Inorg. Chem. **2000,** *39,* 1809−1811

Notes

Layered $K_4[Re_6S_{10}(CN)_2]$ and Chainlike $K_4[Re_6Se_{10}(CN)_4]$: New Types of Chalcocyanide Cluster Compounds with Bridging Chalcogenide Ligands

Yuri V. Mironov,[†] **Vladimir E. Fedorov,**[‡]
Craig C. McLauchlan,[§] **and James A. Ibers***[,§]

Lehlstuhl für Analytische Chemie, Ruhr-Universität Bochum,
D-44780 Bochum, Germany, Institute of Inorganic
Chemistry, Ak. Lavrent'ev prosp. 3,
Novosibirsk 630090, Russia, and Department of Chemistry,
Northwestern University, 2145 Sheridan Road,
Evanston, Illinois 60208-3113

Received August 4, 1999

Introduction

Chalcocyanide cluster compounds of the early transition metals have been studied intensively in the past few years. These compounds crystallize with either molecular or polymeric structures. Isolated chalcocyanide cluster anions, including $[Re_6Q_8(CN)_6]^{4-}$ (Q = S,[1−3] Se,[4,5] Te[4,6]), $[Re_4Q_4(CN)_{12}]^{4-}$ (Q = S,[6−8] Se,[6] Te[9]), $[Mo_4S_4(CN)_{12}]^{8-}$,[10] $[Mo_4Te_4(CN)_{12}]^{7-}$,[11] $[W_4Te_4(CN)_{12}]^{6-}$,[11] $[Nb_4OTe_4(CN)_{12}]^{6-}$,[12] $[Mo_3Se_4(CN)_9]^{5-}$,[13] $[W_3Se_4(CN)_9]^{5-}$,[13] and $[Mo_3Te_7(CN)_6]^{2-}$,[14] have been characterized structurally. The polymeric layered compound $[Cu_4(OH)_4][Re_4Te_4(CN)_{12}]$[15] and a series of compounds based on the cluster anions $[Re_6Q_8(CN)_6]^{4-}$ (Q = S, Se) and transition metal cations (Mn^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+}, Zn^{2+}, Cd^{2+})[16−21] have also been synthesized. In these polymeric compounds all or some of the CN^- ligands are bridging. Despite the variety of reported structures, there are no known examples of chalcocyanide complexes containing terminal or bridging chalcogenido ligands or both.

A useful method for preparing chalcocyanide cluster compounds is the reaction of metal chalcogenide or metal chalcohalide complexes with molten KCN at high temperature.[2,5] In the process of developing a synthesis of rhenium chalcocyanide cluster compounds, we have studied the reactions of ReS_2 and $ReSe_2$ with KCN at high temperatures. These reactions have led to the formation of two new unusual chalcocyanide compounds, $K_4[Re_6S_{10}(CN)_2]$ (**1**) and $K_4[Re_6Se_{10}(CN)_4]$ (**2**), that contain bridging ligands, S^{2-} (**1**) or Se_2^{2-} (**2**), together with terminal CN^- ligands. We describe these results here.

Experimental Section

Syntheses. KCN (99.7%), Re (99.997%), S (99.5%), and Se (99.9%) were obtained from commercial sources and used without further purification. The starting compounds ReS_2 and $ReSe_2$ were prepared from stoichiometric amounts of the elements in fused silica tubes at 700 °C for 3 days.[22,23] Compounds $K_4[Re_6S_{10}(CN)_2]$ (**1**) and $K_4[Re_6Se_{10}(CN)_4]$ (**2**) were prepared by the reaction of ReS_2 or $ReSe_2$ with molten KCN in a 1:2 molar ratio. The syntheses were carried out in evacuated fused silica tubes at 800 °C (**1**) and 650 °C (**2**) for 2 days. The tubes were cooled at 10 °C/h to promote crystal growth. The reaction mixtures were washed with methanol. Appropriate red, air-stable single crystals were manually isolated from the reaction mixtures in low yield for **1** and 86% yield for **2** (based on Re). Semiquantitative elemental analyses were made with the use of an energy-dispersive spectrometry (EDS)-equipped Hitachi S-4500 scanning electron microscope: for $K_4[Re_6S_{10}(CN)_2]$ (**1**), K/Re/S is 4.2:6:9.6; for $K_4[Re_6Se_{10}(CN)_4]$ (**2**), K/Re/Se is 4.5:6:10.7.

