Inorg. Chem. **2006**, *45*, 1611–1616

Inorganic Chemistry

Article

Synthesis, Structural Evolution, and Electrical Properties of the Novel Mo_{12} Cluster Compounds $K_{1+x}Mo_{12}S_{14}$ ($x = 0$, 1.1, 1.3, and 1.6) with a Tunnel Structure

Soazig Picard, Patrick Gougeon,* and Michel Potel

Université de Rennes 1, Laboratoire de Chimie du Solide et Inorganique Moléculaire,
U.M.R. 6511, Avenue du Général Leclerc, 35042 Rennes Cedex, France

Received September 21, 2005

The new structural type (**1**) $K_{2.3}Mo_{12}S_{14}$ was prepared by solid-state reaction at 1500 °C in a sealed molybdenum crucible. The compound crystallizes in the trigonal space group $P\bar{3}1c$, $Z = 2$, (**1**) $a = 9.1720(7)$ Å, $c = 16.403(4)$ Å. Its crystal structure was determined from single-crystal X-ray diffraction data and consists of interconnected $Mo_{12}S_{14}$ units that form an original and unprecedented three-dimensional framework in which large tunnels are occupied randomly by a part of the K^+ ions. The remaining K^+ ions are localized between two consecutive $Mo_{12}S_{14}$ units along the *c* axis. By carrying out topotactic oxydo-reduction reactions at low temperature (<100 °C), we were able to remove or insert K^+ ions in the channels and thus form isostructural phases $K_{1+x}Mo_{12}S_{14}$ ($0 \leq x \leq 1.6$). Thus, we have solved the crystal structures for the following three compositions: (**2**) $K_{2.1}Mo_{12}S_{14}$, (**3**) $KMo_{12}S_{14}$, and (**4**) $K_{2.6}Mo_{12}S_{14}$ ((**2**) $a = 9.1476(4)$ Å, $c = 16.421(1)$ Å; (**3**) $a = 9.0797(9)$ Å, $c = 16.412(6)$ Å; and (**4**) $a = 9.1990(4)$ Å, $c = 16.426(4)$ Å). Electrical resistivity measurements carried out on single crystals of $K_{2.3}Mo_{12}S_{14}$ and $KMo_{12}S_{14}$ indicate that the former is semiconducting, whereas the latter is metallic. The evolution of the Mo–Mo distances with respect to the stoichiometry in potassium is discussed.

Introduction

Inorganic compounds containing low-valence molybdenum are generally characterized by metal clusters of diverse sizes and geometries. Thus, in reduced molybdenum oxides, 22 different types of discrete molybdenum clusters, of which the nuclearities goes from 3 to 36, are known to date. Clusters with nuclearities higher than 8 generally result from the one-dimensional condensation of Mo_6 clusters via opposite edge-sharing. This process leads to Mo_{4n+2} oligomers that are observed, for example, in the series $M_{n-x}Mo_{4n+2}O_{6n+4}$ ($n =$ 2, 3, 4, and 5).[1] Chalcogenide compounds containing octahedral Mo_6 clusters[2] are the most abundant and present interesting physical properties.[3,4] Molybdenum clusters with higher nuclearities, such as Mo_9,[5] Mo_{12},[6] Mo_{15},[7] Mo_{18},[8] Mo_{21},[9] Mo_{24}[10], Mo_{30},[10] and Mo_{36},[11] can also be obtained and result from the one-dimensional trans face-sharing of Mo_6 octahedra. Most of the chalcogenide compounds containing the latter clusters present a well-defined stoichiometry in cations when they are synthesized by classical solid-state reactions at high temperatures (1000 °C − 1800 °C). However, it is possible to use topotactic oxydo-reduction reactions at low temperatures ($T <$ 600 °C) to modify the stoichiometry of the cations and thus the number of electrons borne by the molybdenum clusters on which the physical properties depend. For example, the solid-state synthesized compound $Ag_{3.6}Mo_9Se_{11}$[5] with 36 electrons per Mo_9 cluster is semi-

---

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

(1) (a) Hibble, S. J.; Cheetham, A. K.; Bogle, A. R. L.; Wakerley, H. R.; Cox, D. E. *J. Am. Chem. Soc*. **1988**, *110*, 3295. (b) Dronskowski, R.; Simon, A. *Angew. Chem., Int. Ed.* **1989**, *28*, 758. (c) Gougeon, P.; Potel, M.; Sergent, M. *Acta Crystallogr., Sect. C* **1990**, *46*, 1188. (d) Gougeon, P.; Gall, P.; Sergent, M. *Acta Crystallogr., Sect. C* **1991**, *47*, 421. (e) Dronskowski, R.; Simon, A.; Mertin, W. *Z. Anorg. Allg. Chem*. **1991**, *602*, 49. (f) Gall, P.; Gougeon, P. *Acta Crystallogr., Sect. C* **1994**, *50*, 7. (g) Gall, P.; Gougeon, P. *Acta Crystallogr., Sect. C* **1994**, *50*, 1183. (h) Dronskowski, R.; Simon, A.; Mertin. W. *Z. Anorg. Allg. Chem*. **1991**, *602*, 49. (i) Dronskowski, R.; Simon, A. *Acta Chem. Scand*. **1991**, *45*, 850. (j) Schimek, G. L.; Chen, S. C.; McCarley, R. E. *Inorg. Chem.* **1995**, *34*, 6130. (k) Schimek, G. L.; Nagaki, D. A.; McCarley, R. E. *Inorg. Chem.* **1994**, *33*, 1259. (l) Dronskowski, R.; Mattausch, H. J.; Simon, A. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1397. (m) Schimek, G. L.; McCarley, R. E. *J. Solid State Chem*. **1994**, *113*, 345.

