5000 *Inorg. Chem.* **2000,** *39,* 5000−5001

A Cyanide-Bridged Chain of Mo_6Se_8 Clusters: A Product of Cyanide-Melt Cluster Synthesis

Carmela Magliocchi, Xiaobing Xie, and Timothy Hughbanks*

Department of Chemistry, Texas A&M University, P.O. Box 30012, College Station, Texas 77842-3012

Received July 25, 2000

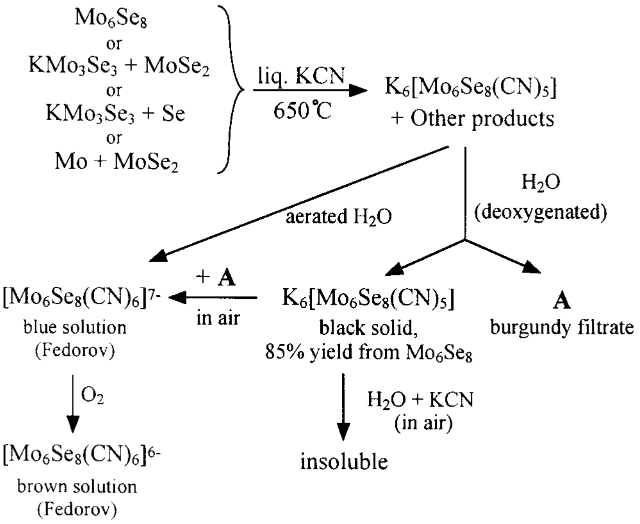
"Chevrel phases", $M_xMo_6Q_8$ (Q = S, Se, Te), possess structures in which Mo_6Q_8 clusters are tightly cross-linked by Mo−Q bonds into a 3-dimensional network. In the 1970s and 1980s these compounds attracted intense interest because they exhibit diverse physical and chemical properties, such as high-critical-field (H_{c2}) superconductivity,[1] magnetic ordering,[2−5] fast ion conductivity,[6] and catalytic activity for hydrodesulfurization.[7]

There has been considerable recent interest in preparation of molecular Mo_6Q_8 complexes. Such preparative work has involved the Q/Cl exchange, starting with $[Mo_6Cl_8]^{4+}$,[8] or synthesis from smaller cluster fragments.[9] In a distinct departure from these approaches, Fedorov's group has recently discovered that the binary Chevrel phase compound, Mo_6Se_8, serves as a precursor to discrete $[Mo_6Se_8(CN)_6]^{6/7-}$ clusters when reacted with molten KCN.[10] Though the reactivity and ligand field strength of cyanide make it an attractive nucleophile for such a "cluster excision" process,[11] it is remarkable that the Mo_6Se_8 seems to be extricated intact from the tightly cross-linked Chevrel phase structure. Molten cyanides are also effective in excising Re_6Q_8 (Q = Se, Te) clusters from less tightly crosslinked Re_6Q_8-based solids.[12−15]

Intrigued by the opportunities offered by the redox active $[Mo_6Se_8(CN)_6]^{6/7-}$ clusters, we have investigated this system further. Here we report the synthesis, structure, and characterization of the first example of an extended structure, $K_6Mo_6Se_8(CN)_5$ (**1**), in which hexanuclear clusters are bridged by cyanide ligands. We also show that the KCN melt can serve as a medium for the synthesis of Mo_6Se_8 clusters from simple starting materials.

Scheme 1 shows that there are several synthetic routes to **1**. Although the binary Chevrel phase precursor, Mo_6Se_8, works well,[16] it is not necessary to begin with a compound containing clusters. **1** is the major phase obtained in all these reactions, but more unreacted starting material is observed in XRD powder patterns when Mo_6Se_8 is not used. The formation of Mo_6Se_8 clusters in a direct reaction of the $MoSe_2$ and Mo metal at relatively low temperatures is especially remarkable given that the binary Mo_6Se_8 is commonly prepared by direct solid-state reaction at 1200 °C for 24 h.[17,18] Fedorov and co-workers have recently reported the synthesis of compounds containing Re_6Q_8 (Q = S, Se) clusters by reaction of ReQ_2 in molten KCN.[19]

Scheme 1



The formation of $[Mo_6Se_8(CN)_6]^{6/7-}$ clusters from **1** is a somewhat subtle process (Scheme 1). As noted by the Fedorov group, the direct dissolution of the cyanide melt in aerated water yields $[Mo_6Se_8(CN)_6]^{6/7-}$ clusters. However, when the wash water is deoxygenated, **1** remains insoluble and can be isolated. If the filtrate (**A**) is removed, the insolubility persists even if **1** is added to an aqueous KCN solution in the presence of oxygen or if the $[Mo_6Se_8(CN)_6]^{6-}$ ion is added in hopes of catalyzing dissolution. The clear implication of these observations is that there are species in the filtrate that are air-oxidized and those oxidized species are necessary to facilitate the dissolution of **1**. We have not identified minor products formed when Mo_6Se_8 is reduced to form $[Mo_6Se_8(CN)_6]$,$^{7-}$ though cluster disproportionation is a plausible