Crystallographic Studies. The structures of both compounds have been determined by single-crystal X-ray diffraction methods. The unit cell was obtained at 113 K from the setting angles of 25 reflections that had been centered on a Picker diffractometer[24] for compound **1** and at 293 K from the setting angles of 15 reflections that had been centered on Siemens P4 X-ray diffractometer for compound **2**. Both

---

[†] Ruhr-Universität Bochum.

[‡] Institute of Inorganic Chemistry.

[§] Northwestern University.

(1) Mironov, Y. V.; Virovets, A. V.; Fedorov, V. E.; Podberezskaya, N. V.; Shishkin, O. V.; Struchkov, Y. T. *Polyhedron* **1995**, *14*, 3171−3173.

(2) Slougui, A.; Mironov, Y. V.; Perrin, A.; Fedorov, V. E. *Croat. Chem. Acta* **1995**, *68*, 885−890.

(3) McLauchlan, C. C.; Ibers, J. A. Unpublished results.

(4) Mironov, Y. V.; Cody, J. A.; Albrecht-Schmitt, T. E.; Ibers, J. A. *J. Am. Chem. Soc.* **1997**, *119*, 493−498.

(5) Naumov, N. G.; Virovets, A. V.; Podberezskaya, N. V.; Federov, V. E. *J. Struct. Chem. (Engl. Trans.)* **1997**, *38*, 857−862; *Zh. Strukt. Khim.* **1997**, *38*, 1020−1026.

(6) Laing, M.; Kiernan, P. M.; Griffith, W. P. *J. Chem. Soc., Chem. Commun.* **1977**, 221−222.

(7) Fedin, V. P.; Elsegood, M. R. J.; Clegg, W.; Sykes, A. G. *Polyhedron* **1996**, *15*, 485−488.

(8) Müller, A.; Krickemeyer, E.; Bögge, H.; Ratajczak, H.; Armatage, A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 770−773; *Angew. Chem.* **1994**, *106*, 800.

(9) Mironov, Y. V.; Albrecht-Schmitt, T. E.; Ibers, J. A. *Z. Kristallogr.* **1997**, *212*, 308.

(10) Müller, A.; Eltzner, W.; Bögge, H.; Jostes, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 795−796; *Angew. Chem.* **1982**, *94*, 783.

(11) Fedin, V. P.; Kalinina, I. V.; Virovets, A. V.; Podberezskaya, N. V.; Sykes, A. G. *J. Chem. Soc., Chem. Commun.* **1998**, 237−238.

(12) Fedin, V. P.; Kalinina, I. V.; Virovets, A. V.; Podberezskaya, N. V.; Neretin, I. S.; Slovokhotov, Y. L. *J. Chem. Soc., Chem. Commun.* **1998**, 2579−2580.

(13) Fedin, V. P.; Lamprecht, G. J.; Kohzuma, T.; Clegg, W.; Elsegood, M. R. J.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1997**, 1747−1751.

(14) Fedin, V. P.; Imoto, H.; Saito, T.; McFarlane, W.; Sykes, A. G. *Inorg. Chem.* **1995**, *34*, 5097−5098.

(15) Mironov, Y. V.; Virovets, A. V.; Artemkina, S. B.; Fedorov, V. E. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2507−2509; *Angew. Chem.* **1998**, *110*, 2656−2658.

