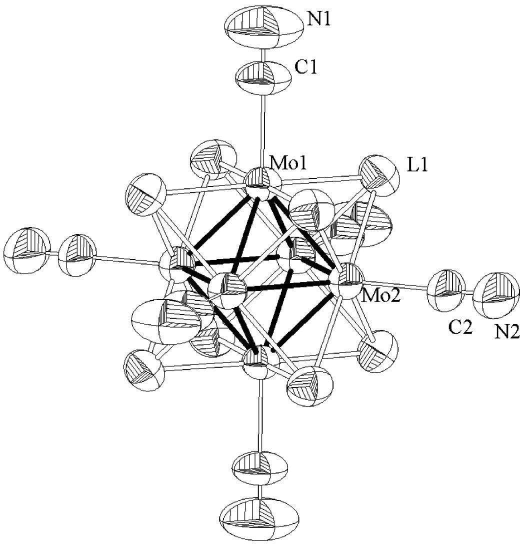


Figure 4. The $[(Mo_6L^i{}_8)(CN)^a{}_6]^{4-}$ cluster anion in the structure of $Cs_{0.4}K_{0.6}(Et_4N)_{11}[(Mo_6Br_6S_2)(CN)_6]_3{\cdot}16H_2O$. Ellipsoids are drawn at the 50% probability level.

(Figure 4). The two chalcogen atoms are randomly distributed on the eight inner ligand positions. As found for **1** and **2**, the average $[(Mo_6Br^i{}_6Y^i{}_2)(CN)^a{}_6]^{4-}$ units deduced from X-ray analyses do not give any information about the number of isomeric units present in the structures. However, the three signals observed in the ^{77}Se NMR spectra of compound **4** suggest that the three possible isomers—that are theoretically deduced from a $(Mo_6Br_6Y_2)$ core—are available in solution of **4** and obviously in parent **2** compound (see below).

The interatomic distances of the four title compounds are reported in Table 2. Their weighted average values are given in Table 3 together with those of other Mo_6 compounds for comparison. As expected, the units of these four compounds characterized by 24 valence electrons per cluster exhibit Mo−Mo distances roughly equal to 2.63 Å in agreement with those reported in other Mo_6 bromide complexes with the same VEC value. Indeed, a lower VEC would lead to larger Mo−Mo bond lengths owing to fewer valence electrons involved in the Mo−Mo bonding states of the molecular orbital diagram. The Mo−L^i average distances are similar in **1** and **2** and close to the corresponding ones in $PbMo_6Br_{14}$[2d] or $Cu_2Mo_6Br_{14}$.[2e] On the other hand, the Mo−Br^a bond lengths are significantly larger in **1** and **2** than in the two latter bromides, in relation with a lower cationic charge of the $(Mo_6L^i{}_8)^{n+}$ cluster core (2+ for **1** and **2** ; 4+ for $PbMo_6Br_{14}$ and $Cu_2Mo_6Br_{14}$). Indeed, the higher is the charge, the shorter is the Mo−Br^a bond length due to greater electrostatic interactions. The Mo−L^i average interatomic distances in **3** and **4** are close to the corresponding ones observed in $(Ph_4P)_2[(Mo_6Br_8)(CN)_6]{\cdot}4H_2O$[14] and similar to those observed in the two starting compounds. The mean Mo−C and C−N distances (2.21 and 2.23 Å; 1.09 and 1.12 Å for compounds **3** and **4** respectively) are in agreement with those found in other molybdenum cyanides.[12,13,25] The charge of the cluster core does not influence greatly these Mo−C bond lengths which are only slightly larger in **3** and **4** than in $(Ph_4P)_2[(Mo_6Br_8)(CN)_6]{\cdot}4H_2O$. Notice that these CN-substituted compounds reveal a slight elongation of the