(2) Chevrel, R.; Sergent, M. In *Superconducting in Ternary Compounds, Part I*; Fischer, Ø., Maple, M. B., Eds.; Springer-Verlag: Berlin, 1982.

(3) Fischer, Ø. *Appl. Phys.* **1978**, *16*, 1.

(4) Maple, M. B.; Fischer, Ø. In *Superconducting in Ternary Compounds, Parts I, II*; Fischer, Ø., Maple, M. B., Eds.; Springer-Verlag: Berlin, 1982.

10.1021/ic051622u CCC: $33.50

conducting, whereas the metastable binary o-Mo_9Se_{11},[12] obtained by topotactic silver deintercalation and with 32 electrons per Mo_9 cluster, exhibits a metallic behavior with a superconducting transition at 5.5 K.

We present here the syntheses and crystal structures of the $K_{1+x}Mo_{12}S_{14}$ ($x = 0$, 1.1 1.3, and 1.6) compounds, which crystallize in a new structural type built with $Mo_{12}S_{14}$ units. Also reported are the electrical resistivity measurements on the compounds with $x = 0$ and 1.3.

Experimental Section

Syntheses. Starting materials used for the solid-state syntheses were MoS_2, K_2MoS_4, and Mo, all in powder form. Before use, Mo powder (Plansee, 99.999%) was reduced under H_2 flowing gas at 1000 °C for 10 hours, eliminating any trace of oxygen. The molybdenum disulfide was prepared by the reaction of sulfur (Fluka, 99.999%) with H_2-reduced Mo in a 2:1 S:Mo ratio in an evacuated (ca. 10^{-2} Pa Ar residual pressure) and flame-baked silica tube, heated at about 700 °C for 2 days. The thiomolybdate of potassium was obtained by the sulfuration of K_2MoO_4 at 400 °C for 2 days using CS_2 gas in a flowing argon carrier. The molybdate K_2MoO_4 was synthesized by heating an equimolar ratio of MoO_3 and K_2CO_3 (CERAC, 99.95 and 99.9%, respectively) in an alumina vessel at 800 °C in air for 2 days. The purity of all starting reagents was checked by powder X-ray diffraction on an Inel curve sensitive position detector CPS 120. Furthermore, to avoid any contamination by oxygen and moisture, we kept and handled the starting reagents in a purified argon-filled glovebox.

$K_{2.3}Mo_{12}S_{14}$. Single crystals of $K_{2.3}Mo_{12}S_{14}$ were synthesized by a high-temperature solid-state reaction from a mixture of K_2MoS_4, MoS_2, and Mo with an overall composition of $K_{0.25}Mo_{0.375}S_{0.5}$. The powders were mixed, ground together in a mortar, and then cold-pressed. The pellet (ca. 3 g) was then loaded in a molybdenum crucible (depth = 2.5 cm; diameter = 1.5 cm), which was previously cleaned by being heated at 1500 °C in a high-frequency furnace for 15 min under a dynamic vacuum of about 10^{-3} Pa and then sealed under a low argon pressure (300 h Pa) using an arc welding system. The crucible was heated at a rate of 300 °C h^{-1} up to 1500 °C and held there for 6 h; it was then cooled at 100 °C h^{-1} to 1000 °C and finally furnace-cooled to room temperature.

$K_{2.1}Mo_{12}S_{14}$ and $KMo_{12}S_{14}$. The $K_{2.1}Mo_{12}S_{14}$ and $KMo_{12}S_{14}$ compounds were prepared by oxidation of single crystals of $K_{2.3}Mo_{12}S_{14}$ in an aqueous solution of iodine at 90 °C for 2 and 48 h, respectively, according to the following reaction:

$$K_{2.3}Mo_{12}S_{14} + xI_2 \rightarrow K_{2.3-2x}Mo_{12}S_{14} + 2xKI$$

$K_{2.6}Mo_{12}S_{14}$. Single crystal of $K_{2.6}Mo_{12}S_{14}$ were obtained by treating crystals of $K_{2.3}Mo_{12}S_{14}$ in a basic reducing solution of $K_2S_2O_3$/KOH at 60 °C for 3 days. The proposed reaction involved here is:

$$(4/x)K_{2.3}Mo_{12}S_{14} + 8K^+ + S_2O_3^{2-} + 6OH^- \rightarrow (4/x)K_{2.3+x}Mo_{12}S_{14} + 2SO_3^{2-} + 4K^+ + 3H_2O$$