(16) Naumov, N. G.; Virovets, A. V.; Solokov, M. N.; Artemkina, S. B.; Fedorov, V. E. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1943−1945; *Angew. Chem.* **1998**, *110*, 2043−2045.

(17) Beauvais, L. G.; Shores, M. P.; Long, J. R. *Chem. Mater.* **1998**, *10*, 3783−3786.

(18) Naumov, N. G.; Virovets, A. V.; Artemkina, S. B.; Naumov, D. Yu.; Howard, J. A.K.; Fedorov, V. E. *Supramol. Chem.*, in press.

(19) Naumov, N. G.; Virovets, A. V.; Mironov, Y. I.; Artemkina, S. B.; Fedorov, V. E. *Ukr. Khim. Zh.* **1999**, *65*, 21−27.

(20) Shores, M. P.; Beauvais, L. G.; Long, J. R. *J. Am. Chem. Soc.* **1999**, *121*, 775−779.

(21) Shores, M. P.; Beauvais, L. G.; Long, J. R. *Inorg. Chem.* **1999**, *38*, 1648−1649.

(22) Briscoe, H. V. A.; Robinson, P. L.; Stoddart, E. M. *J. Chem. Soc.* **1931**, 1439−1443.

(23) Alcock, N. W.; Kjekshus, A. *Acta Chem. Scand.* **1965**, *19*, 79−94.

(24) Huffman, J. C. Ph.D. Dissertation, Indiana University, 1974.

10.1021/ic990936c CCC: $19.00

Table 1. Crystallographic Data for $K_4[Re_6S_{10}(CN)_2]$ (**1**) and $K_4[Re_6Se_{10}(CN)_4]$ (**2**)

compound	$K_4[Re_6S_{10}(CN)_2]$	$K_4[Re_6Se_{10}(CN)_4]$
empirical formula	$C_2K_4N_2Re_6S_{10}$	$C_4K_4N_4Re_6Se_{10}$
fw	1646.24	2167.28
a, Å	11.183(11)	9.725(6)
b, Å	9.198(9)	13.164(5)
c, Å	10.028(9)	10.738(6)
β, (deg)	90	106.28(4)
V, Å^3	1032(2)	1319(1)
space group	*Pmna*	$P2_1/n$
Z	2	2
λ, Å	0.710 73	0.710 73
ρ_{calc}, g cm^{-3}	5.300	5.455
μ, cm^{-1}	368.7	418.4
temp, K	113(2)	293(2)
$R_1(F)^a$	0.0522	0.0545
$wR2(F_o^2)^b$	0.100	0.114

[a] $R_1(F) = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $wR2(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum wF_o^4]^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (0.04F_o^2)^2$ for $F_o^2 > 0$; $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 = 0$.

instruments used Mo Kα radiation. Intensity data for both compounds were processed and corrected for absorption by an analytical method.[25] The structures were solved by direct methods and refined with the use of the SHELXTL PC[26,27] crystallographic program package. All atomswere refined anisotropically except for atom N(1) of **1**. The refinement of the K positions in **1** presented some difficulties that were not satisfactorily resolved. There are three independent K atoms in the asymmetric unit. Refinement of the occupancies of K sites indicates that the K(1) site is fully occupied, whereas the K(2) and K(3) sites are half-occupied. Nevertheless, the displacement ellipsoids on these K atoms remain large. Since this model of random occupancy of the K(2) and K(3) sites leads to K(2)$\cdots$K(3) interactions of 2.54 Å, there must be some additional order. No evidence of a supercell was found. An alternative solution could not be found in the lower symmetry space group $Pmn2_1$. Except for diminished precision, the structure of the $[Re_6S_{10}(CN)_2]^{4-}$ anion is unaffected by these problems. Additional experimental details are given in Table 1 and in Supporting Information.