Table 2. Interatomic Distances (Å) and Angles (deg) for $Cs_4Mo_6Br_{12}S_2$ (**1**), $Cs_4Mo_6Br_{12}Se_2$ (**2**), $Cs_{0.4}K_{0.6}(Et_4N)_{11}[(Mo_6Br_6S_2)(CN)_6]_3{\cdot}16H_2O$ (**3**), and $Cs_{0.5}K_{0.5}(Et_4N)_{11}[(Mo_6Br_6Se_2)(CN)_6]_3{\cdot}16H_2O$ (**4**)

1		**2**		**3**		**4**	
Mo1−Mo2	2.623(2)	Mo1−Mo2	2.634(1)	Mo1−Mo2	2.6456(11)	Mo1−Mo2	2.6532(8)
Mo1−Mo3	2.640(2)	Mo1−Mo3	2.642(1)	Mo2−Mo2	2.6428(14)	Mo2−Mo2	2.647(1)
Mo1−Mo4	2.633(2)	Mo1−Mo4	2.638(1)				
Mo1−Mo5	2.646(2)	Mo1−Mo5	2.645(2)				
Mo2−Mo3	2.638(2)	Mo2−Mo3	2.642(1)				
Mo2−Mo4	2.614(2)	Mo2−Mo4	2.633(1)				
Mo2−Mo6	2.630(2)	Mo2−Mo6	2.636(2)				
Mo3−Mo5	2.645(2)	Mo3−Mo5	2.647(1)				
Mo3−Mo6	2.627(2)	Mo3−Mo6	2.631(1)				
Mo4−Mo5	2.624(2)	Mo4−Mo5	2.630(1)				
Mo4−Mo6	2.620(2)	Mo4−Mo6	2.637(1)				
Mo5−Mo6	2.624(2)	Mo5−Mo6	2.638(1)				
Mo1−L7	2.619(2)	Mo1−L7	2.614(1)	Mo1−L1	2.5895(13)	Mo1−L1	2.6006(6)
Mo1−L8	2.616(2)	Mo1−L8	2.618(1)	Mo2−L1	2.5987(9)	Mo2−L1	2.6042(5)
Mo1−L9	2.585(2)	Mo1−L9	2.608(1)				
Mo1−L10	2.603(2)	Mo1−L10	2.601(1)				
Mo2−L8	2.615(2)	Mo2−L8	2.614(1)				
Mo2−L9	2.592(2)	Mo2−L9	2.600(1)				
Mo2−L12	2.557(3)	Mo2−L12	2.581(1)				
Mo2−L13	2.622(2)	Mo2−L13	2.618(1)				
Mo3−L7	2.603(2)	Mo3−L7	2.601(1)				
Mo3−L8	2.599(2)	Mo3−L8	2.603(2)				
Mo3−L13	2.610(2)	Mo3−L13	2.604(1)				
Mo3−L14	2.604(2)	Mo3−L14	2.606(2)				
Mo4−L9	2.590(2)	Mo4−L9	2.603(2)				
Mo4−L10	2.646(2)	Mo4−L10	2.635(1)				
Mo4−L11	2.554(3)	Mo4−L11	2.585(2)				
Mo4−L12	2.566(3)	Mo4−L12	2.588(1)				
Mo5−L7	2.640(2)	Mo5−L7	2.627(1)				
Mo5−L10	2.614(2)	Mo5−L10	2.603(1)				
Mo5−L11	2.566(3)	Mo5−L11	2.601(1)				
Mo5−L14	2.597(2)	Mo5−L14	2.605(1)				
Mo6−L11	2.549(3)	Mo6−L11	2.581(1)				
Mo6−L12	2.544(3)	Mo6−L12	2.584(1)				
Mo6−L13	2.641(2)	Mo6−L13	2.627 (1)				
Mo6−L14	2.626(2)	Mo6−L14	2.624(1)				
Mo1−Br1	2.643(2)	Mo1−Br1	2.644(2)	Mo1−C1	2.21(2)	Mo1−C1	2.228(15)
Mo2−Br2	2.648(2)	Mo2−Br2	2.655(1)	Mo2−C2	2.208(14)	Mo2−C2	2.223(10)
Mo3−Br3	2.662(2)	Mo3−Br3	2.664(1)				
Mo4−Br4	2.651(2)	Mo4−Br4	2.657(1)				
Mo5−Br5	2.660(2)	Mo5−Br5	2.654(2)				
Mo6−Br6	2.647(2)	Mo6−Br6	2.655(2)				
				C1−N1	1.07(3)	C1−N1	1.114(19)
				C2−N2	1.101(16)	C2−N2	1.121(13)
				Mo1−C1−N1	180.	Mo1−C1−N1	180.
				Mo2−C2−N2	180 0(1)	Mo2−C2−N2	180.0(8)
				(Cs,K)1−N1	3.45(2)	(Cs,K)1−N1	3.394(15)