Single-Crystal X-ray Studies. Black single crystals of $K_{2.3}Mo_{12}S_{14}$ (**1**), $K_{2.1}Mo_{12}S_{14}$ (**2**), $KMo_{12}S_{14}$ (**3**), and $K_{2.6}Mo_{12}S_{14}$ (**4**) with approximately spherical shapes were selected and mounted on glass fibers. They were investigated by the $\omega-2\theta$ scan method at room temperature on an automatic X-ray Nonius CAD-4 diffractometer equipped with graphite-monochromatized Mo K_α radiation ($\lambda = 0.71073$ Å). Lattice parameters were obtained by least-squares refinement of the setting angles of 25 reflections. In all cases, three orientation and three intensity reference reflections were checked every 250 reflections and every hour, respectively, and showed no significant fluctuation during data collection. For the four single crystals measured, the intensities were collected in the (h,k,l) ranges: 0/14, −14/0, 0/26 for **1**, −18/0, 0/18, 0/32 for **2**, 0/16, 0/16,−29/+29 for **3**, and 0/19, 0/19,−35/+35 for **4**. The raw data were then corrected for Lorentz polarization and for absorption using the ψ-scan or spherical technique with the aid of the WINGX program.[13] Systematic absences (hhl) $l = 2n+1$ were only consistent with $P31c$ and $P\bar{3}1c$ space groups. Atomic scattering factors and anomalous dispersion corrections were taken from *Tables for X-ray Crystallography* (1974).

$K_{2.3}Mo_{12}S_{14}$(1). The initial positions for all the molybdenum and sulfur atoms as well as for one potassium atom K1 were determined with the direct-methods program SHELXS[14] in the $P\bar{3}1c$ space group using the 3728 collected reflections (1107 unique reflections with $I/\sigma(I) > 2$; $R_{int} = 0.054$). At this stage, an electron-density difference map revealed a quasicontinuous electron density along the c axis with three maxima at the levels $z = 0$, 0.14, and 0.25, which we assigned to potassium atoms K2, K3, and K4, respectively (Figure 1a). The refinement of the positional and anisotropic displacement parameters for all atoms and occupancy factor parameters for the K2, K3, and K4 sites using the JANA2000 Program[15] led to the values of $R(F_o) = 0.0289$ and $R_w(F_o) = 0.0304$ for the 1107 independent data having $I/\sigma(I) > 2$, with no residual peaks higher than 1.55 and −1.24 e Å^{-3} in the channel. Attempts to refine the K2, K3, and K4 atoms using anharmonic atomic displacement parameters were unsuccessful. The stoichiometry deduced from the refinement was $K_{2.3(1)}Mo_{12}S_{14}$.

$K_{2.1}Mo_{12}S_{14}$ (2), $KMo_{12}S_{14}$ (3), and $K_{2.6}Mo_{12}S_{14}$ (4). The structures were refined in the trigonal space group $P\bar{3}1c$ on F by full-matrix least-squares techniques with the JANA2000 program. Atomic positions of the atoms forming the $KMo_{12}S_{14}$ skeleton were used in the first step of refinement of **2**, **3**, and **4** on the corrected data sets. At this stage, although no electron density was found in the channel along the c axis for **3**, we observed three maxima of electron density for **2** and **4** along the c axis, as in **1** (Figure 1b, c). For **4**, the excess of potassium goes principally on the K3 site, whose the population increases from 24% in **1** to 39% in **4**. It is also interesting to note that the population of the K4 site decreases slightly from 52% in **1** to 42% in **4**. For **2**, the diminishing of the potassium stoichiometry results principally from a decrease in the population of the K2 site from 32% in **1** to 3% in **2**. The final values of the different R factors are given in Table 1. For **1**, **2**, and **4**, calculations of probability density function show that for the K

---

(5) Gougeon, P.; Padiou, J.; Le Marouille, J.-Y.; Potel, M.; Sergent, M. *J. Solid State Chem.* **1984**, *51*, 226.

(6) (a) Gougeon, P.; Potel, M.; Padiou, J.; Sergent, M. *Mater. Res Bull.* **1987**, *22*, 1087. (b) Gautier, R.; Picard, S.; Gougeon, P.; Potel, M. *Mater. Res. Bull.* **1999**, *34*, 93.

(7) (a) Gougeon, P.; Potel, M.; Sergent, M. *Acta Crystallogr., Sect. C* **1989**, *45*, 182. (b) Gougeon, P.; Potel, M.; Sergent, M. *Acta Crystallogr., Sect. C* **1989**, *45*, 1413.

(8) Gougeon, P.; Potel, M.; Padiou, J.; Sergent, M. *Mater. Res Bull.* **1988**, *23*, 453.

(9) Picard, S.; Gougeon, P.; Potel, M. *Acta Crystallogr., Sect. C* **1997**, *53*, 1519.

(10) Gougeon, P. Ph.D. Thesis, Université de Rennes, France, 1984.

(11) Picard, S.; Gougeon, P.; Potel, M. *Angew. Chem.* **1999**, *38*, 2034.

(12) Gougeon, P.; Potel, M.; Padiou, J.; Sergent, M.; Boulanger, C.; Lecuire, J.-M. *J. Solid State Chem.* **1984**, *218*, 226.

(13) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.

(14) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

(15) Petricek, V.; Dusek, M. *Jana2000, Structure Determination Software Programs*; Institute of Physics: Praha, Czech Republic, 2000.

