Inorg. Chem. **2008**, *47*, 7271−7278

Inorganic Chemistry

Article

# Synthesis and Study of Hexanuclear Molybdenum Clusters Containing Thiolate Ligands

**Lisa F. Szczepura,*,† Karen A. Ketcham,† Betty A. Ooro,† Julia A. Edwards,† Jeffrey N. Templeton,† David L. Cedeño,† and Alan J. Jircitano‡**

*Department of Chemistry, Campus Box 4160, Illinois State University, Normal, Illinois 61790, and School of Science, Penn State Erie, The Behrend College, Erie, Pennsylvania 16563*

Received April 4, 2008

Four hexanuclear molybdenum chloride cluster complexes containing terminal thiolate ligands have been synthesized and fully characterized. $(Bu_4N)_2[Mo_6Cl_8(SEt)_6]$ was prepared by reacting $Na_2[Mo_6Cl_8(OMe)_6]$ with an excess of ethanethiol in refluxing tetrahydrofuran. $(PPN)_2[Mo_6Cl_8(SBu)_6]$, $(Bu_4N)_2[Mo_6Cl_8(SBn)_6]$, and $(Bu_4N)_2[Mo_6Cl_8(SNC_8H_6)_6]$ ($C_8H_6NS^- =$ 3-indolylthiolate) were subsequently prepared in the reaction of $[Mo_6Cl_8(SEt)_6]^{2-}$ with an excess of HSR (R = Bu, Bn or 3-indolyl). Single crystal X-ray diffraction analyses were performed on two of these complexes: $(PPN)_2[Mo_6Cl_8(SEt)_6] \cdot Et_2O$, crystallizes in the triclinic space group $P\bar{1}$ with $a = 12.3894(11)$, $b = 13.7651(12)$, $c = 15.0974(13)$, $\alpha = 103.975(2)$, $\beta = 99.690(2)$, $\gamma = 98.062(2)$, and $Z = 1$; $(PPh_3Me)_2[Mo_6Cl_8(SBn)_6] \cdot 2NO_2CH_3$, also crystallizes in the $P\bar{1}$ space group with $a = 12.1574(16)$, $b = 13.4441(17)$, $c = 14.2132(18)$, $\alpha = 89.654(2)$, $\beta = 88.365(2)$, $\gamma = 71.179(2)$, and $Z = 1$. Our studies demonstrate that $[Mo_6Cl_8(SEt)_6]^{2-}$ displays luminescent properties and that the same complex undergoes substitution reactions with different thiols, as well as reaction with electrophilic reagents such as MeI.

## Introduction

Thiolate ligands ($RS^-$) play an important role in the coordination chemistry of transition metal complexes in that they exhibit unique properties compared to their $NR_2^-$ and $OR^-$ counterparts. For example, mononuclear transition metal complexes containing only monodentate thiolate ligands are much less common than mononuclear complexes containing oxygen and nitrogen donor ligands. This is due to a number of factors, including the following: the unpleasant odor of thiols, the fact that thiolate ligands readily bridge metal centers ($\mu_2$-SR and $\mu_3$-SR ligands are quite common and tend to stabilize metal sulfide cluster cores), and that complexes containing these ligands are difficult to work with because of air sensitivity of thiols and the resulting complexes, and solubility problems.[1–5]

Little was known about transition metal thiolate complexes until the field of bioinorganic chemistry emerged in the 1970s with the initial modeling of ferredoxins.[6,7] Holm and coworkers incorporated simple thiolates, such as benzylthiolate, in their initial ferredoxin models in place of the naturally occurring cysteine.[8,9] The fact that numerous other metalloproteins, including nitrogenase, hydrogenase, and the metallothioneins, contain cysteine as well has made thiolates a key component of the structural and functional models of the active sites of these proteins.[10–14] An extensive body of research now exists on the synthesis and reactivity, as well as magnetic and spectral properties, of discrete transition metal (mostly Fe and Mo) clusters containing $SR^-$

---

* To whom correspondence should be addressed. E-mail: lfszcze@ilstu.edu. Phone: 1-309-438-2359.

† Illinois State University.

‡ Penn State Erie, The Behrend College.

(1) Blower, P. J.; Dilworth, J. R. *Coord. Chem. Rev.* **1987**, *76*, 121.
(2) Krebs, B.; Henkel, G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 769.
(3) Muller, A.; Diemann, E. In *Comprehensive Coordination Chemistry I*; Wilkinson, G., Ed.; Pergamon Press: Oxford, 1987; p 526.
(4) Dance, I. G. *Polyhedron* **1986**, *5*, 1037.
(5) Eichhorn, D. M.; Goswami, N. *Comments Inorg. Chem.* **2003**, *24*, 1.
(6) Holm, R. H. *Acc. Chem. Res.* **1977**, *10*, 427.
(7) Berg, J. M.; Holm, R. H. In *Iron-Sulfur Proteins*; Spiro, T. G., Ed.; Wiley-Interscience: New York, 1982; Chapter 1.
(8) Herskovitz, T.; Averill, B. A.; Holm, R. H.; Ibers, J. A.; Phillips, W. D.; Weiher, J. F. *Proc. Nat. Acad. Sci. U.S.A.* **1972**, *69*, 2437.
(9) Averill, B. A.; Herskovitz, T.; Holm, R. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 3523.
(10) Venkateswara Rao, P.; Holm, R. H. *Chem. Rev.* **2004**, *104*, 527–559.
(11) González-Duarte, P. In *Comprehensive Coordination Chemistry II*; McCleverty, J. A., Meyer, T. J., Eds.; Elsevier, Ltd.: Oxford, U.K., 2004; Vol. *8*, pp 213−228.
(12) Evans, D. J.; Pickett, C. J. *Chem. Soc. Rev.* **2003**, *32*, 268.
(13) Barriere, F. *Coord. Chem. Rev.* **2003**, *236*, 71.
(14) Dilworth, J. R.; Hu, J. *Adv. Inorg. Chem.* **1993**, *40*, 411.

10.1021/ic800613d CCC: $40.75

ligands.[10,15,16] Notably, the reactivity studies of these cluster complexes have contributed immensely to the study of the chemistry of these S donor ligands. Therefore, we now have a much better handle on the synthesis, reactivity, and structural features of discrete thiolate complexes despite the inherent problems associated with metal−thiolate chemistry. However, much of our current understanding about the chemistry of this ligand type is based on biologically relevant iron based clusters.

This paper focuses on studies involving thiolate complexes of hexanuclear molybdenum chloride cluster complexes. These clusters have little biological relevance but are of interest because they are highly symmetric and robust, which makes them ideal building blocks in the preparation of 3D solids,[17] and they have demonstrated interesting redox and photophysical properties.[18,19] Octahedral hexanuclear clusters have the basic formula $[M_6(\mu_3\text{-}X)_8]^{n+}$ and $[M_6(\mu_2\text{-}X)_{12}]^{n+}$ (often written as $[M_6X_8]^{n+}$ and $[M_6X_{12}]^{n+}$, respectively, for the sake of simplicity), and a variety of metals and nonmetal bridging ions have been incorporated into these structural motifs.[20,21] However, the synthetic versatility of these clusters remains limited in terms of the type of terminal ligands incorporated and by the lack of synthetic routes for the preparation of mixed terminal ligand cluster complexes. The types of ligands coordinated to hexanuclear cluster cores are essentially limited to halides, pseudohalides such as $CN^-$, trialkylphosphines, and N donor ligands such as pyridine and triaklylamines. This situation is especially noticeable in light of the synthetic chemistry established for single metal octahedral complexes. One cannot even begin to compare these clusters to single metal complexes which contain such a diverse group of ligands (containing different donor atoms and/or substituents which can vary the steric and electronic properties of the ligands).