Table 3. Average Interatomic Distances for Mo_6 Bromides, Mo_6 Chalcobromides, and Mo_6 CN-Substituted Compounds

compound	ref	VEC	space group	Mo−Mo (Å)	Mo−L^i (Å)	Mo−L^a (Å)
$Cs_4[(Mo_6Br_6S_2)Br_6]$	this work	24	*Pbca*	2.630	2.598^a	2.656
$Cs_4[(Mo_6Br_6Se_2)Br_6]$	this work	24	*Pbca*	2.638	2.605^a	2.655
$Pb[(Mo_6Br_8)Br_6]$	2d	24	*Pn*-3	2.621	2.587	2.616
$Cu_2[(Mo_6Br_8)Br_6]$	2e	24	*Pn*-3	2.628	2.592	2.610
$(Et_4N)_3[(Mo_6Br_7S)Cl_6]$	6	24	$P4_2/mnm$	2.638	2.606^a	2.464
$(n\text{-}Bu_4N)_2[(Mo_6Br_7S)Cl_6]$	6	23	$P2_1/n$	2.653	2.596^a	2.425
$Cs_{0.4}K_{0.6}(Et_4N)_{11}[(Mo_6Br_6S_2)(CN)_6]_3{\cdot}16H_2O$	this work	24	*Pm*-3*m*	2.645	2.597^a	2.21
$Cs_{0.4}K_{0.6}(Et_4N)_{11}[(Mo_6Br_6Se_2)(CN)_6]_3{\cdot}16H_2O$	this work	24	*Pm*-3*m*	2.651	2.603^a	2.23
$K_7[(Mo_6S_8)(CN)_6]{\cdot}8H_2O$	12	21	*Fm*-3*m*	2.666	2.456	2.204
$K_7[(Mo_6Se_8)(CN)_6]{\cdot}8H_2O$	13	21	*Fm*-3*m*	2.700	2.562	2.17
$(Me_4N)_4K_2[(Mo_6Se_8)(CN)_6]{\cdot}10H_2O$	13	20	*P*-1	2.711	2.573	2.20
$(Ph_4P)_2[(Mo_6Br_8)(CN)_6]{\cdot}4H_2O$	14	24	*P*1	2.637	2.590	2.201

[a] L^i positions randomly occupied by bromine and chalcogen.

Mo−Mo bond length compared to that observed in the starting Mo_6 unit: 2.645(1) Å vs 2.630(9) Å and 2.651(3) Å vs 2.638(5) Å for compounds **3** and **1** and compounds **4** and **2**, respectively. Similar elongation of the average Mo−Mo distance was found for $(Ph_4P)_2[(Mo_6Br_8)(CN)_6]{\cdot}4H_2O$ compared to $Pb[(Mo_6Br_8)Br_6]$: 2.637(7) Å vs 2.621(7) Å, respectively. This might be due to the strong π-acceptor capability of the cyanide ligand, withdrawing some electronic density from the Mo_6 core orbitals.

Localization of the Countercations and Water Molecules. In **1,** the cesium atoms fully occupy four crystallographic sites and exhibit complex coordinations involving apical bromines and inner ligands (shortest Cs−Br distance: 3.523(3) Å). The cesium sites are larger in **2** than in **1**; consequently the four cesium atoms are slightly shifted from the initial positions found in **1**.