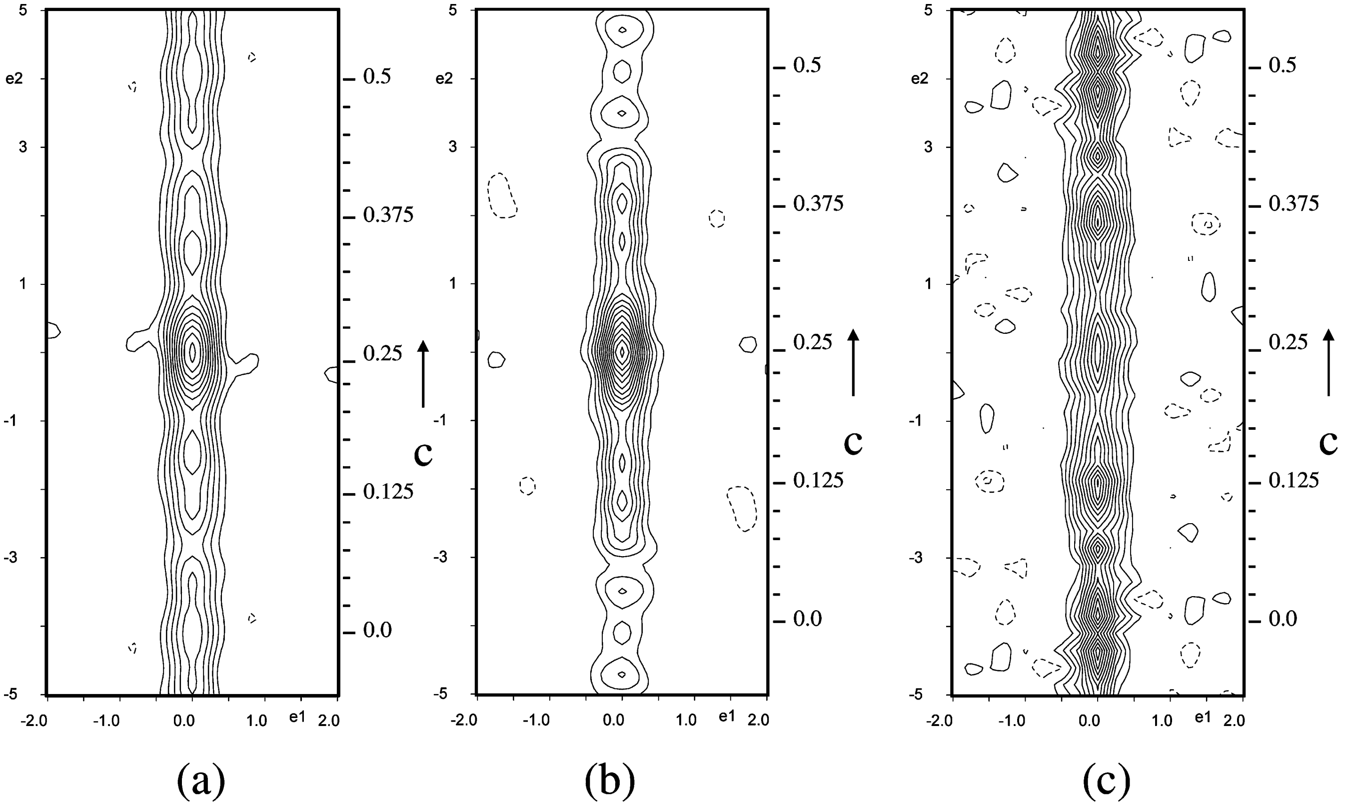


Figure 1. Fourier difference maps along the *c* axis in (a) $K_{2.3}Mo_{12}S_{14}$, (b) $K_{2.1}Mo_{12}S_{14}$, and (c) $K_{2.6}Mo_{12}S_{14}$ (step: 1 e Å^{-3}).

Table 1. X-ray Crystallographic and Experimental Data for $K_{2.3}Mo_{12}S_{14}$, $K_{2.6}Mo_{12}S_{14}$, $K_{2.1}Mo_{12}S_{14}$, and $KMo_{12}S_{14}$

	$K_{2.3}Mo_{12}S_{14}$	$K_{2.6}Mo_{12}S_{14}$	$K_{2.1}Mo_{12}S_{14}$	$KMo_{12}S_{14}$
fw (g mol^{-1})	1690.0	1701.8	1682.2	1639.2
space group	$P\bar{3}1c$ (No. 163)			
a (Å)	9.1720(7)	9.1990(4)	9.1476(4)	9.0797(9)
c (Å)	16.403(4)	16.426(4)	16.421(1)	16.412(6)
Z	2			
V (Å^3)	1195.0(3)	1203.8(3)	1190.0(1)	1171.7(4)
ρ_{calcd} (g cm^{-3})	4.695	4.693	4.693	4.646
T (°C)	20			
λ (Mo K$_\alpha$; Å)	0.71073			
μ (mm^{-1})	7.676	7.676	7.705	7.621
R1a ($I/\sigma(I) > 2$)	0.0289	0.0361	0.0265	0.0243
wR2b ($I/\sigma(I) > 2$)	0.0304	0.0391	0.0297	0.0249

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o - F_c)^2]/\sum[w(F_o)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o) + 0.00005F_o^2]$.