In our quest to develop new $[Mo_6Cl_8]^{4+}$ containing precursors and to further investigate the reactivity of $[Mo_6Cl_8L_6]^n$ cluster complexes, we synthesized $[Mo_6Cl_8(SEt)_6]^{2-}$, and subsequently studied its utility in the preparation of cluster complexes containing the $[Mo_6Cl_8]^{4+}$ core.[22] While Schoonover et al. previously published the preparation and Raman studies of the phenylthiolate cluster, $[Mo_6Cl_8(SPh)_6]^{2-}$, reactivity studies involving this complex were never reported.[23] Our main interest in synthesizing $[Mo_6Cl_8(SEt)_6]^{2-}$ was to test the fundamental properties and reactivity of a hexanuclear cluster containing thiolate ligands and compare our findings to other complexes containing similar ligands. We chose ethanethiolate as our thiolate ligand of choice because reaction with electrophiles often leads to the generation of volatile byproducts (e.g., HSEt) which can be easily removed in vacuo. Not only does this aid in the purification of product complexes, but it can also be used to drive reactions to completion.

Here we report the synthesis, characterization, and X-ray structural analysis of $[Mo_6Cl_8(SEt)_6]^{2-}$. We also discuss the general reactivity of this complex in terms of its use as a starting material for the preparation of new complexes. Along these lines, we demonstrate how $[Mo_6Cl_8(SEt)_6]^{2-}$ can be used to prepare other thiolate cluster complexes, $[Mo_6Cl_8(SR)_6]^{2-}$ (R = Bu, Bn, 3-indolyl, and Ph). These studies are significant in that they broaden the fundamental chemistry of thiolate ligands and add to the synthetic methodologies for hexanuclear cluster complexes.

## Experimental Section

**Reagents and General Procedures.** $Mo_6Cl_{12}$ and $Na_2[Mo_6Cl_8(OMe)_6]$ were prepared according to previously published procedures.[24,25] 3-Indolylthiol was prepared following a slight modification of the published procedure (see Supporting Information).[26] All manipulations involving thiolate complexes were done under an inert atmosphere using either Schlenk line or glovebox techniques. All chemicals and solvents were used as received. Reprecipitations were performed by dissolving the compound in a minimal amount of solvent (usually MeCN or $CH_2Cl_2$) and dripping it into ∼100 fold (v:v) excess of $Et_2O$; recrystallizations were performed using the vapor diffusion technique.

**Instrumentation.** NMR spectra were recorded on a Varian 400 MHz Mercury Spectrophotometer. Elemental analyses and X-ray crystallographic information were performed at the University of Illinois, Urbana, by the Microanalysis Laboratory and the George L. Clark X-Ray Facility and 3M Materials Laboratory, respectively. Mass spectral data was also obtained at the University of Illinois; for the complexes subjected to MS analysis, the highest mass envelope was assigned. Electrochemical measurements were made

---

(15) Lee, S. C.; Holm, R. H. *Chem. Rev.* **2004**, *104*, 1135.

(16) Holm, R. H. *Adv. Inorg. Chem.* **1992**, *38*, 1–71.

(17) (a) Perruchas, S.; Flores, S.; Jousselme, B.; Lobkovsky, E.; Abruña, H.; DiSalvo, F. J. *Inorg. Chem.* **2007**, *46*, 8976. (b) Roland, B. K.; Flora, W. H.; Armstrong, N. R.; Zheng, Z. *C. R. Chimie* **2005**, *8*, 1798. (c) Bennett, M. V.; Beauvais, L. G.; Shores, M. P.; Long, J. R. *J. Am. Chem. Soc.* **2001**, *123*, 8022.

(18) (a) Gray, T. G.; Rudzinski, C. M.; Meyer, E. E.; Holm, R. H.; Nocera, D. G. *J. Am. Chem. Soc.* **2003**, *125*, 4755. (b) Kitamura, N.; Ueda, Y.; Ishizaka, S.; Yamada, K.; Aniya, M.; Sasaki, Y. *Inorg. Chem.* **2005**, *44*, 6308. (c) Maverick, A. W.; Najdzionek, J. S.; MacKenzie, D.; Nocera, D. G.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 1878.

(19) (a) Baudron, S. A.; Batail, P.; Coulon, C.; Clérac, R.; Canadell, E.; Laukhin, V.; Melzi, R.; Wzietek, P.; Jérome, D.; Auban-Senzier, P.; Ravy, S. *J. Am. Chem. Soc.* **2005**, *127*, 11785. (b) Yoshimura, T.; Umakoshi, K.; Sasaki, Y.; Ishizaka, S.; Kim, H.-B.; Kitamura, N. *Inorg. Chem.* **2000**, *39*, 1765. (c) Yoshimura, T.; Chen, Z.-N.; Itasaka, A.; Abe, M.; Sasaki, Y.; Ishizaka, S.; Kitamura, N.; Yarovoi, S. S.; Solodovnikov, S. F.; Fedorov, V. E. *Inorg. Chem.* **2003**, *42*, 4857.

(20) Recent review articles: (a) Fedorov, V. E.; Mironov, Y. V.; Naumov, N. G.; Sokolov, M. N.; Fedin, V. P. *Russ. Chem. Rev.* **2007**, *76*, 529. (b) Welch, E. J.; Long, J. R. *Prog. Inorg. Chem.* **2005**, *54*, 1. (c) Gabriel, J.-C. P.; Boubekeur, K.; Uriel, S.; Batail, P. *Chem. Rev.* **2001**, *101*, 2037. (d) Prokopuk, N.; Shriver, D. F. *Adv. Inorg. Chem.* **1999**, *46*, 1. (e) Saito, T. *Adv. Inorg. Chem.* **1997**, *44*, 45.

(21) (a) Eckermann, A. L.; Wunder, M.; Fenske, D.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.* **2002**, *41*, 2004. (b) Goddard, C. A.; Long, J. R.; Holm, R. H. *Inorg. Chem.* **1996**, *35*, 4347. (c) Cecconi, F.; Ghilardi, C. A.; Midollini, S.; Orlandini, A. *Inorg. Chim. Acta* **1983**, *76*, L183. (d) Xie, X.; Reibenspies, J. H.; Hughbanks, T. *J. Am. Chem. Soc.* **1998**, *120*, 11391.

(22) We were recently made aware of a technical government report which contains the preparation of $Na_2[Mo_6Cl_8(SEt)_6]$ via a different route (Michel, J. B. *ERDA Energy Research Abstracts*, Vol 2, Issue 16, 1977). Our studies complement those previously published in that we have completely characterized the $[Mo_6Cl_8(SEt)_6]^{2-}$ complex ion using NMR, UV-vis, EA, MS, electrochemistry, and X-ray crystallography.

(23) Schoonover, J. R.; Zietlow, T. C.; Clark, D. L.; Heppert, J. A.; Chisholm, M. H.; Gray, H. B.; Sattelberger, A. P.; Woodruff, W. H. *Inorg. Chem.* **1996**, *35*, 6606.

(24) Koknat, F. W.; Adaway, T. J.; Erzerum, S. I.; Syed, S. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 307.

(25) Nannelli, P.; Block, B. P. *Inorg. Chem.* **1968**, *7*, 2423.