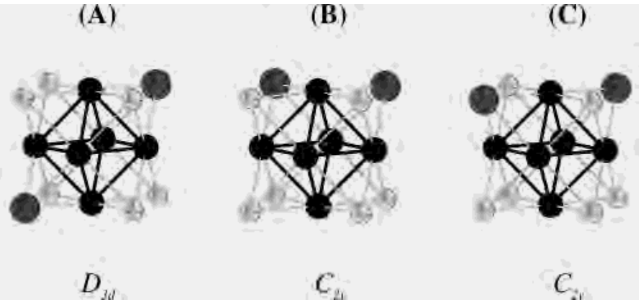
In compounds **3** and **4**, alkali atoms are located at the origin of the unit cell. They lie in an ideal octahedral environment formed by six N1 atoms from CN groups with (Cs,K)−N distances of 3.45(2) Å and 3.39(2) Å for **3** and **4**, respectively. These two structures contain two independent tetraethylammonium cations. One of them is orientationally disordered over two positions centered on the faces of the unit cell with the nitrogen on a 3*c* Wyckoff position. The second one is located in the octants of the unit cell and orientationally disordered over three positions with the nitrogen on an 8*g* Wyckoff position. In these two compounds, the water molecules form hydrogen bonds with N of CN ligands and with other water molecules. It is noteworthy that in **3** and **4** the alkali metals and $[(Mo_6Br_6Y_2)(CN)_6]^{4-}$ anions form a $\{M[(Mo_6Br_6Y_2)(CN)_6]_3\}^{11-}$ framework with a topology related to that found in Super Prussian Blue series,[26] in particular cluster expanded Prussian Blue analogues widely studied during last years.[27,28] The structure brings to mind the unit cell of classical Prussian Blue but with missing central anion and transition metal atoms located at the faces, and with tetraethylammonium cations compensating the negative charge of $\{M[(Mo_6Br_6Y_2)(CN)_6]_3\}^{11-}$. This framework occupies only 28.5% (for sulfur) and 28.7% (for selenium) of unit cell volume. Other voids are filled by tetraethylammonium cations and water molecules. In molecular cyanometalates, the closest analogue of this framework is the compound $\{(SnMe_3)_3[Co^{III}(CN)_6]\}$.[26a]

Electrochemistry. The cyclic voltammograms (CV) of **3** and **4** showed one quasi-reversible oxidation wave at almost the same potential given in Table 4. No distinct reduction peaks were observed in the region as low as −1.2 V vs SCE in CH_3CN. The peak-to-peak differences were 0.090 and 0.094 V for **3** and **4**, respectively. These values are comparable with that measured for ferrocene in similar conditions (0.086 V). The shape of the signals does not give any indications on the presence of species with different redox potentials (Supporting Information). At potentials above 0.5 V, clusters undergo an irreversible multielectron oxidation followed by decomposition.[29]

In Table 4, comparison of $E_{1/2}$ of **3** and **4** with other Mo$_6$ complexes shows that substitution of inner halogen ligands by chalcogen ones drastically decreases oxidation potentials (for example, +1.38 V for (Mo_6Br_8), +0.55 V for (Mo_6Br_7S), and −0.056 V for $(Mo_6Br_6S_2)$) while the nature of chalcogen itself affects the potential only slightly. Substitution of subsequent inner halogen atoms should lead to a similar cathodic shift with clusters having VEC = 24 and should allow stabilization of species with a lower number of valence electrons. Accordingly, the anion with eight inner chalcogen ligands exists only with 21 and 20 valence electrons per cluster.[12,13]

IR Spectra. The infrared spectra of compounds **3** and **4** exhibit a strong sharp ν_{CN} stretching vibration, which has almost the same frequency in both cases. They lie between 2120 cm^{-1} for $[(Mo_6Br_8)(CN)_6]^{4-}$ [14] and 2080−2095 cm^{-1} for fully substituted $[(Mo_6Y_8)(CN)_6]^{n-}$ (Y = S, Se).[12,13]

^{77}Se NMR Spectra. Despite the random Br/Se distribution on inner positions, owing to the −4 anionic charge and the 24 VEC value of each cluster unit in **4**, that compound is built from anions having the same Br:Se stoichiometry: $[Mo_6Br_6Se_2(CN)_6]^{4-}$. Such an anion can exist as three geometric isomers with different arrangements of inner ligands: A, B, and C with D_{3d}, C_{2v}, and C_{2v} symmetry, respectively.