Table 2. Selected Interatomic Distances (Å) for $K_{2.6}Mo_{12}S_{14}$, $K_{2.3}Mo_{12}S_{14}$, $K_{2.1}Mo_{12}S_{14}$, and $KMo_{12}S_{14}$

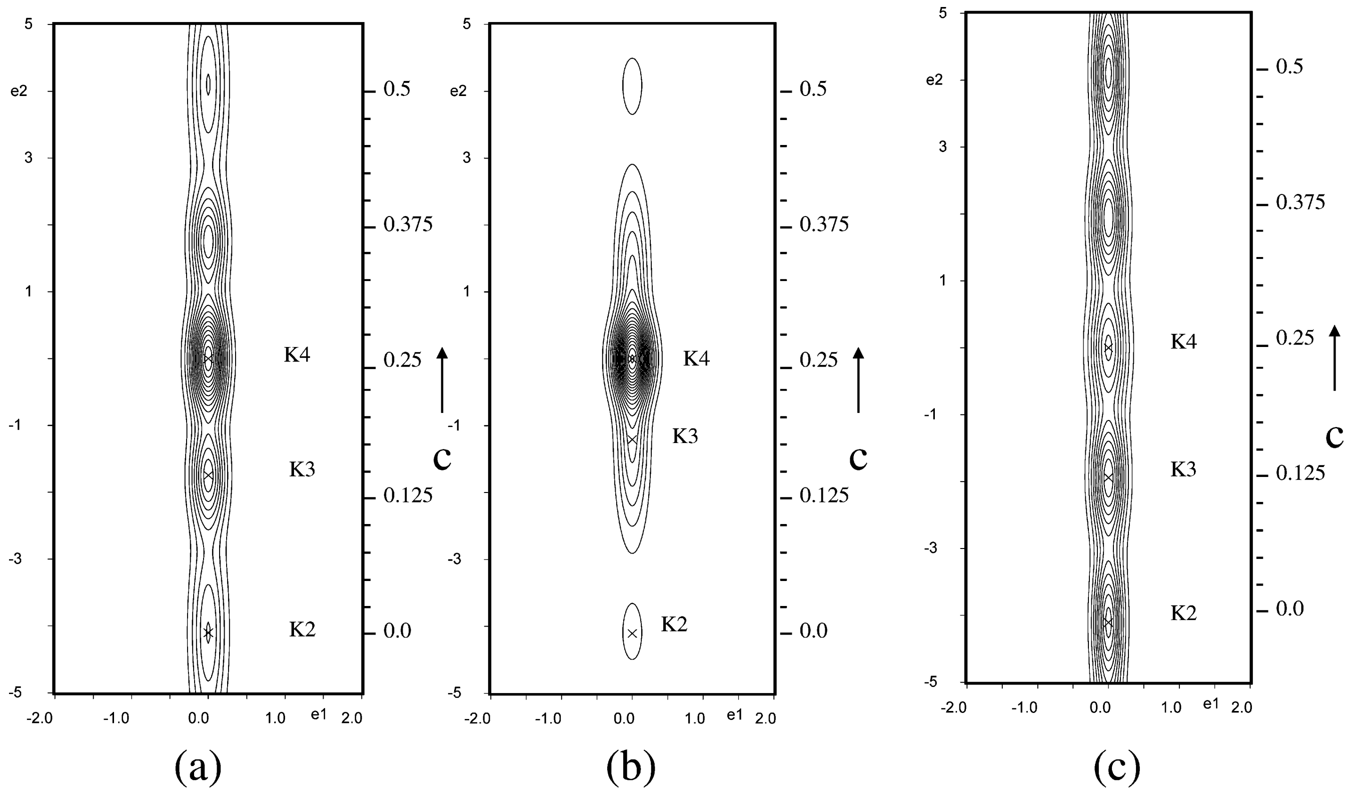
	$K_{2.6}Mo_{12}S_{14}$	$K_{2.3}Mo_{12}S_{14}$	$K_{2.1}Mo_{12}S_{14}$	$KMo_{12}S_{14}$
Intratriangle				
Mo1−Mo1 (×2)	2.6386(4)	2.6515(7)	2.6639(3)	2.6856(3)
Mo2−Mo2 (×2)	2.6797(4)	2.6784(7)	2.6823(5)	2.6942(4)
Intertriangle				
Mo1−Mo2	2.7208(3)	2.7265(6)	2.7356(3)	2.7542(3)
	2.7964(3)	2.8056(6)	2.8177(3)	2.8411(3)
Mo2−Mo2	2.6515(4)	2.6461(6)	2.6480(4)	2.6346(4)
	2.6833(2)	2.6791(5)	2.6816(2)	2.6739(2)
Average				
Mo−Mo	2.686	2.690	2.697	2.709
Intercluster				
Mo1−Mo1	3.2631(4)	3.2283(8)	3.2000(4)	3.1351(4)
Intratriangle				
Mo1−S1	2.452(1)	2.449(3)	2.446(1)	2.438(1)
	2.482(1)	2.475(2)	2.475(1)	2.4560(9)
Mo2−S2	2.4722(8)	2.469(2)	2.4710(7)	2.4597(7)
	2.4826(9)	2.480(2)	2.4822(7)	2.4761(7)
Intertriangle				
Mo1−S2 (×2)	2.6028(9)	2.607(1)	2.6160(6)	2.6136(5)
Mo2−S1 (×2)	2.4486(9)	2.441(2)	2.4380(9)	2.4215(7)
Mo2−S2 (×2)	2.5873(8)	2.578(2)	2.5760(8)	2.5587(7)
Mo1−S3 (×2)	2.3891(9)	2.387(1)	2.3877(9)	2.3881(8)
Intercluster				
Mo1−S1	2.4843(7)	2.469(1)	2.4607(6)	2.4338(5)
K1−S2 (×6)	3.346(1)	3.331(2)	3.3164(8)	3.2816(8)
K1−S3 (×2)	2.995(1)	2.989(2)	2.992(1)	2.988(1)
K2−S1 (×6)	3.170(1)	3.159(2)	3.1434(9)	
K3−S2 (×3)	3.310(8)	3.261(1)	3.185(1)	
K3−S1 (×3)	3.260(1)	3.32(3)	3.61(9)	
K4−S2 (×6)	3.407(1)	3.395(2)	3.3812(8)	

atoms in the channels, the position of the density maximum coincides with the refined position (Figure 2). The crystallographic and experimental data of the four compounds investigated are listed in Table 1, and selected interatomic distances in Table 3.