(26) Harris, R. L. N. *Tetrahedron Lett.* **1969**, *51*, 4465.

using a BAS CV-50W and were conducted in an inert atmosphere glovebox using a three electrode cell consisting of a glassy C working electrode, a Pt auxiliary electrode, and Ag/AgNO$_3$ (0.01 M) reference electrode. Prior to use, the working electrode was polished using 1.0 $\mu$m alumina paste; after polishing, the electrode was pretreated by scanning once to the potential limit. The electrolyte concentration was 0.2 M Bu$_4$NBF$_4$ in MeCN, and all potentials are reported as V vs the FeCp$_2$$^{+/0}$ couple. Electronic absorption data were recorded on a Varian Cary 5E UV−vis−NIR spectrophotometer. Steady state emission spectra were obtained using a Perkin-Elmer LS55 fluorimeter at various excitation wavelengths that corresponded to absorption wavelengths. Excitation and emission slits were set to optimize the emission spectrum. Time resolved emission signals were obtained using either a pulsed nitrogen laser (337 nm, 3 Hz, PTI GL-3300) or a dye laser (PTI GL-301, Coumarin 456 dye as lasing medium) pumped by a nitrogen laser used for excitation wavelengths in the range 420−460 nm. Deoxygenated acetonitrile solutions of the clusters were contained in tightly capped quartz cuvettes (10 mm optical path). Upon laser excitation, the emitted light was collected at a 90 degree angle using a collimating lens system, passed through a long wavelength pass filter ($\lambda$ > 600 nm), and focused into an amplified fast silicon photovoltaic detector (Thorlabs DET 110). The signal was fed (50 Ω load) into a digital storage oscilloscope (400 MHz, LeCroy 9314CM). The average trace of at least 50 laser pulses was recorded and stored in a computer for further analysis using Sigma Plot 9.0. All determinations were made at 296 ± 1 K.

**A$_2$[Mo$_6$Cl$_8$(SEt)$_6$] (A = Bu$_4$N$^+$ or PPN$^+$).** A 378 mg quantity of (0.346 mmol) Na$_2$[Mo$_6$Cl$_8$(OMe)$_6$] was slurried with 6 mL of tetrahydrofuran (THF) in a Schlenk flask, and 0.8 mL (10.8 mmol) of ethanethiol was added via syringe. The solution was heated at reflux for 20 h. After cooling, 2.1 equiv of Bu$_4$NBr or PPNCl was added and the resulting solution filtered to remove the unwanted salt (NaBr or NaCl). After reducing the filtrate to dryness in vacuo, the solid was dissolved in MeCN, filtered through Celite, and precipitated by dripping into Et$_2$O. The product was further purified by recrystallization using a mixture of MeCN/CH$_2$Cl$_2$ and Et$_2$O. (Bu$_4$N)$_2$[Mo$_6$Cl$_8$(SEt)$_6$]: Yield: 340 mg (58%). $^1$H NMR (CDCl$_3$, ppm): 1.03 (t, 24H, Bu$_4$N$^+$), 1.30 (t, 18H, SCH$_2$C*H*$_3$), 1.48 (sextet, 16H, Bu$_4$N$^+$), 1.68 (m, 16H, Bu$_4$N$^+$), 2.68 (q, 12H, SC*H*$_2$CH$_3$), 3.25 (m, 16H, Bu$_4$N$^+$). $^{13}$C NMR (CDCl$_3$, ppm): 13.82 (Bu$_4$N$^+$), 19.95 (Bu$_4$N$^+$), 21.15 (SCH$_2$*C*H$_3$), 24.29 (Bu$_4$N$^+$), 27.48 (S*C*H$_2$CH$_3$), 58.86 (Bu$_4$N$^+$). UV/vis (in MeCN) nm ($\varepsilon$ in M$^{-1}$ cm$^{-1}$): 220 sh, 242 (107 000); 271 sh (70 000). Anal. Calcd for C$_{44}$H$_{102}$N$_2$Cl$_8$S$_6$Mo$_6$: C, 30.89; H, 6.01; N, 1.64. Found: C, 30.67; H, 5.95; N, 1.53. ESI$^-$ MS: *m*/*z* 1468.5 ([M − Bu$_4$N]$^-$).

**Ligand Substitution Studies.** A 100 mg quantity of (Bu$_4$N)$_2$[Mo$_6$Cl$_8$(SEt)$_6$] or (PPN)$_2$[Mo$_6$Cl$_8$(SEt)$_6$] was dissolved in 10 mL of MeCN, and an excess (20−40 mol equiv) of benzylthiol, phenylthiol, or 1-butanethiol was added via syringe. The solution was then heated at reflux for 20 h. After cooling, the solution was reduced to dryness in vacuo and taken back into the glovebox. The residue was dissolved in MeCN or a mixture of MeCN/CH$_2$Cl$_2$, filtered through Celite, and precipitated by dripping into Et$_2$O. Further purification was completed by recrystallization using MeCN/Et$_2$O or MeCN/CH$_2$Cl$_2$/Et$_2$O at 0 °C. (Bu$_4$N)$_2$[Mo$_6$Cl$_8$(SBn)$_6$]: Yield: 90 mg (74%). $^1$H NMR (CDCl$_3$, ppm): 0.90 (t, 24H, Bu$_4$N$^+$), 1.29 (m, 32H, Bu$_4$N$^+$), 2.89 (m, 16H, Bu$_4$N$^+$), 3.86 (s, 12H, SC*H*$_2$C$_6$H$_5$), 7.08 (false t, 6H, SCH$_2$C$_6$*H*$_5$), 7.19 (false t, 12H, SCH$_2$C$_6$*H*$_5$), 7.37 (d, 12H, SCH$_2$C$_6$*H*$_5$). $^{13}$C NMR (CDCl$_3$, ppm): 13.78 (Bu$_4$N$^+$), 19.74 (Bu$_4$N$^+$), 23.86 (Bu$_4$N$^+$), 37.70 (S*C*H$_2$C$_6$H$_5$), 58.49 (Bu$_4$N$^+$), 125.36 (SCH$_2$*C*$_6$H$_5$), 127.96 (SCH$_2$*C*$_6$H$_5$), 128.68 (SCH$_2$*C*$_6$H$_5$), 145.67 (SCH$_2$*C*$_6$H$_5$). UV/vis (in MeCN) nm ($\varepsilon$ in M$^{-1}$ cm$^{-1}$): 245 (157 000); 275 sh (104 000). Anal. Calcd for C$_{74}$H$_{114}$N$_2$Cl$_8$S$_6$Mo$_6$: C, 42.54; H, 5.46; N, 1.34. Found: C, 42.19; H, 5.37; N, 1.49. (Bu$_4$N)$_2$[Mo$_6$Cl$_8$(SPh)$_6$]: Yield: 67 mg (61%). $^1$H NMR (acetone-*d*$_6$, ppm): 0.97 (t, 24H, Bu$_4$N$^+$), 1.43 (sextet, 16H, Bu$_4$N$^+$), 1.79 (quintet, 16H, Bu$_4$N$^+$), 3.41 (m, 16H, Bu$_4$N$^+$), 6.90 (false t, 6H, SC$_6$*H*$_5$), 7.07 (false t, 12H, SC$_6$*H*$_5$), 7.21 (d, 12H, SC$_6$*H*$_5$). $^{13}$C NMR (acetone-*d*$_6$, ppm): 13.78 (Bu$_4$N$^+$), 20.25 (Bu$_4$N$^+$), 24.28 (Bu$_4$N$^+$), 59.19 (Bu$_4$N$^+$), 123.36 (S*C*$_6$H$_5$), 127.92 (S*C*$_6$H$_5$), 135.69 (S*C*$_6$H$_5$), 148.18 (S*C*$_6$H$_5$). UV/vis (in MeCN) nm ($\varepsilon$ in M$^{-1}$ cm$^{-1}$): 282 (105 000). Anal. Calcd for C$_{68}$H$_{102}$N$_2$Cl$_8$S$_6$Mo$_6$: C, 40.86; H, 5.11; N, 1.40. Found: C, 40.77; H, 5.09; N, 1.54. (PPN)$_2$[Mo$_6$Cl$_8$(SBu)$_6$]: Yield: 57 mg (69%). $^1$H NMR (CDCl$_3$, ppm): 0.76 (t, 18H, SCH$_2$CH$_2$CH$_2$C*H*$_3$), 1.32 (m, 12H, SCH$_2$CH$_2$C*H*$_2$CH$_3$), 1.54 (q, 12H, SCH$_2$C*H*$_2$CH$_2$CH$_3$), 2.63 (t, 12H, SC*H*$_2$CH$_2$CH$_2$CH$_3$), 7.47 (m, 12H, PPN$^+$), 7.66 (m, 48H, PPN$^+$). $^{13}$C NMR (CDCl$_3$, ppm): 14.10 (SCH$_2$CH$_2$CH$_2$*C*H$_3$), 22.47 (SCH$_2$CH$_2$*C*H$_2$CH$_3$), 33.01 (SCH$_2$*C*H$_2$CH$_2$CH$_3$), 38.17 (S*C*H$_2$CH$_2$CH$_2$CH$_3$), 126.84 (d, PPN$^+$), 129.57 (m, PPN$^+$), 132.01 (m, PPN$^+$), 133.96 (s, PPN$^+$). UV/vis (in MeCN) nm ($\varepsilon$ in M$^{-1}$ cm$^{-1}$): 227 (174 000); 267 (74 000); 274 (73 000). Anal. Calcd for C$_{96}$H$_{114}$N$_2$Cl$_8$P$_4$S$_6$Mo$_6$: C, 46.65; H, 4.65; N, 1.13. Found: C, 46.58; H, 4.59; N, 1.30.