Each isomer contains one type of selenium atom that corresponds to one resonance in the ^{77}Se NMR spectrum.

---

(25) (a) Corden, B. J.; Cunningham, J. A.; Eisenberg, R. *Inorg. Chem.* **1970**, *9*, 356. (b) Muller, A.; Jostes, R.; Eltzner, W.; Chong- Shi Nie; Diemann, E.; Bogge, H.; Zimmermann, M.; Dartmann, M.; Reinsch-Vogell, U.; Shun Che; Cyvin, S. J.; Cyvin, B. N. *Inorg. Chem.* **1985**, *24*, 2872. (c) Szalay, P. S.; Dunbar, K. R. *Inorg. Chem. Commun.* **2000**, *3*, 49. (d) Smit, J. P.; Purcell, W.; Roodt, A.; Leipoldt, J. G. *J. Chem. Soc., Chem. Commun.* **1993**, 1388. (e) Fedin, V. P.; Samsonenko, D. G.; Virovets, A. V.; Kalinina, L. V.; Naumov, D. Yu. *Izv. Akad. Nauk SSSR, Ser. Khim.* **2000**, 18. (f) Nowicka, B.; Samotus, A.; Szklarzewicz, J.; Burgess, J.; Fawcett, J.; Russell, D. R. *Polyhedron* **1998**, *17*, 3167. (g) Novotny, M.; Lewis, D. F.; Lippard, S. J. *J. Am. Chem. Soc.* **1972**, *94*, 6961. (h) Potvin, C.; Bregeault, J.-M.; Manoli, J.-M. *J. Chem. Soc., Chem. Commun.* **1980**, 664. (i) Leipoldt, J. G.; Basson, S. S.; Bok, L. D. C. *Inorg. Chim. Acta* **1980**, *38*, L99. (j) Greco, G. E.; O'Donoghue, M. B.; Seidel, S. W.; Davis, W. M.; Schrock, R. R. *Organometallics* **2000**, *19*, 1132.

(26) (a) Yunlu, K.; Hock, N.; Fischer D. *Angew. Chem., Int. Ed. Engl.* **1985**, *24* 879. (b) Siebel, E.; Fischer, R. D.; Davies, N. A.; Apperley, D. C.; Harris, R. K. *J. Organomet. Chem.* **2000**, *604*, 34. (c) Schwarz, P.; Siebel, E.; Fischer, R. D.; Apperley, D. C.; Davies, N. A.; Harris, R. K. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1197. (d) Behrens, U.; Brimah, A. K.; Soliman, T. M.; Fischer, R. D.; Apperley, D. C.; Davies, N. A.; Harris, R. K. *Organometallics* **1992**, *11*, 1718.

(27) (a) Naumov, N. G.; Virovets, A. V.; Sokolov, M. N.; Artemkina, S. B.; Fedorov, V. E. *Angew. Chem., Int. Ed.* **1998**, *37*, 1943. (b) Naumov, N. G.; Virovets, A. V.; Fedorov, V. E. *J. Struct. Chem. Engl. Tr.* **2000**, *41*, 499. (c) Naumov, N. G.; Virovets, A. V.; Fedorov, V. E. *Inorg. Chem. Commun.* **2000**, *3*, 71. (d) Artemkina, S. B.; Naumov, N. G.; Virovets, A. V.; Gromilov, S. A.; Fenske, D.; Fedorov, V. E. *Inorg. Chem. Commun.* **2001**, *4*, 423. (e) Naumov, N. G.; Soldatov, D. V.; Ripmeester, J. A.; Artemkina, S. B.; Fedorov, V. E. *Chem. Commun.* **2001**, 571.