Electrical Resistivity Measurements. The studies of the temperature dependences of the electrical resistivity were carried out on single crystals of $K_{2.3}Mo_{12}S_{14}$ and $KMo_{12}S_{14}$ using a conventional ac four-probe method with a current amplitude of 0.1 mA. Contacts were ultrasonically made with molten indium on single crystals previously characterized on a CAD-4 diffractometer. The ohmic behavior and the invariance of the phase were checked during the different measurements at low and room temperatures.

Results and Discussion

Crystal Structure. The $K_{1+x}Mo_{12}S_{14}$ ($0 \leq x \leq 1.6$) compounds crystallize in a new structural type, the Mo−S three-dimensional framework, which is based on interconnected $Mo_{12}S_{14}$ clusters (Figure 3). The $Mo_{12}S_{14}$ unit, which is centered on a 2d position (1/3; 2/3; 1/4) and thus has here the point symmetry C_{3i}, can be classically described as the result of the mono-axial face-sharing condensation of three Mo_6S_8 units with a loss of S atoms belonging to the shared



(a) (b) (c)

Figure 2. Joint probability density function (jpdf) maps for K2, K3, and K4 along the *c* axis in (a) $K_{2.3}Mo_{12}S_{14}$, (b) $K_{2.1}Mo_{12}S_{14}$, and (c) $K_{2.6}Mo_{12}S_{14}$ (step: 200 $Å^{-3}$).

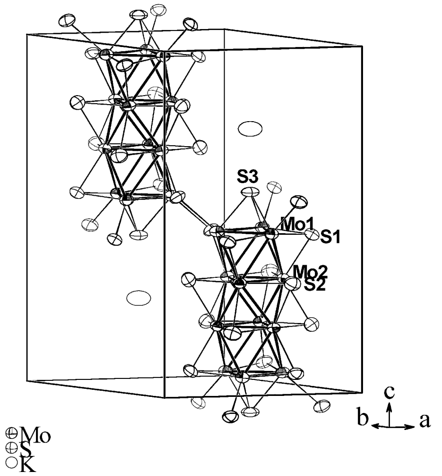


Figure 3. Arrangement of the $Mo_{12}S_{14}$ units and K1 atoms in the $K_{2.3}Mo_{12}S_{14}$ structure (The K2, K3, and K4 atoms have been omitted for clarity; 97% probability level ellipsoids).

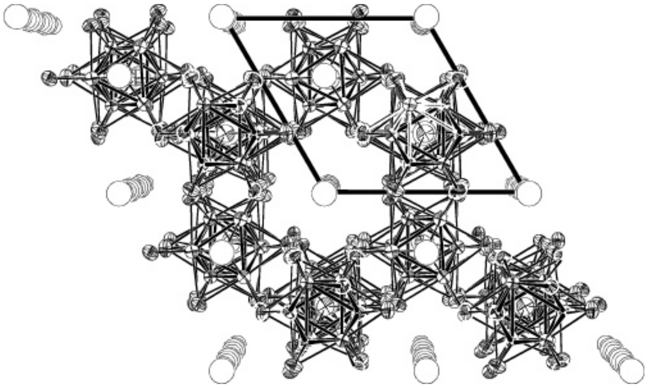


Figure 4. Perspective view of the $K_{1+x}Mo_{12}S_{14}$ structure along the *c* axis.

faces. Such a unit can be also seen as the stacking of four planar Mo_3S_3 instead of two in Mo_6S_8, with two supplementary chalcogen atoms capping the outer triangular faces. The outer Mo1 and the inner Mo2 atoms do not have the same environment. Mo1 atoms of the outer Mo_3 triangles have an environment similar to that encountered in the Mo_6S_8 units of the rhombohedral MMo_6X_8 (M = Na, Pb, RE, etc.; X = S, Se) compounds.[4] They are surrounded by four Mo atoms (two outer Mo1 and two inner Mo2) and four S atoms, which are approximately coplanar, and another S atom that belongs to an adjacent $Mo_{12}S_{14}$ cluster and constitutes the apex of a square-based pyramidal environment. The Mo2 atoms of the inner Mo_3 triangles are surrounded by six Mo atoms (2 outer Mo1 and 2 × 2 inner Mo2) and only four S atoms that belong to the same cluster unit. As observed in previous molybdenum condensed cluster chalcogenides,[10] two kinds of Mo−Mo distances can be distinguished in the units: the Mo−Mo intratriangle distances, which correspond to the distances within the Mo_3 triangles formed by the Mo atoms related through the 3-fold axis and vary between 2.638 and 2.694 Å, and the Mo−Mo distances between the Mo triangles that spread over a wider range (2.634−2.841 Å). The Mo−S bond distances are typical, with the shortest ones at about 2.39 Å for Mo1−S3 and the longest ones at about 2.61 Å for Mo1−S2. Each unit is connected to six adjacent units via 12 interunit Mo1−S1 bonds that are in the 2.434−2.484 Å range, forming a three-dimensional Mo−S framework in which the shortest Mo−Mo intercluster distance varies between 3.135 and 3.263 Å through the $K_{1+x}Mo_{12}S_{14}$ series. The connective formula of the Mo−S network thus created