**(Bu$_4$N)$_2$[Mo$_6$Cl$_8$(SNC$_8$H$_6$)$_6$].** Similar to the above preparations except only 7.5 equiv of 3-indolylthiol was utilized. Yield: 76.8%. $^1$H NMR (acetone-*d*$_6$, ppm): 0.88 (t, 24H, Bu$_4$N$^+$), 1.28 (sextet, 16H, Bu$_4$N$^+$), 1.54 (quintet, 16H, Bu$_4$N$^+$), 3.13 (m, 16H, Bu$_4$N$^+$), 6.49 (s, 6H, 2-H), 6.96 (false t, 6H, 4-H), 7.02 (false t, 6H, 5-H), 7.27 (d, 6H, 6-H), 7.65 (d, 6H, 7-H), 9.14 (s, 6H, NH). $^{13}$C NMR (acetone-*d*$_6$, ppm): 14.00, 20.29, 24.30, 59.00 (4 C from the Bu$_4$N$^+$ cation), 111.46, 116.49, 118.61, 121.15, 121.43, 127.53, 132.66, 136.94 (8 C from the 3-indolylthiolate ligand). UV/vis (in MeCN) nm ($\varepsilon$ in M$^{-1}$ cm$^{-1}$): 222 (159 000); 235sh (150 000); 281 (72 000); 305sh (68 000). Anal. Calcd for C$_{80}$H$_{108}$N$_8$Mo$_6$Cl$_8$S$_6$•2H$_2$O: C, 42.34; H, 4.97; N, 4.94. Found: C, 41.99; H, 4.71; N, 4.87. ESI$^-$ MS: *m*/*z* 874.15 ([M − 2Bu$_4$N]$^{2-}$).

**Reaction of (Bu$_4$N)$_2$[Mo$_6$Cl$_8$(SEt)$_6$] with MeI.** A 121 mg quantity (0.852 mmol) of MeI was dissolved in 5 mL of CH$_2$Cl$_2$ to which 100 mg (0.0584 mmol) of (Bu$_4$N)$_2$[Mo$_6$Cl$_8$(SEt)$_6$] was added. The solution was stirred overnight before drying in vacuo. The solid, (Bu$_4$N)$_2$[Mo$_6$Cl$_8$I$_6$], which is not air-sensitive, was purified by reprecipitation followed by recrystallization out of acetone/Et$_2$O. Yield: 115 mg (93%). $^1$H NMR (CD$_2$Cl$_2$, ppm) 1.04 (t, 24H), 1.46 (sextet, 16H), 1.64 (m, 16H), 3.12 (m, 16H). Anal. Calcd for C$_{32}$H$_{72}$N$_2$Cl$_8$I$_6$Mo$_6$: C, 20.68; H, 3.81; N, 1.27. Found: C, 20.30; H, 3.61; N, 1.38. Monitoring the reaction of (Bu$_4$N)$_2$[Mo$_6$Cl$_8$(SEt)$_6$] with MeI in CDCl$_3$ using NMR spectroscopy, we observed the following peaks after a reaction time of 30 min. $^{13}$C NMR (CDCl$_3$, ppm): −23.18 (unreacted MeI), 13.93 (Bu$_4$N$^+$), 14.53 (EtSMe), 15.21 (EtSMe), 19.97 (Bu$_4$N$^+$), 24.47 (Bu$_4$N$^+$), 28.16 (EtSMe), 59.40 (Bu$_4$N$^+$).

**Reaction of (Bu$_4$N)$_2$[Mo$_6$Cl$_8$(SEt)$_6$] with HCl.** A 101 mg quantity (0.0593 mmol) of (Bu$_4$N)$_2$[Mo$_6$Cl$_8$(SEt)$_6$] was dissolved with 17 mL of MeCN and 16 drops of concentrated HCl were added. The solution changed color from orange to pale yellow immediately. The reaction was stirred for 1 h at room temperature, and then the volume was reduced in vacuo to about 1.5 mL. The resulting yellow precipitate was collected and recrystallized using acetone/Et$_2$O. Yield: 61 mg (66%) $^1$H NMR (acetone-*d*$_6$, ppm): 0.99 (t, 24H), 1.44 (sextet, 16H), 1.83 (quintet, 16H), 3.45 (m, 16H). Anal. Calcd for C$_{32}$H$_{72}$N$_2$Cl$_{14}$Mo$_6$: C, 24.69; H, 4.66; N, 1.80. Found: C, 24.32; H, 4.52; N, 1.79.

**X-ray Crystallography.** Single crystals of (Bu$_4$N)$_2$[Mo$_6$Cl$_8$(SEt)$_6$] were obtained; however, positional disorder of the Bu$_4$N$^+$ cations

**Table 1.** Crystallographic Data for $(PPN)_2[Mo_6Cl_8(SEt)_6]\cdot Et_2O$ and $(PPh_3Me)_2[Mo_6Cl_8(SBn)_6]\cdot 2NO_2CH_3$[a]

| | $(PPN)_2[Mo_6Cl_8(SEt)_6]\cdot Et_2O$ | $(PPh_3Me)_2[Mo_6Cl_8(SBn)_6]\cdot 2NO_2CH_3$ |
|---|---|---|
| chemical formula | $C_{88}H_{100}Cl_8Mo_6N_2OP_4S_6$ | $C_{82}H_{84}Cl_8Mo_6N_2O_4P_2S_6$ |
| formula weight ($g\cdot mol^{-1}$) | 2377.18 | 2275.16 |
| space group | $P\bar{1}$ | $P\bar{1}$ |
| $a$ (Å) | 12.3894(11) | 12.1574(16) |
| $b$ (Å) | 13.7651(12) | 13.4441(17) |
| $c$ (Å) | 15.0974(13) | 14.2132(18) |
| $\alpha$ (deg) | 103.975(2) | 89.654(2) |
| $\beta$ (deg) | 99.690(2) | 88.365(2) |
| $\gamma$ (deg) | 98.062(2) | 71.179(2) |
| $V$ (Å$^3$) | 2418.4(4) | 2198.0(5) |
| $Z$ | 1 | 1 |
| $T$ (K) | 193(2) | 193(2) |
| $\lambda$ (Å) | 0.71073 Å | 0.71073 Å |
| $D_{calc}$ ($g\cdot cm^{-3}$) | 1.632 | 1.719 |
| $\mu$ ($mm^{-1}$) | 1.216 | 1.301 |
| $R(F_o)$ | 0.0419 | 0.0303 |
| $R_w(F_o^2)$ | 0.0860 | 0.0573 |