---

(1) Fischer, O., Maple, M. B., Eds. *Topics in Current Physics, Vol. 32: Superconductivity in Ternary Compounds I: Structural, Electronic, and Lattice Properties*; Springer-Verlag, New York, 1982.

(2) Pena, O.; Sergent, M. *Prog. Solid State Chem.* **1989**, *19*, 165−281.

(3) Burlet, P.; Flouquet, J.; Genicon, J. L.; Horyn, R.; Pena, O.; Sergent, M. *Physica B (Amsterdam)* **1995**, *215*, 127−33.

(4) Pena, O.; LeBerre, F.; Sergent, M.; Horyn, R.; Wojakowski, A. *Physica C (Amsterdam)* **1994**, *235−240*, 771−2.

(5) Giroud, M.; Genicon, J. L.; Tournier, R.; Geantet, C.; Pena, O.; Horyn, R.; Sergent, M. *J. Low Temp. Phys.* **1987**, *69*, 419−50.

(6) Mulhern, P. J.; Haering, R. R. *Can. J. Phys.* **1984**, *62*, 527−31.

(7) McCarty, K. F.; Anderegg, J. W.; Schrader, G. L. *J. Catal.* **1985**, *93*, 375−87.

(8) Hilsenbeck, S. J.; Young, V. G., Jr.; McCarley, R. E. *Inorg. Chem.* **1994**, *33*, 1822−32.

(9) Saito, T.; Yamamoto, N.; Nagase, T.; Tsuboi, T.; Kobayashi, K.; Yamagata, T.; Imoto, H.; Unoura, K. *Inorg. Chem.* **1990**, *29*, 764−70.

(10) Mironov, Y. V.; Virovets, A. V.; Naumev, N. G.; Ikorskii, V. N.; Fedorov, V. E. *Chem.*−*Eur. J.* **2000**, *6*, 1361−5.

(11) Dunbar, K. R.; Heintz, R. A. *Prog. Inorg. Chem.* **1997**, *45*, 283−391.

(12) Mironov, Y. V.; Cody, J. A.; Albrecht-Schmitt, T. E.; Ibers, J. A. *J. Am. Chem. Soc.* **1997**, *119*, 493−8.

(13) Naumov, N. G.; Virovets, A. V.; Podberezskaya, N. V.; Fedorov, V. E. *J. Struct. Chem.* **1997**, *38*, 857−62.

(14) Naumov, N. G.; Virovets, A. V.; Sokolov, M. N.; Artemkina, S. B.; Fedorov, V. E. *Angew. Chem., Int. Ed.* **1998**, *37*, 1943−5.

(15) Beauvais, L. G.; Shores, M. P.; Long, J. R. *J. Am. Chem. Soc.* **2000**, *122*, 2763−72 and references therein.

(16) Following the Fedorov protocol, Mo_6Se_8 (1.00 g, 0.828 mmol) was ground into a fine powder, combined with KCN (1.00 g, 15.385 mmol), and loaded into a fused silica tube. After heating at 650 °C for 36 h, the reaction mixture was cooled and the excess KCN was removed by dissolution in deoxygenated H_2O for 30 min. The mixture was filtered, and a black solid was separated from the burgundy filtrate containing excess KCN. After the solid was dried under vacuum overnight, 1.1 g of black polycrystalline $K_6[Mo_6Se_8(CN)_5]$ (**1**), was recovered (85%, yields in the 75−85% range are typical of this route and the alternatives indicated in Scheme 1). IR (Nujol): $\nu(CN) = 2069, 2016\ cm^{-1}$. Single crystals of **1** were obtained by heating (48 h at 650 °C) of the reaction mixture in a substantial temperature gradient and gathering crystals that had formed at the cooler end of the reaction tube.

(17) De Jonge, R.; Popma, T. J. A.; Wiegers, G. A.; Jellinek, F. *J. Solid State Chem.* **1970**, *2*, 188−92.

(18) Chevrel, R.; Sergent, M.; Prigent, J. *Mater. Res. Bull.* **1974**, *9*, 1487−98.

(19) Mironov, Y. V.; Fedorov, V. E.; McLauchlan, C. C.; Ibers, J. A. *Inorg. Chem.* **2000**, *39*, 1809−11.