Table 3. Atomic Coordinates, Equivalent Isotropic Displacement Parameters (Å^2), Wyckoff Positions, and Site Occupancy Factors (sof) for $K_{2.6}Mo_{12}S_{14}$, $K_{2.3}Mo_{12}S_{14}$, $K_{2.1}Mo_{12}S_{14}$, and $KMo_{12}S_{14}$

atom	*x*	*y*	*z*	U_{eq}[a]	Wyck.	sof
			$K_{2.6}Mo_{12}S_{14}$			
Mo1	0.16218(3)	0.50723(3)	0.544360(14)	0.00819(7)	12i	1
Mo2	0.33135(3)	0.49749(3)	0.683857(13)	0.00742(7)	12i	1
S1	0.03845(10)	0.69191(10)	0.55733(4)	0.0100(2)	12i	1
S2	0.02044(10)	0.35864(10)	0.68032(4)	0.0111(2)	12i	1
S3	0.3333	0.6667	0.43232(7)	0.0117(3)	4f	1
K1	0.3333	0.6667	0.25	0.0232(5)	2c	1
K2	0	0	0	0.20(7)	2b	0.32(5)
K3	0	0	0.131(2)	0.15(3)	4e	0.46(5)
K4	0	0	0.25	0.15(5)	2a	0.33(6)
			$K_{2.3}Mo_{12}S_{14}$			
Mo1	0.16061(6)	0.50626(6)	0.54382(2)	0.00801(14)	12i	1
Mo2	0.33127(5)	0.49705(5)	0.68393(2)	0.00715(14)	12i	1
S1	0.03875(16)	0.69244(16)	0.55751(7)	0.0097(4)	12i	1
S2	0.01966(16)	0.35818(16)	0.68063(7)	0.0111(4)	12i	1
S3	0.3333	0.6667	0.43221(12)	0.0109(4)	4f	1
K1	0.3333	0.6667	0.25	0.0213(7)	2c	1
K2	0	0	0	0.32(19)	2b	0.29(7)
K3	0	0	0.142(4)	0.11(4)	4e	0.25(5)
K4	0	0	0.25	0.11(2)	2a	0.52(5)
			$K_{2.1}Mo_{12}S_{14}$			
Mo1	0.15916(3)	0.50531(3)	0.543433(14)	0.00799(7)	12i	1
Mo2	0.33123(3)	0.49633(3)	0.683973(13)	0.00731(6)	12i	1
S1	0.03893(9)	0.69356(9)	0.55771(4)	0.00961(19)	12i	1
S2	0.01859(8)	0.35711(8)	0.68089(4)	0.01091(18)	12i	1
S3	0.3333	0.6667	0.43221(7)	0.0111(2)	4f	1
K1	0.3333	0.6667	0.25	0.0216(4)	2c	1
K2	0	0	0	0.06(6)	2b	0.031(13)
K3	0	0	0.175(14)	0.30(11)	4e	0.27(6)
K4	0	0	0.25	0.073(10)	2a	0.55(11)
			$KMo_{12}S_{14}$			
	0.15603(3)	0.50328(3)	0.542721(11)	0.00636(6)	12i	1
Mo2	0.33087(3)	0.49413(3)	0.684483(11)	0.00676(6)	12i	1
S1	0.03902(8)	0.69397(8)	0.55834(3)	0.00821(18)	12i	1
S2	0.01687(8)	0.35662(8)	0.68091(3)	0.00997(19)	12i	1
S3	0.3333	0.6667	0.43205(6)	0.0094(2)	4f	1
K1	0.3333	0.6667	0.25	0.0196(4)	2c	1

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

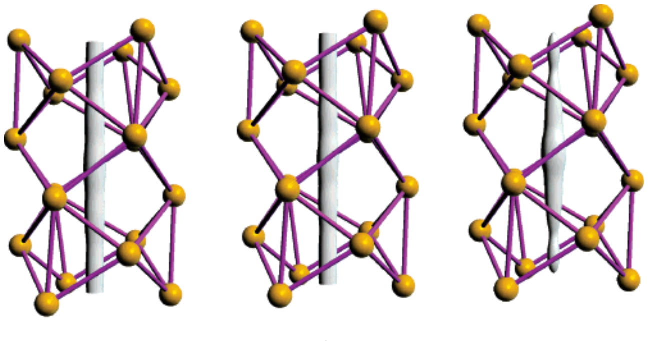

(a) (b) (c)

Figure 5. Three-dimensional surface plot of the jpdf of K2, K3, and K4 with their sulfur environment in (a) $K_{2.6}Mo_{12}S_{14}$, (b) $K_{2.3}Mo_{12}S_{14}$, and (c) $K_{2.1}Mo_{12}S_{14}$ (isosurface at 95% density probability).