[a] $R$ defined as $\Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w$ defined as $(\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[wF_o^4])^{1/2}$.

prevented a complete solution of the structure. Subsequently, single crystals containing $(PPN)_2[Mo_6Cl_8(SEt)_6]$ were grown out of a $MeCN/CH_2Cl_2$ mixture and $Et_2O$ via vapor diffusion at −20 °C and subjected to X-ray diffraction analysis. A red-orange crystal with the dimensions 0.08 × 0.14 × 0.16 mm was mounted using oil (paratone-N, Exxon) to a thin glass fiber and centered on a Bruker CCD Smart System diffractometer with graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation at 193 K. Details about data collection and solution refinement are given in Table 1. Data collection and reduction were performed using the Bruker SMART (Version 5.00) and Bruker Saint (Version 5.00) package of programs. The data were not corrected for absorption. The structure was solved and refined using SHELXS97 and SHELXL97, respectively. The structure was refined by full-matrix least-squares on $F$.[2] Hydrogens were placed in geometrically idealized positions and included as riding atoms. A molecule of $Et_2O$ co-crystallizes with a molecule of the cluster, disordered about an inversion center at the oxygen. The adjacent carbon was modeled in two positions with 0.6 and 0.4 occupancy and could be reasonably refined but with large displacement parameters. Hydrogen atoms were not included in the model. There is little evidence of disorder in the cluster or counterion.

Single crystals containing $(PPh_3Me)_2[Mo_6Cl_8(SBn)_6]$ were grown via vapor diffusion using a $CH_2Cl_2/NO_2CH_3$ mixture and toluene at −20 °C and subjected to X-ray diffraction analysis. An orange crystal with the dimensions 0.10 × 0.14 × 0.18 mm was mounted using oil (paratone-N, Exxon) and centered on a Bruker CCD Smart System diffractometer with graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation at 193 K. Details about data collection and solution refinement are also provided in Table 1. Data collection, reduction, solution, and refinement were performed using the same programs mentioned above. The data were corrected for absorption and refined by full-matrix least-squares on $F$.[2] All non-hydrogen atoms were located through difference Fourier maps. Hydrogens were placed in geometrically idealized positions and included as riding atoms. Two molecules of $NO_2CH_3$ were found to co-crystallize with the cluster. The cation and anion appear to be largely free of disorder. Although the solvent displacement parameters are large, this disorder was not accounted for.

## Results and Discussion

**Synthesis and Characterization.** Reaction of $Na_2[Mo_6Cl_8(OMe)_6]$ with an excess of HSEt in refluxing THF generates $[Mo_6Cl_8(SEt)_6]^{2-}$ in high yield. Metathesis of the $Na^+$ cation with $Bu_4N^+$ or $PPN^+$ substantially increases the solubility of this cluster complex in organic solvents, which enabled us to purify the material via recrystallization using a mixture of $MeCN/CH_2Cl_2$ and $Et_2O$. The preparation of $[Mo_6Cl_8(SEt)_6]^{2-}$ is similar to that reported for the preparation of $[Mo_6Cl_8(SPh)_6]^{2-}$.[23] However, the coordination of ethanethiolate required a larger excess of thiol and a longer reaction time. $[Mo_6Cl_8(SR)_6]^{2-}$ (R = Bu, Bn and 3-indolyl) were prepared via ligand substitution of $[Mo_6Cl_8(SEt)_6]^{2-}$ with BuSH, BnSH, and 3-indolylthiol; $[Mo_6Cl_8(SBn)_6]^{2-}$ can also be prepared via reaction of $Na_2[Mo_6Cl_8(OMe)_6]$ with an excess of HSBn in refluxing THF. Like many thiolate complexes, the newly prepared $[Mo_6Cl_8(SR)_6]^{2-}$ complexes are readily oxidized by air. All clusters were characterized using $^1H$ and $^{13}C$ NMR spectroscopy, UV−vis spectroscopy, and elemental analysis. ($^1H$ NMR spectra can be found in the Supporting Information. Values for the HH coupling constants were not included but were routine.) In addition, mass spectral data was obtained for $[Mo_6Cl_8(SEt)_6]^{2-}$ and $[Mo_6Cl_8(SNC_8H_6)_6]^{2-}$, and electrochemical studies were performed on the hexaethanethiolate complex. X-ray diffraction analyses were performed on two of these thiolate cluster complexes; see details below.

**Structural Studies.** Oak Ridge Thermal Ellipsoid Plot (ORTEP) diagrams of $[Mo_6Cl_8(SEt)_6]^{2-}$ and $[Mo_6Cl_8(SBn)_6]^{2-}$ are shown in Figures 1 and 2 while information regarding the X-ray data collection and refinement is summarized in Table 1. The thiolate ligands do not appear to affect the cluster core as can be seen by comparing the bond lengths and angles of the $[Mo_6Cl_8]^{4+}$ core with similar cluster complexes. For example, in $[Mo_6Cl_8(SEt)_6]^{2-}$ the average Mo−Cl bond length is 2.483(6) Å and the average Mo−Cl−Mo bond angle is 63.7(1)°, while in $[Mo_6Cl_8(SBn)_6]^{2-}$ the average Mo−Cl bond length is 2.481(2) Å and the average Mo−Cl−Mo bond angle is 63.6(1)°. This can be compared to $[Mo_6Cl_8]^{4+}$ containing clusters in which Mo−Cl(internal) bond lengths have been reported to range from 2.45 to 2.50 Å, and Mo−Cl−Mo angles reportedly

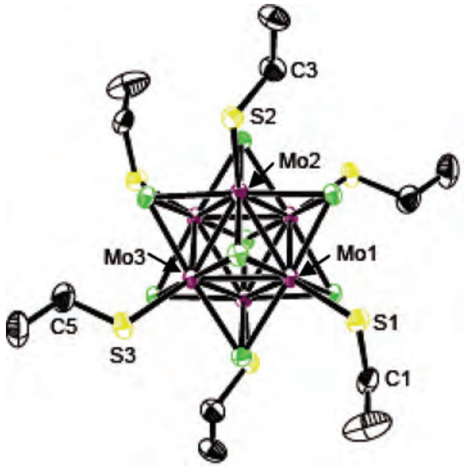

**Figure 1.** ORTEP diagram of $[Mo_6Cl_8(SEt)_6]^{2-}$ with hydrogen atoms and solvent molecules omitted for clarity (ellipsoids at 50% probability).

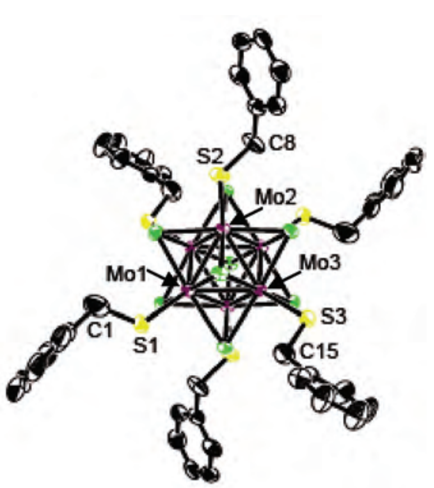

**Figure 2.** ORTEP diagram of $[Mo_6Cl_8(SBn)_6]^{2-}$ with hydrogen atoms and solvent molecules omitted for clarity. Ellipsoids at 50% probability.

range from 62.8 to 64.1°.[27] The average Mo−Mo bond length is 2.622(4) Å in $[Mo_6Cl_8(SEt)_6]^{2-}$ and 2.616(2) Å in $[Mo_6Cl_8(SBn)_6]^{2-}$. Although these distances are longer than the average Mo−Mo bond distance (2.606 Å) of $[Mo_6Cl_8]^{4+}$ containing cluster complexes, they are still within the range of those observed.[27]