10.1021/ic000833q CCC: $19.00

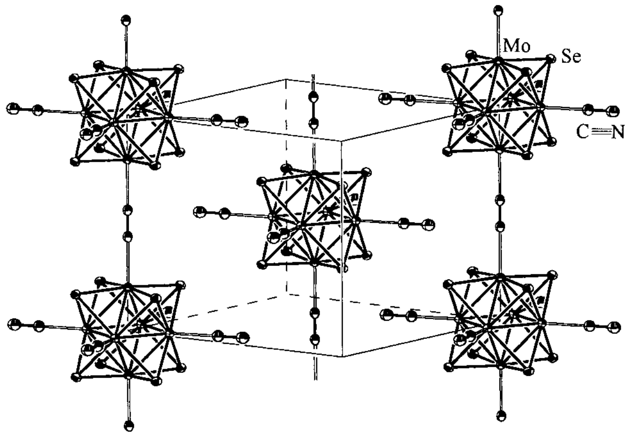


Figure 1. Cell packing diagram of $[Mo_6Se_8(CN)_5]^{6-}$. Thermal ellipsoids are shown at the 90% probability level; chains in the foreground and background were omitted for clarity.

explanation. Similar uncertainties apply, for example, when ReS_2 is reduced in cyanide melts to give compounds with the $[Re_6S_8]^{2+}$ core.[10,19]

The body-centered tetragonal structure of $K_6Mo_6Se_8(CN)_5$ was determined by single-crystal X-ray diffraction;[20] a cell packing diagram is shown in Figure 1. The molybdenum atoms in the basal plane of each $[Mo_6Se_8]^-$ cluster are bound to four terminal CN^- ligands, and clusters are linked by cyanide ligands into linear chains, $[Mo_6Se_8(CN)_4(CN)_{2/2}{}^{6-}]_n$, that propagate up the *c*-axis. The basal plane in each Mo_6 octahedron is contracted so that the Mo_b-Mo_b distances (2.6711(4) Å) are shorter than distances between the apical and basal molybdenum atoms (Mo_a-Mo_b = 2.7193(4) Å). The Mo_6Se_8 cluster is otherwise fairly regular: ($\bar{d}$(Mo−Se) = 2.5763 Å, range: 2.5683(3)−2.5873(3) Å). Mo_b−CN distances to terminal cyanides (2.204(3) Å) are only slightly shorter than the mean distance involving bridging atoms ($\bar{d}$(Mo_a−C/N) = 2.217(4) Å). We found no evidence for long-range order of the bridging cyanides; neither systematic absence violations nor superlattice reflections can be detected.

Theoretical treatments indicate that Mo_6Q_8 clusters accommodate up to 24 e in M−M bonding orbitals, and for the ideal O_h-symmetry case, the HOMO has e_g symmetry.[1,21−25] For $[Mo_6Se_8]^-$, there are 21 cluster bonding electrons and an $e_g{}^1$ electron configuration (^2E_g state) is expected. In the observed tetragonal environment (nominally D_{4h}), the e_g (O_h) orbital set splits such that the a_{1g} (D_{4h}) descendent is the SOMO (singly occupied MO) and the b_{1g} (D_{4h}) orbital is unoccupied (Figure 2d). In an extended Hückel band structure calculation performed on a single $[Mo_6Se_8(CN)_4(CN)_{2/2}{}^{6-}]_n$ chain, the orbital splitting, $\Delta E(b_{1g} - a_{1g})$, is calculated to be 0.10 eV. The splitting is an evident consequence of the differential stabilization conferred on the a_{1g} orbital by the shortening of the basal Mo−Mo bonds.

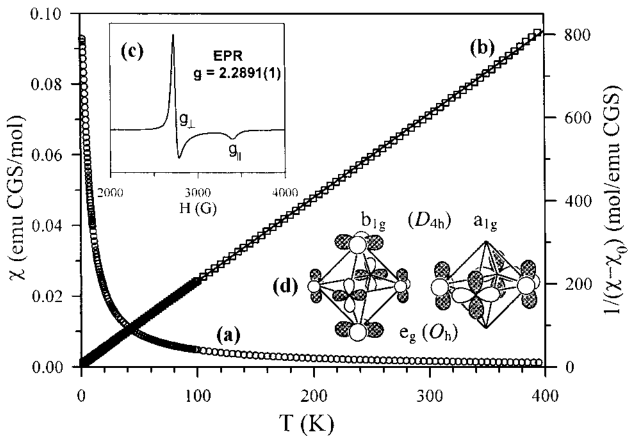


Figure 2. (a) Molar susceptibility versus temperature for $K_6[Mo_6Se_8(CN)_5]$. (b) Reciprocal molar susceptibility (corrected for temperature independent terms). The line is the linear regression fit. (c) X-band EPR powder spectrum at 10 K. (d) e_g orbitals for the Mo_6Se_8 cluster.