Results and Discussion

Compound **1**, $K_4[Re_6S_{10}(CN)_2]$ ($=K_4\{[Re_6S^i_8]S^{a-a}_{4/2}(CN)^a_2\}$),[28] consists of layers built from the $[Re_6S_8]^{2+}$ cluster units linked in two dimensions by four S^{2-} ligands (Figure 1). The geometry of the $[Re_6S_8]^{2+}$ cluster unit, which has idealized D_{4h} symmetry,contains an Re_6 octahedron inscribed in an S_8 cube and is close to that of several compounds reported previously.[17,29−32] The Re−Re distances range from 2.587(3) to 2.646(2) Å; the Re−S^i distances range from 2.369(6) to 2.425(6) Å. Four Re atoms have apical S^{2-} ligands that bridge between $[Re_6S_8]$ cluster units in a Re−S^{a-a}−Re fashion to form the layers. The remaining two Re atoms are trans to one another and are ligated by terminal CN^- ligands. The Re−S^{a-a} distances (2.387(4)−2.412(4) Å) do not differ significantly from the Re−S^i distances. Re−C distances (2.05(3) Å) are similar to those found in other related clusters.[1,5,16] The interlayer space is occupied by two K^+ ions spread over three crystallographically distinct sites.

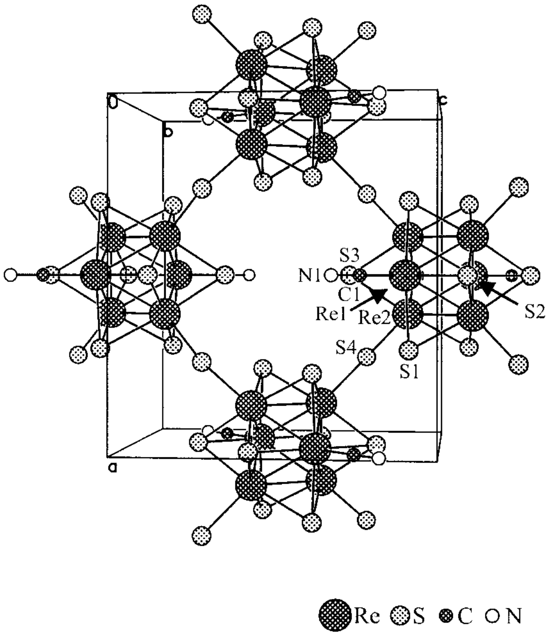

Figure 1. View of the $[Re_6S_{10}(CN)_2]^{4-}$ layer along [010].

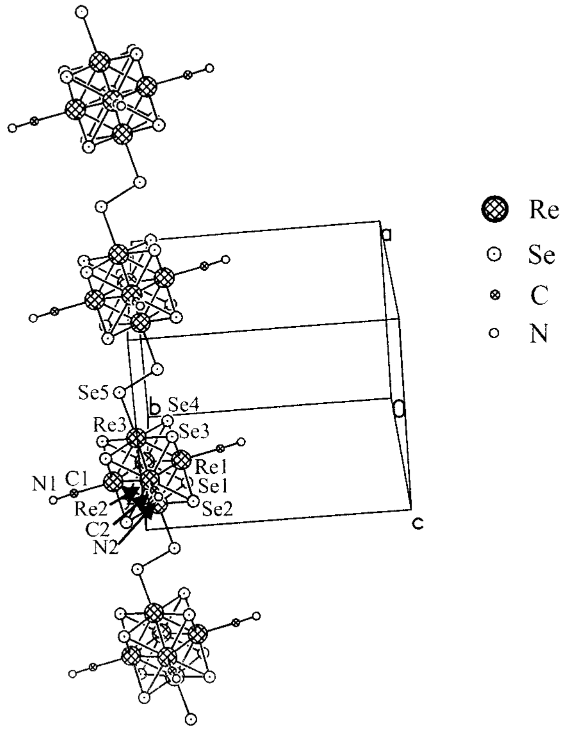

Figure 2. View of a $[Re_6Se_{10}(CN)_4]^{4-}$ chain.