The three unique Mo−S bond lengths in $[Mo_6Cl_8(SEt)_6]^{2-}$ are Mo1−S1 = 2.4821(14), Mo2−S2 = 2.4695(13), and Mo3−S3 = 2.4709(13); in $[Mo_6Cl_8(SBn)_6]^{2-}$, they are Mo1−S1 = 2.4472(13), Mo2−S2 = 2.4842(14), and Mo3−S3 = 2.4838(14). The average Mo−S−C bond angles are 105.8(3)° for $[Mo_6Cl_8(SEt)_6]^{2-}$ and 108.2(3)° for $[Mo_6Cl_8(SBn)_6]^{2-}$. While there are significant differences in the Mo−S bond distances for both clusters and in the Mo−S−C bond angles in the hexabenzylthiolate complex, these do not impact the cluster core. There are a limited number of Mo(II) complexes containing monodentate alkyl or aryl thiolate ligands. Comparing our data with some of these complexes we find that the bond lengths and angles observed for our hexathiolate cluster complexes fall within the range of those previously reported. For example, Richards and co-workers determined the structure of *trans*-[Mo(S*n*-Bu)$_2$(dppe)$_2$] and found Mo−S = 2.361(1) Å, Kamata et al. reported a Mo−S distance of 2.37 Å for [Mo(S*t*-Bu)$_2$(*t*-BuNC)$_4$], and Bishop et al. reported Mo−S bond distances ranging from 2.302 to 2.524 Å for some nitrosyl thiolato complexes of molybdenum.[28] In addition, Schoonover reported the average Mo−S bond length in $[Mo_6Cl_8(SPh)_6]^{2-}$ to be 2.489(3) Å and the Mo−S−C angle to be 111.14°.[23]

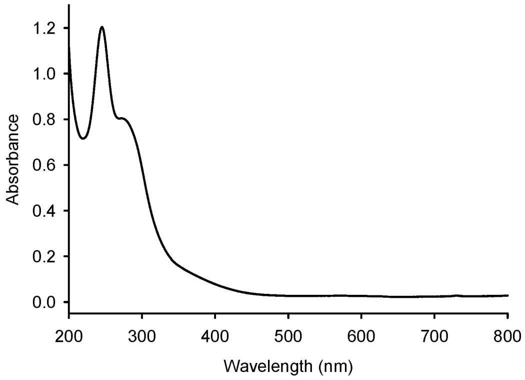

**Figure 3.** UV−vis spectrum of $(Bu_4N)_2[Mo_6Cl_8(SEt)_6]$ in acetonitrile.

**UV−vis Spectroscopy.** The electronic absorption spectrum of $(Bu_4N)_2[Mo_6Cl_8(SEt)_6]$ in MeCN (Figure 3) shows one peak at $\lambda_{max}$ = 242 nm and a substantial shoulder at 271 nm (a small shoulder at 220 nm also exists). The spectra of $(Bu_4N)_2[Mo_6Cl_8(SBn)_6]$ and $(PPN)_2[Mo_6Cl_8(SBu)_6]$ are similar to the hexaethanethiolate cluster in that $[Mo_6Cl_8(SBn)_6]^{2-}$ has a peak at 245 nm and a shoulder at 275 nm, while $(PPN)_2[Mo_6Cl_8(SBu)_6]$ has a peak at 227 nm and an absorption around 270 nm (vide infra). The spectra of $[Mo_6Cl_8(SPh)_6]^{2-}$ and $[Mo_6Cl_8(SNC_8H_6)_6]^{2-}$ differ slightly from those described above in that the hexaphenythiolate complex has only one broad peak at $\lambda_{max}$ = 282 nm and the hexaindolylthiolate complex has two peaks (222 and 281 nm) and two shoulders (237 and 304 nm). Looking closely at the spectra of the ethyl-, benzyl-, and butylthiolate complexes, there appears to be a subtle shoulder at ∼380 nm which extends into the blue region up to about 460 nm.

Gray and co-workers recorded the electronic absorption spectrum of $(Bu_4N)_2[Mo_6Cl_{14}]$ (or $(Bu_4N)_2[Mo_6(\mu_3\text{-}Cl)_8Cl_6]$) in MeCN from 250−600 nm.[29,30] This cluster shows a broad peak at $\lambda_{max}$ = 330 nm with an extinction coefficient of 3000 $M^{-1}\ cm^{-1}$. Because the spectra of our hexathiolate complexes contain peaks at ∼230 nm, we were interested in seeing if $(Bu_4N)_2[Mo_6Cl_{14}]$ absorbed light at shorter wavelengths. Therefore, we measured the UV−vis spectrum of $(Bu_4N)_2[Mo_6Cl_{14}]$ and found a peak at $\lambda_{max}$ = 222 nm ($\varepsilon$ = $2.04 \times 10^5\ M^{-1}\ cm^{-1}$) in addition to the previously reported peak at 330 nm. Perchenek and Simon reported the electronic spectra of analogous O-donor complexes: $[Mo_6Cl_8(OMe)_6]^{2-}$

---

(27) Based on a Cambridge Structural Database analysis of 65 cluster complexes containing the $[Mo_6Cl_8]^{4+}$ core.

(28) (a) Povey, D. C.; Richards, R. L.; Shortman, C. *Polyhedron* **1986**, *5*, 369. (b) Bishop, P. T.; Dilworth, J. R.; Hutchinson, J.; Zubieta, H. *J. Chem. Soc., Dalton Trans.* **1986**, 967. (c) Kamata, M.; Hirotsu, K.; Higuchi, T.; Tatsumi, K.; Hoffmann, R.; Yoshida, T.; Otsuka, S. *J. Am. Chem. Soc.* **1981**, *103*, 5772.

(29) Maverick, A. W.; Gray, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 1298.

(30) Maverick, A. W.; Najdzionek, J. S.; MacKenzie, D.; Nocera, D. G.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 1878.

(31) Perchenek, N.; Simon, A. *Z. Anorg. Allg. Chem.* **1993**, *619*, 103.

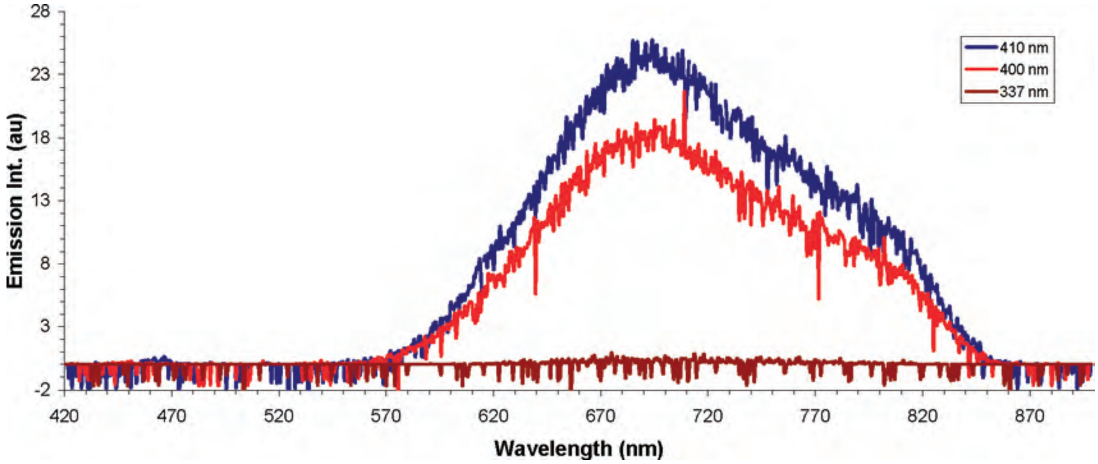

**Figure 4.** Emission spectra of $(Bu_4N)_2[Mo_6Cl_8(SEt)_6]$ in MeCN at excitation wavelengths 410, 400, and 337 nm (top to bottom respectively).

and $[Mo_6Cl_8(OPh)_6]^{2-}$.[31] Both of these complexes contain ligand-to-metal charge transfer (LMCT) bands at 222 and 218 nm, respectively, with high extinction coefficients (0.6 to 3.0 × $10^5$ $M^{-1}$ $cm^{-1}$). $[Mo_6Cl_8(OPh)_6]^{2-}$ contains additional absorptions due to the phenolate ligands. Therefore, the high extinction coefficients observed for the UV bands of these hexathiolate complexes are consistent with the spectra of similar complexes. The UV−vis spectra of our complexes also contain characteristics of the free thiols and countercation ($PPN^+$). For example, the electronic spectrum of PPNCl exhibits two sharp bands at 267 and 274 nm; however, these appear to be superimposed over another transition in the spectrum of the $(PPN)_2[Mo_6Cl_8(SBu)_6]$ complex.