(28) (a) Bennett, M. V.; Beauvais, L. G.; Shores, M. P.; Long, J. R. *J. Am. Chem. Soc.* **2001**, *123*, 8022. (b) Bennett, M. V.; Shores, M. P.; Beauvais, L. G.; Long, J. R. *J. Am. Chem. Soc.* **2000**, *122*, 6664. (c) Beauvais, L. G.; Shores, M. P.; Long, J. R. *J. Am. Chem. Soc.* **2000**, *122*, 2763. (d) Shores, M. P.; Beauvais, L. G.; Long, J. R. *J. Am. Chem. Soc.* **1999**, *121*, 775. (e) Beauvais, L. G.; Shores, M. P.; Long, J. R. *Chem. Mater.* **1998**, *10*, 3783.

(29) In contrast to cyanide cluster anions $[Mo_6Br_6Y_2(CN)_6]^{4-}$ the cyclic voltammograms of $[Mo_6Y_2Br_{12}]^{4-}$ anions in **1** and **2** in acetonitrile demonstrated complex curves with poorly resolved waves. Such behavior might be due to solvation of $[Mo_6Y_2Br_{12}]^{4-}$ anion and presence in solution of $[(Mo_6Y_2Br_6)Br_{6-x}(CH_3CN)_x]^{4-x-}$ species [ref 7]. Detailed study of electrochemical behavior is in progress.

Table 4. Oxidation Potentials for Mo_6 Complexes

compound	VEC	$E_{1/2}$, V (SCE)	ref
$[(Mo_6Cl_8)Cl_6]^{2-}$	24/23	+1.56	4
$[(Mo_6Br_8)Br_6]^{2-}$	24/23	+1.38	4
$[(Mo_6Cl_7S)Cl_6]^{2-}$	24/23	+0.69	4
$[(Mo_6Cl_7Se)Cl_6]^{2-}$	24/23	+0.64	4
$[(Mo_6Br_7S)Cl_6]^{3-}$	24/23	+0.55	4
$[(Mo_6Br_6S_2)(CN)_6]^{4-}$	24/23	−0.056	this work
$[(Mo_6Br_6Se_2)(CN)_6]^{4-}$	24/23	−0.068	this work
$[(Mo_6Se_8)(CN)_6]^{7-}$	21/20	+0.63 (NHE)	13

Theoretically in the case of statistic distribution of the isomers the spectrum should have three resonances with intensities 1:3:3.

In fact the ^{77}Se NMR spectrum of a solution of tetraphenylphosphonium salt of $[Mo_6Br_6Se_2(CN)_6]^{4-}$ prepared in a similar way as for compound **4** exhibits three sharp signals at −166.2, −175.9, and −277.0 ppm with relative intensities 1.8:6.5:1 (Supporting Information).

NMR study of isomers of octahedral cluster complexes was recently reported for $[Re_6Te_{8-x}Se_x(CN)_6]^{4-}$,[30,31] for $[Re_6Se_6Br_8]^{2-}$,[32] and $[W_6S_8L_{6-n}(PR_3)_n]$ ($n = 0-6$) complexes.[33] In refs 31 and 32 the authors have made assignments of isomers using simple additive model of influence of neighbor ligands on chemical shifts of selenium and tellurium, previously suggested by Dean and Evans for $[MF_6]^{n-}$ complexes.[34]

The limited number of resonances in the spectrum of **4** (three lines for three isomers) does not allow us to definitively assign species, but we could make some assumptions. Two close resonances of −166.2 and −175.9 ppm could correspond to isomers with selenium atoms located on edge and face diagonal of L_8 cube (B and C isomers). This assumption is in agreement with the influence of bromine localization on the shift of selenium atoms found for $[Re_6Se_6Br_8]^{2-}$.[32] The signal at −277.0 ppm could correspond to the isomer with selenium atoms located on body diagonal of L_8 cube (A isomer). This attribution correlates with a lowest concentration expected for this isomer and the small intensity found for this signal. In addition, the shift is in agreement with the larger distance between selenium atoms. Further ^{77}Se NMR study of other members of $[Mo_6Br_xSe_{8-x}(CN)_6]^{n-}$ series that are planned could provide more information about influence of ligand arrangement on chemical shift of selenium atoms.

