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$Mo_2S_4^{2+}$ Core: New Syntheses, New Complexes, and Electrochemical Diversity

Sir:

Recognition of the importance of sulfide ligation in the heterogeneous Mo catalysts used in industrial redox processes[1] and in the Mo-containing site of the enzyme nitrogenase[2] has directed increasing attention to the coordination chemistry of sulfidomolybdenum complexes. Efforts to develop mononuclear, polynuclear, and heteronuclear Mo sulfide entities which serve as structural or reactivity models for these catalytic systems have led to the synthesis of several novel Mo-[3] and Mo–Fe sulfide complexes.[4] However, progress has been significantly restricted

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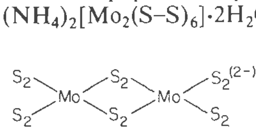
ble I. Infrared and Electrochemical Data for $Mo_2S_4^{2+}$ Complexes

designation	complex	ν (Mo–S_t), cm^{-1}	E,[a] V, vs. SCE
3	$[(C_2H_5)_4N]_2[Mo_2S_4(SC_6H_5)_4]$	525 s, 512 m	−1.51,[b] −0.70[c]
4	$Mo_2S_4(C_6H_4SNH_2)_2$	542 s	−0.78,[b] −1.22,[b] −1.8
5	$[(C_2H_5)_4N]_2[Mo_2S_4(C_6H_4SNH)_2]$	510 s, 490 sh	−1.80
6	$Mo_2S_4[S_2CN(C_2H_5)_2]_2$[e]	546 s, 535 m	−0.92,[d] −1.53[d]
7	$[(C_2H_5)_4N]_2[Mo_2S_4(SCH_2CH_2S)_2]$	522 s, 510 sh	−1.88
8	$Mo_2S_4(CH_3NHCH_2C(CH_3)_2S)_2$	546 s, 534 sh	−0.99, −1.50

[a] Complexes display quasi-reversible behavior unless otherwise noted [E = (Epc + Epa)/2]. Voltammograms obtained from 3.0 mM solu-ns of complex in DMF vs. SCE with 0.1 M $(C_2H_5)_4NClO_4$. Scan rate = 0.04 V/s. [b] Peak potential for irreversible reduction. [c] Peak po-ıtial for irreversible oxidation. [d] Scan rate = 0.4 V/s. [e] See ref 19.

the lack of appropriate sulfidomolybdenum starting materials. hile the thiomolybdate series $MoO_xS_{4-x}^{2-}$ (X = 0–3) has been ɜful,[3,4] the only other well-characterized complexes containing ɔlybdenum–terminal-sulfide moieties are mononuclear sulfi-molybdenum halide complexes,[5] complexes containing cyclo-ntadienyl ligands,[6] and dithiolate complexes containing a oOS_3^{2+}[7] or $Mo_2S_4^{2+}$ core.[8] Unfortunately, the utility of the ter series has been limited by the requirement for bidentate hiolate ligands and by the low yields of the reactions in which ɜse complexes are prepared.[8b,c]

Recently, Müller and co-workers have reported a series of lynuclear molybdenum complexes which contain disulfide (S_2^{2-}) ands.[9] In this paper, we report the use of one of these com-:xes, $(NH_4)_2[Mo_2(S{-}S)_6]\cdot 2H_2O$ (**1**),[9a] in a general procedure



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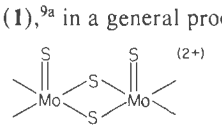

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· the preparation of complexes containing the $Mo_2S_4^{2+}$ core. is reaction involves a novel redox process whereby a Mo sulfide ·e, **2**, is generated via the reduction of the disulfide linkages complex **1**. The resulting availability of $Mo_2S_4^{2+}$ complexes :h a variety of ligand types has allowed us to investigate trends physical and chemical properties.[10]

Reaction of **1** with 30 equiv of the sodium salt of thiophenol CH_3CN containing $(C_2H_5)_4N^+Br^-$, for 1 h at room temperature, ·lds a red-orange crystalline solid upon precipitation with iso-ɔpyl alcohol. Analytical[11a] and spectroscopic properties (vide ra) indicate this complex to be $[(C_2H_5)_4N]_2[Mo_2S_4(SC_6H_5)_4]$, Similarly, reaction of **1** in ethanol with 60 equiv of *o*-amino-ızenethiol ($C_6H_4SHNH_2$) yields, depending upon the workup, ɔ distinct complexes containing the $Mo_2S_4^{2+}$ core. The addition of HCl after 2 h yields a maroon solid which elemental analysis[11b] indicates to be $Mo_2S_4(C_6H_4SNH_2)_2$, **4**. Treatment of **4** with base, followed by the addition of $(C_2H_5)_4N^+Br^-$, leads to the isolation of a red-brown solid, identified as $[(C_2H_5)_4N]_2[Mo_2S_4(C_6H_4SNH)_2]$, **5**.[11c] Complexes **4** and **5** differ in the degree of protonation of the amino group. The isolation of **4** is unusual in that there is a strong tendency for Mo complexes of *o*-aminobenzenethiol to have monodeprotonated amine groups.[12] Presumably, the π-donor properties of the sulfur atoms which make up the $Mo_2S_4^{2+}$ core reduce the acidity normally associated with the aromatic amino groups coordinated to metals in high oxidation states. The yields of the new complexes, **3**, **4**, and **5**, by the procedures described above are 82, 80, and 90%, respectively.