There has been a great deal of interest in the electronic spectra of hexanuclear octahedral clusters because of their interesting photophysical properties. For example, Maverick and Gray were the first to report the long excited-state lifetime of the hexachloro cluster, $(Bu_4N)_2[Mo_6Cl_{14}]$;[29,30] subsequently, studies involving the excited-state spectra of $[Re_6Se_8]^{2+}$ containing clusters were reported by Nocera, Holm and co-workers as well as by Sasaki and co-workers.[32,33] We found that the emission spectrum of the $[Mo_6Cl_8(SEt)_6]^{2-}$ cluster is quite similar to that reported by Maverick and Gray for $[Mo_6Cl_{14}]^{2-}$ in solution.[29] The emission band is broad expanding on a range of about 300 nm. There is a maximum at ~700 nm but there seems to be a convolution of various emission bands. Gray and co-workers first reported a corrected emission maximum at 760 nm for the $[Mo_6Cl_{14}]^{2-}$ complex, although they later reported an emission maximum at 805 nm.[29,18c] However, the emission spectrum of $[Mo_6Cl_{14}]^{2-}$ (in MeCN) prepared in our laboratory is quite similar to those shown in Figure 4 with a maximum at 700 nm and a shoulder around 800 nm.

An exponential fit to the decay part of the emission signal (included in the Supporting Information) according to the expression:$y = y_0 + ae^{-t/\tau}$ reveals that the lifetime ($\tau$) of the luminescent excited-state is 6.2 ± 1.1 $\mu$s (average of six independent determinations). The lifetime of the emitting state was determined at excitation wavelengths of 337 nm and in the 420−460 nm range. The lifetime is independent of the excitation wavelength selected. It was found, however, that the amount of light emitted is dependent on the excitation wavelength and that it is larger at wavelengths above 300 nm, with larger emission intensities when the excitation is set above 400 nm (see Figure 4). Closer inspection of the spectrum reveals a weak absorption band in the blue region, which is associated with the luminescent state. This behavior is quite similar to that found by Gray and co-workers for the $[Mo_6X_{14}]^{2-}$ clusters (X = Cl, Br, I).[29,18c] The lifetime of the emitting state is about 26 times shorter than the one reported for $[Mo_6Cl_{14}]^{2-}$ in MeCN solution.[29] It is evident that the presence of sulfur in the terminal ligands of the cluster yields a shorter lived emitting state. Luminescent studies of the other hexathiolate complexes reported here are currently underway.

**Electrochemical Studies.** Electrochemical measurements were performed on $[Mo_6Cl_8(SEt)_6]^{2-}$ to compare the redox properties of one of the thiolate complexes with the well studied $[Mo_6Cl_{14}]^{2-}$ complex. (We were unable to measure the electrochemistry of the starting hexamethoxy complex, $Na_2[Mo_6Cl_8(OMe)_6]$, because of poor solubility.) Starting at the rest potential (−0.60 V) and scanning in a negative direction, a reductive peak at $E_{p,c} = -2.39$ V is observed. As shown in Figure 5 a small peak ($E_{p,a} = -2.27$ V) which corresponds to the cathodic peak at −2.39 V is observed on the return scan. However, because of the large $\Delta E_p$, the magnitude of the anodic peak current, and the shift of the $E_{p,c}$ with a change in scan rate, we assign this couple as irreversible. Nocera and Gray report that $[Mo_6Cl_{14}]^{2-}$ contains two redox couples: one reversible oxidative wave at +1.56 V and one quasireversible wave at −1.53 V vs SCE in MeCN which were assigned to the $[Mo_6Cl_{14}]^{2-/-}$ and $[Mo_6Cl_{14}]^{2-/3-}$ couples, respectively.[29,34] (We observed these couples at +1.26 V and −1.81 V vs the $FeCp_2^{+/0}$ couple in MeCN.) By analogy, we assign the reductive process in our cyclic voltammogram to the irreversible reduction of

---

(32) (a) Gray, T. G.; Rudzinski, C. M.; Meyer, E. E.; Holm, R. H.; Nocera, D. G. *J. Am. Chem. Soc.* **2003**, *125*, 4755. (b) Gray, T. G.; Rudzinski, C. M.; Nocera, D. G.; Holm, R. H. *Inorg. Chem.* **1999**, *38*, 5932.

(33) Yoshimura, T.; Ishizaka, S.; Umakoshi, K.; Sasaki, Y.; Kim, H.-B.; Kitamura, N. *Chem. Lett.* **1999**, 697.

(34) Nocera, D. G.; Gray, H. B. *J. Am. Chem. Soc.* **1984**, *106*, 824–825.

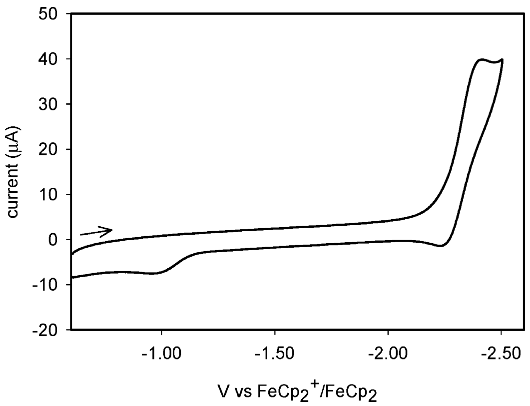

**Figure 5.** Cyclic Voltammogram of $(Bu_4N)_2[Mo_6Cl_8(SEt)_6]$ in MeCN (2.2 × $10^{-3}$M, 100 mV sec).

$[Mo_6Cl_8(SEt)_6]^{2-}$ to $[Mo_6Cl_8(SEt)_6]^{3-}$. Within the −0.60 V to −2.50 V window an anodic peak at $E_{p,a} = -1.00$ V is also apparent. This is only observed after accessing the irreversible reductive peak at −2.39 V which indicates that the peak at −1.00 V is due to decomposition of the reduced species. Notably, $SEt^-$ has been shown to undergo an irreversible oxidation at $E_{p,a} = -0.54$ V vs SCE.[35] This corresponds to a potential of ∼−1.00 V vs $FeCp_2^{+/0}$ in MeCN, which matches the anodic peak we observe. Therefore, it is possible that generation of the reduced cluster, $[Mo_6Cl_8(SEt)_6]^{3-}$, leads to the formation of free ethanethiolate. Scanning in the positive direction (out to +0.90 V) no oxidative peaks were observed. The window for the glassy carbon electrode did not allow us to scan out farther, so it is likely that the window is not large enough for us to observe the $[Mo_6Cl_8(SEt)_6]^{2-/-}$ process.[36]

Holm and co-workers report that $[Fe_4S_4(SEt)_4]^{2-/3-}$ ($E_{1/2} = -1.32$ V vs SCE in MeCN) is more difficult to reduce than $[Fe_4S_4Cl_4]^{2-/3-}$ ($E_{1/2} = -0.79$ V vs SCE in MeCN).[37,38] Qualitatively we observe the same trend when we compare the $E_{1/2}$ of the $[Mo_6Cl_{14}]^{2-/3-}$ couple with the reductive peak ($E_{p,c}$) of $[Mo_6Cl_8(SEt)_6]^{2-/3-}$. (Such a comparison must be made with caution as the measured potential values for irreversible peaks cannot be directly compared with their thermodynamic equilibrium potentials.[39]) This shift is likely due to the fact that thiolate ligands are stronger Brønsted bases than chloride. Thiolates are better able to donate electron density to the cluster, making it more electron rich and, consequently, more difficult to reduce.