Let us note that the ratio of intensities is different from that was expected; obviously, the C isomer has an “extra stability”. Similar distribution of isomers in unit with two selenium atoms was found for $[Re_6Te_6Se_2(CN)_6]^{4-}$ complexes.[31]

Conclusion

The two $Cs_4Mo_6Br_{12}S_2$ and $Cs_4Mo_6Br_{12}Se_2$ chalcobromides reported in this paper with two inner chalcogens constitute new data of the $(Mo_6Br^i_{8-x}Y^i_x)$ cluster core series ($0 < x < 8$) poorly investigated up to now. The reaction of these two compounds with KCN solution provides a straightforward access to the new $[(Mo_6Br^i_{8-x}Y^i_x)(CN)_6]^{4-}$ anionic units in the two first Mo_6 cyano-chalcobromides, $Cs_{0.4}K_{0.6}(Et_4N)_{11}[(Mo_6Br_6S_2)(CN)_6]_3\cdot 16H_2O$ and $Cs_{0.4}K_{0.6}(Et_4N)_{11}[(Mo_6Br_6Se_2)(CN)_6]_3\cdot 16H_2O$. The complete $[(Mo_6Br^i_{8-x}Y^i_x)Br_6]^{n-}$ series and the related $[(Mo_6Br^i_{8-x}Y^i_x)(CN)_6]^{n-}$ cyano substituted units that we plan to obtain will allow study of the influence of the inner Y/Br ratio on the structural and electronic properties and on the reactivity of these anionic units. In addition, for the same inner Y/Br ratio, different arrangements of the chalcogen and bromine around the Mo_6 cluster, which are theoretically possible, will give access to a comparative study of different isomer units. Such an extended study will give valuable information, particularly useful in the field of nanoscience. Indeed, these units of about 1 nm dimension, could be used as building blocks of nanostructured materials, for instance by complexation of the cyano units by transition elements in order to obtain low dimensional materials, as previously made in Re_6 cluster chemistry.[35]

Acknowledgment. This work was supported by INTAS (Grant N2000-00689). N.G.N. is grateful to CNRS for a 9 month position at LCSIM. The “Centre de Diffractométrie de l’Université de Rennes 1” is acknowledged for the data collection on the Nonius KappaCCD X-ray diffractometer. In particular, we greatly thank Dr. T. Roisnel for the useful advice. We also acknowledge “Fondation Langlois” for financial support.

Supporting Information Available: X-ray crystallographic data in CIF format, ^{77}Se NMR spectrum, and voltammogram curves. This material is available free of charge via the Internet at http://pubs.acs.org.

IC034443Q

---

(30) Mironov, Y. V.; Cody, J. A.; Albrecht-Schmitt, T. E.; Ibers, J. A. *J. Am. Chem. Soc.* **1997**, *119*, 493.

(31) Fedorov, V. E.; Tkachev, S. V.; Naumov, N. G.; Mironov, Y. V.; Mironov, Y. I. *Russ. J. Inorg. Chem.* **1998**, *43*, 1562.

(32) Yarovoi, S. S.; Solodovnikov, S. F.; Tkachev, S. V.; Mironov, Y. V.; Fedorov, V. E. *Russ. Chem. Bull. Int. Ed.* **2003**, *52*, 68.

(33) Jin, S.; Adamchuk, J.; Xiang, B. S.; DiSalvo, F. J. *J. Am. Chem. Soc.* **2002**, *124*, 9229.

(34) Dean, P. A.; W.; Evans, D. F. *J. Chem. Soc. A* **1968**, 1154.

(35) Naumov, N. G.; Virovets, A. V.; Fedorov, V. E. *J. Struct. Chem.* **2000**, *41*, 499.