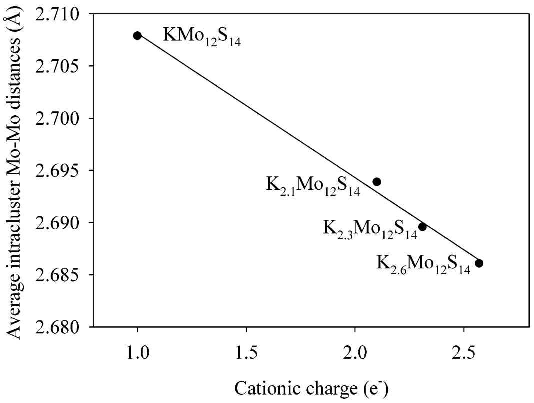


Figure 6. Variations of the average of the Mo–Mo distances within the Mo_{12} cluster as a function of the cationic charge.

is $[Mo_{12}S_8{}^{i}S_{6/2}{}^{i-a}]S_{6/2}{}^{a-i}$ in Schäfer's notation.[16] As shown by the perspective view of the crystal structure along the *c* axis (Figure 4), this arrangement results in large channels extending along the *c* axis being created in which the potassium K2, K3, and K4 ions reside. The other potassium atoms (i.e., K1) are located between two consecutive $Mo_{12}S_{14}$ units along the 3-fold axis.

The K1 cations are eight-coordinated with six S2 atoms, forming an octahedron compressed along the 3-fold axis, and the remaining two S3 atoms cap two opposite faces of the octahedron. As shown by the 3D surface plots of the joint probability density functions of K2, K3, and K4, the latter atoms quasicontinuously occupy the channel running along the *c* axis (Figure 5). The maxima of density correspond to sites formed by six sulfur atoms in a distorted octahedral arrangement.

Evolution of the Mo–Mo distances. Previous studies on ternary chalcogenides containing Mo_6 and Mo_9 clusters have shown that the Mo–Mo distances are greatly affected by

---

(16) Schäfer, H.; Von Schnering, H. G. *Angew. Chem.* **1964**, *20*, 833.

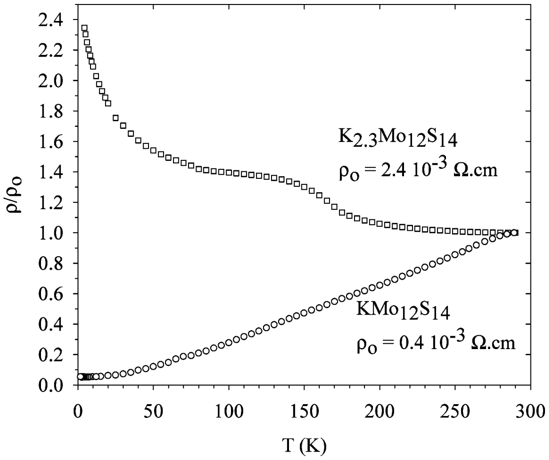


Figure 7. Temperature dependences of the resistivity of $K_{2.3}Mo_{12}S_{14}$ and $KMo_{12}S_{14}$ single crystals, normalized to 290 K.

the modification of the charge transfer from the cations to the clusters. In our case, the augmentation of the charge transfer to the Mo_{12} cluster when going from $KMo_{12}S_{14}$ to $K_{2.6}Mo_{12}S_{14}$ results, if we except the intertriangle Mo2−Mo2 distances, which slightly augment, in a decrease in the other Mo−Mo distances. On average, the Mo−Mo distances within the trioctahedral Mo_{12} cluster decrease when the charge borne by the cluster augments as shown in Figure 6.

Resistivity Properties. Variable-temperature resistivity data for single crystals of $K_{2.3}Mo_{12}S_{14}$ and $KMo_{12}S_{14}$ in the temperature range 4−290 K are presented in Figure 7. $KMo_{12}S_{14}$ exhibits a metallic behavior with a room-temperature resistivity of 0.4 10^{-3} Ω cm. For $K_{2.3}Mo_{12}S_{14}$, the temperature dependence of the resistivity indicates a semiconducting behavior. Such a behavior difference essentially results from the number of electrons per Mo_{12} cluster, which increases from 45 in $KMo_{12}S_{14}$ to 46.3 in $K_{2.3}Mo_{12}S_{14}$.

Conclusion

The four new compounds $K_{1+x}Mo_{12}S_{14}$ ($x = 0$, 1.1, 1.3, and 1.6) were synthesized either by solid-state reaction at high temperature ($x = 1.3$) or by "chimie douce" for the other members. Single-crystal X-ray diffraction studies showed that their structures contain, for the first time, quasi-isolated $Mo_{12}S_{14}$ units that form an original three-dimensional network characterized by a tunnel in which the potassium cations reside. The increase in the cationic charge leads to a decrease in the average of the Mo−Mo distances within the Mo_{12} cluster and to a change from a metallic behavior to a semiconducting one. The crystal structure of the $K_{1+x}Mo_{12}S_{14}$ compounds are particularly adapted for topotactic reaction by "chimie douce", and further works are in progress to insert other cations in the empty channels of $KMo_{12}S_{14}$ either by low-temperature or electrochemical reactions.

Supporting Information Available: X-ray crystallographic files for the $K_{1+x}Mo_{12}S_{14}$ ($x = 0$, 1.,1 1.3, and 1.6) compounds in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC051622U