Magnetic susceptibility and EPR measurements (Figure 2) are fully consistent with the electronic description given above for this extended chain compound. The EPR spectrum (T = 10 K) is characteristic of an axial system; averaging of $g_\perp$ (2.4425(1)) and $g_\parallel$ (1.9822(1)) gives a g value of 2.2891(1). Over the temperature range 1.8−400 K, magnetic susceptibility data are well described by the Curie−Weiss relation, $\chi = \chi_0 + C/(T + \theta)$; $\chi_0 = 1.216 \times 10^{-5}$ emu/mol, C = 0.497 emu·K/mol, and θ = 2.74 K. Magnetic ordering was not observed at any temperature. The magnetic moment obtained from the Curie constant C is 1.99 μ_B ($\mu_{eff} = 2.828C^{1/2}$), in close agreement with the moment calculated using the g value obtained from EPR and assuming a doublet state for the clusters ($S = {}^1/_2$; $\mu_{eff} = g[{}^1/_2({}^1/_2 + 1)]^{1/2}$ = 1.98 μ_B).

Cyanide ligands would provide significant antiferromagnetic coupling if their π or π^* orbitals had a nonzero overlap with the cluster SOMO. The conspicuous absence of coupling (ferro- or antiferromagnetic) in the magnetic data means that overlap between the CN π^* orbitals and the cluster SOMO is virtually zero. This is consistent with the claim that the odd electron resides in one of the e_g (O_h) orbitals (we argue for the a_{1g} (D_{4h}) descendent on structural grounds). For any open-shell Mo_6Q_8 cluster (21-23 cluster bonding electrons), it is the e_g (O_h) orbitals that will be partially occupied. This must be borne in mind as we seek to more systematically synthesize cyanide-bridged Mo_6Q_8-cluster networks; electronic coupling of the clusters by conjugation through the CN π^* orbitals is precluded by symmetry.

Acknowledgment. We thank Dr. Rodolphe Clérac for help in obtaining magnetic susceptibility data and Mr. Gang Xing for assistance with EPR measurements. We also thank Prof. Arnold Guloy (University of Houston) for his help in acquiring powder X-ray diffraction patterns. We gratefully acknowledge the Robert A. Welch Foundation for its support through Grant A-1132, the National Science Foundation for its support through Grant CHE-9623255, and the Texas Advanced Research Program through Grant 010366-0038b-1997.

Supporting Information Available: X-ray crystallographic file in CIF format for the structure determination of $K_6[Mo_6Se_8(CN)_5]$ (**1**). This material is available free charge via the Internet at http://pubs.acs.org.

IC000833Q

---

(20) Crystal data for **1**: M_r = 1572.02, tetragonal, space group $I4/m$, a = 11.50585(4) Å, b = 11.5085(4) Å, c = 9.5177(4) Å, V = 1260.58(8) Å^3, Z = 2, D_c = 4.142 g/cm^3. A Bruker SMART CCD (charge coupled device) equipped diffractometer with Mo Kα radiation (λ = 0.71073 Å) and a LT-2 low-temperature apparatus was used to collect data from a black rectangular crystal with dimensions of 0.12 × 0.10 × 0.01 mm^3 at 90(1) K. A total of 10391 reflections ($5° < 2\theta < 72.64°$, $\pm h$, $\pm k$, $\pm l$) were collected, and 1601 were unique (R_{int} = 0.0554). All atoms were refined anisotropically. Superlattice reflections were not observed in data collected at 298 or 90 K. Bridging cyanides were refined using a disordered model with a 50/50 superposition of carbon and nitrogen at the unique bridging atom site. Full-matrix least-squared refinement on F^2 (43 variables) converged to R = 0.0410, wR2 = 0.0457 (all data).

(21) Hughbanks, T.; Hoffmann, R. *J. Am. Chem. Soc.* **1983**, *105*, 1150−62.

(22) Andersen, O. K.; Klose, W.; Nohl, H. *Phys. Rev. B* **1978**, *17*, 1209−37.

(23) Mattheiss, L. F.; Fong, C. Y. *Phys. Rev. B* **1977**, *15*, 1760−8.

(24) Bullett, D. W. *Phys. Rev. Lett.* **1977**, *39*, 664−6.

(25) Jarlborg, T.; Freeman, A. J. *J. Magn. Magn. Mater.* **1980**, *15−18*, 1579−80.