**Ligand Reactivity Studies.** To compare the reactivity of the thiolate ligands coordinated to the molybdenum chloride cluster core to other thiolate complexes reported in the literature, we examined reactions of $[Mo_6Cl_8(SEt)_6]^{2-}$ with other thiols and with electrophilic reagents such as MeI and HCl. The hexaethanethiolate cluster complex reported here was found to undergo ligand substitution reactions with various thiols (RSH where R = nBu, Bn, Ph, 3-indolyl) as shown in eq 1.

$$[Mo_6Cl_8(SEt)_6]^{2-} + \mathrm{xs}\ RSH \rightarrow [Mo_6Cl_8(SR)_6]^{2-} + 6EtSH \qquad (1)$$

This chemistry is similar to that initially observed by Holm and co-workers for the reaction of $[Fe_4S_4(S\mathit{t}Bu)_4]^{2-}$ with *p*-tolylthiol and has been observed in a few other systems.[40–42] Monitoring the reaction of $[Mo_6Cl_8(SEt)_6]^{2-}$ with ∼8 equiv of HSPh, we found that within 5 h a small amount of the ethanethiolate had been substituted by phenylthiolate at room temperature. To prepare the substituted complexes in high yield, we combined $[Mo_6Cl_8(SEt)_6]^{2-}$ with an excess of RSH (∼20 equiv) and heated the solution at reflux for 20 h. We later observed that the reaction of $[Mo_6Cl_8(SEt)_6]^{2-}$ with 7.5 equiv of 3-indolylthiol went to completion in the same amount of time; therefore, heating the solution for a longer period of time is more important than the number of equivalents. Substitution of the thiolate ligands coordinated to the $[Fe_4S_4]^{2+}$ core is facile. For example, $[Fe_4S_4(S\mathit{t}Bu)_4]^{2-}$ is quantitatively converted to $[Fe_4S_4(SPh)_4]^{2-}$ within 15 min via reaction with 4.5 equiv of phenylthiol.[41] It is not surprising that thiolate substitution at molybdenum is slower than substitution at iron because molybdenum is a second row transition metal. However, it is interesting to note that Lang et al. reported that substitution of the thiolate ligands in the tungsten(II) complex, $[W(CO)_2(phen)(S\text{-}\mathit{t}Bu)_2]$, with HSPh and $H_2S$ was also complete within minutes at room temperature.[43]

Holm and co-workers also studied the reaction of tetralkylthiolate iron cubane clusters with electrophilic reagents such as HCl, $CH_3COCl$, $CH_3CO_2H$, and $CF_3SO_3CH_3$.[44] We found that $[Mo_6Cl_8(SEt)_6]^{2-}$ reacts with MeI, generating $[Mo_6Cl_8I_6]^{2-}$ and EtSMe, and with HCl leading to the formation of $[Mo_6Cl_{14}]^{2-}$. These cluster complexes have been reported previously; however, these studies demonstrate the basic reactivity of the coordinated thiolate ligands. We have also tried other electrophilic reagents such as $Me_3OBF_4$, benzyl bromide, and $HPnBu_3BF_4$; $^1H$ NMR spectra show that the peaks due to the ethanethiolate groups are either no longer present or are diminished, indicating reactivity with the thiolate ligands. However, further studies need to be conducted to determine the exact products formed in these reactions.

These substitution studies indicate that the thiolate ligands

---

(35) Krger, H.-J.; Holm, R. H. *Inorg. Chem.* **1989**, *28*, 1148.

(36) Electrochemical measurements were also made using a Pt working electrode. Under these conditions, the irreversible reductive peak which was reported with the glassy C electrode was also observed; however, it was not well defined. Because the Pt working electrode has a larger window, we were able to extend our oxidative scan to +1.50 V, and we did observe an irreversible oxidative peak at ($E_{p,a} = +1.18$ V).

(37) Wong, G. B.; Bobrik, M. A.; Holm, R. H. *Inorg. Chem.* **1978**, *17*, 578.

(38) Zhou, C.; Raebiger, J. W.; Segal, B. M.; Holm, R. H. *Inorg. Chim. Acta* **2000**, *300–302*, 892.

(39) Heinze, J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 831.

(40) Bobrik, M. A.; Que, L., Jr.; Holm, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 285.

(41) Que, L.; Bobrik, M. A.; Ibers, J. A.; Holm, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 4168.

(42) (a) Rakowski DuBois, M.; VanDerveer, M. C.; DuBois, D. L.; Haltiwanger, R. C.; Miller, W. K. *J. Am. Chem. Soc.* **1980**, *102*, 7456. (b) Christou, G.; Garner, C. D.; Mabbs, F. E. *Chem. Commun.* **1979**, 91. (c) Mayerle, J. J.; Denmark, S. E.; DePamphilis, B. V.; Ibers, J. A.; Holm, R. H. *J. Am. Chem. Soc.* **1975**, *97*, 1032.

(43) Lang, R. F.; Ju, T. D.; Kiss, G.; Hoff, C. D.; Bryan, J. C.; Kubas, G. J. *Inorg. Chem.* **1994**, *33*, 3899.

(44) Johnson, R. W.; Holm, R. H. *J. Am. Chem. Soc.* **1978**, *100*, 5338.

in $[Mo_6Cl_8(SEt)_6]^{2-}$ react in a similar manner to other coordinated thiolate ligands and that this complex could be used as a starting material in the preparation of new and interesting cluster complexes containing the molybdenum chloride core.

## Conclusions

This report contains a complete study of the chemical and physical properties of the $[Mo_6Cl_8(SR)_6]^{2-}$ cluster complexes which adds significantly to the chemistry of transition metal thiolate complexes. We demonstrated that $[Mo_6Cl_8(SEt)_6]^{2-}$ can act as a precursor for the preparation of new cluster complexes and that it undergoes reactions with electrophilic reagents such as MeI. The reactivity of the thiolate ligand in these clusters appears to be consistent with what has been observed with the thiolate ligands coordinated to the $[Fe_4S_4]^{2+}$ cluster core. This is in contrast to our previous studies involving the oxidation of phosphine ligands coordinated to the molybdenum chloride core. In that study, we examined the oxidation of coordinated phosphine ligands and found that they reacted differently than one would expect for phosphine ligands coordinated to a single transition metal center.[45]

**Acknowledgment.** This material is based on work supported by the National Science Foundation under Grant CHE-0239805 and the Research Corporation (CC5192).

**Supporting Information Available:** X-ray crystallographic data in CIF format for $(PPN)_2[Mo_6Cl_8(SEt)_6]\cdot Et_2O$ and $(PPh_3Me)_2[Mo_6Cl_8(SBn)_6]\cdot 2NO_2CH_3$ is included along with $^1H$ NMR spectral data for the $[Mo_6Cl_8(SR)_6]^{2-}$ complexes, the time-resolved emission of $[Mo_6Cl_8(SEt)_6]^{2-}$ in MeCN, and the synthesis of 3-indolylthiol and $(PPh_3Me)_2[Mo_6Cl_8(SBn)_6]$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

IC800613D

---

(45) Szczepura, L. F.; Ooro, B. A.; Wilson, S. R. *J. Chem. Soc., Dalton Trans.* **2002**, 3112.