Compound **2**, $K_4[Re_6Se_{10}(CN)_4]$ ($=K_4\{[Re_6Se^i_8](Se_2)^{a-a}_{2/2}(CN)^a_4\}$), consists of chains built from the $[Re_6Se_8]^{2+}$ cluster units linked one-dimensionally by two Se_2^{2-} bridging ligands (Figure 2). The Se−Se distance in the bridging Se_2^{2-} group is 2.365(5) Å. The cluster units are typical for Re_6Se_8 octahedral clusters[4,30,33−35] with Re−Re distances ranging from 2.624(2)

---

(25) de Meulenaer, J.; Tompa, H. *Acta Crystallogr.* **1965**, *19*, 1014−1018.

(26) Sheldrick, G. M. *SHELXTL, An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data*, PC version 5.0; Siemens Analytical X-Ray Instruments, Inc.: Madison, WI, 1994.

(27) Sheldrick, G. M. *SHELXTL*, DOS/Windows/NT version 5.10; Bruker Analytical X-Ray Instruments, Inc.: Madison, WI, 1997.

(28) A complete description of the “a, i” notation may be found in ref 30.

(29) Bronger, W.; Miessen, H.-J. *J. Less-Common Met.* **1982**, *83*, 29−38.

(30) Long, J. R.; McCarty, L. S.; Holm, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 4603−4616.

(31) Willer, M. W.; Long, J. R.; McLauchlan, C. C.; Holm, R. H. *Inorg. Chem.* **1998**, *37*, 328−333.

(32) Slougui, A.; Ferron, S.; Perrin, A.; Sergent, M. *Eur. J. Solid State Inorg. Chem.* **1996**, *33*, 1001−1013.

(33) Long, J. R.; Williamson, A. S.; Holm, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 226−229; *Angew. Chem.* **1995**, *107*, 248.

(34) Zheng, Z.; Long, J. R.; Holm, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 2163-2171.

(35) Bronger, W.; Koppe, C.; Schmitz, D. *Z. Anorg. Allg. Chem.* **1997**, *623*, 239−242.

to 2.642(1) Å and Re−Se^i distances ranging from 2.525(2) to 2.543(3) Å. Two Re atoms trans to one another have apical Se ligands at an Re−Se distance of 2.566(3) Å. The apical Se atom from one cluster unit bonds to a similar Se atom of another cluster unit in a Re−Se^a−Se^a−Re fashion to form infinite chains of $[Re_6Se_8]^{2+}$ clusters with Se_2^{2-} bridging ligands. The four remaining Re atoms have terminal CN^- ligands; Re−C distances are 2.09(2) and 2.12(2) Å.

Previously known chalcocyanide clusters contain chalcogen atoms in the core and terminal cyano groups that enter into bridges. The present compounds are the first to contain both terminal chalcogen and cyano groups that are accessible for intercluster bridging; in these compounds, at least, the chalcogen atoms bridge whereas the cyano groups do not. The geometries of these bridges are similar to those in related clusters.[29,35−37]

Acknowledgment. This research was supported by the National Science Foundation (Grant No. DMR97-09351) and Russian Foundation for Basic Research (Grant N99-03-32789). Y. V. Mironov thanks the Alexander von Humboldt Foundation for a fellowship.

Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of $K_4[Re_6S_{10}(CN)_2]$ (**1**) and $K_4[Re_6Se_{10}(CN)_4]$ (**2**). This material is available free of charge via the Internet at http://pubs.acs.org.

IC990936C

---

(36) Bronger, W.; Miessen, H.-J.; Neugröschel, R.; Schmitz, D.; Spangenberg, M. *Z. Anorg. Allg. Chem.* **1985**, *525*, 41−53.

(37) Bronger, W.; Loevenich, M.; Schmitz, D.; Schuster, T. *Z. Anorg. Allg. Chem.* **1990**, *587*, 91−102.