The syntheses of two reported $Mo_2S_4^{2+}$ complexes, $Mo_2S_4(S_2CN(C_2H_5)_2)_2$ (**6**)[8b] and $[(C_2H_5)_4N]_2[Mo_2S_4(SCH_2CH_2S)_2]$ (**7**),[8c] were undertaken to evaluate the efficacy of our method for the preparation of complexes containing the $Mo_2S_4^{2+}$ core. When **1** is refluxed in CH_3OH with 20 equiv of $Na(S_2CN(C_2H_5)_2)$ for 2 h, an 82% yield of analytically pure **6** is obtained.[11d] Similarly, the reaction of **1** with 25 equiv of the disodium salt of 1,2-dimercaptoethane for 30 min at room temperature, followed by the addition of $(C_2H_5)_4N^+Br^-$, results in a 75% yield of **7**.[11e] These yields are to be compared with reported yields of 32% for 6[8b] and 3 or 6% (depending on the isomer) for **7**.[8c]

The key conversion in the reactions described above is the reduction of the disulfide ligands in **1** to coordinated and free sulfide ions. The oxidation state of molybdenum and the Mo–Mo bond are not affected by this reaction. The excess thiolate ligand serves both as the reductant and as a ligand in this reaction (eq 1). Alternative reductants can assume the redox function of the

$$[(S{-}S)_2Mo(S{-}S)_2Mo(S{-}S)_2]^{2-} + 16C_6H_5S^- \rightarrow [Mo_2S_4(SC_6H_5)_4]^{2-} + 6C_6H_5S{-}SC_6H_5 + 8S^{2-} \quad (1)$$

thiolate. Thus, addition of $(C_6H_5)_3P$ to a solution of **1** and 4 equiv of $Na(S_2CN(C_2H_5)_2)$ at room temperature results in the instantaneous formation of **6** and $(C_6H_5)_3PS$, according to eq 2.

$$Mo_2(S{-}S)_6^{2-} + 6(C_6H_5)_3P + 2S_2CN(C_2H_5)_2^- \rightarrow Mo_2S_4(S_2CN(C_2H_5)_2)_2 + 6(C_6H_5)_3PS + 2S^{2-} \quad (2)$$

The use of $(C_6H_5)_3P$ as a reductant obviates the need for excess thiols, an important consideration when less common thiols are involved.

Ligand substitution reactions provide an additional alternative procedure for preparation of $Mo_2S_4^{2+}$ complexes. Reaction of **3** with the bidentate ligand $CH_3NHCH_2C(CH_3)_2SH$[13] in CH_3CN containing $(C_2H_5)_3N$ results in the formation of an orange solid identified as $Mo_2S_4(CH_3NHCH_2C(CH_3)_2S)_2$, **8**, in 76% yield[11f] (eq 3). The formation of the chelated complex and the insolubility

$$Mo_2S_4(SC_6H_5)_4^{2-} + 2CH_3NHCH_2C(CH_3)_2SH + 2(C_2H_5)_3N \rightarrow Mo_2S_4(CH_3NHCH_2C(CH_3)_2S)_2 + 2(C_2H_5)_3NH^+ + 4C_6H_5S^- \quad (3)$$

of the product in CH_3CN supply the driving force for this reaction.

Two structural isomers, a C_{2v} isomer designated syn (**2**) and a C_{2h} isomer designated anti, have been identified for the $Mo_2S_4^{2+}$

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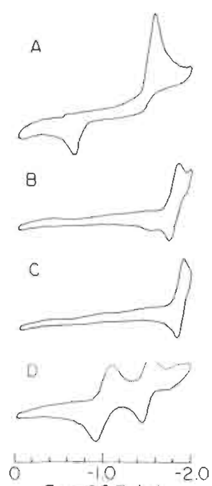

Figure 1. Cyclic voltammograms of 3-mM solutions in 0.1 M $(C_2H_5)_4NClO_4$ vs. SCE in DMF at a platinum button electrode, scan rate 0.4 V/s. (A) $[(C_2H_5)_4N]_2[Mo_2S_4(SC_6H_5)_4]$, (B) $[(C_2H_5)_4N]_2[Mo_2S_4(C_6H_4SNH)_2]$, (C) $[(C_2H_5)_4N]_2[Mo_2S_4(SCH_2CH_2S)_2]$, (D) $Mo_2S_4(CH_3NHCH_2C(CH_3)_2S)_2$.

core. Complex **6** has been found only in the syn isomeric form[14] while complex **7** has been crystallographically characterized in both isomeric forms.[8c,15] The infrared spectra of complexes **3–8** (Table I) all contain a strong $Mo–S_t$ stretching vibration and in most cases a second, much weaker, absorption at lower wavenumbers, consistent with the predominant or exclusive formation of the syn isomer.[17] The dianionic complexes display lower $Mo–S_t$ stretching frequencies than the neutral complexes, presumably due to additional electron density on the $Mo_2S_4^{2+}$ core. Comparison of the neutral and dianionic complexes of the *o*-aminobenzenethiol ligand, **4** and **5**, where $\nu(Mo–S_t)$ occurs at 512 and 510 cm^{-1}, respectively, illustrates this effect.

The cyclic voltammograms of complexes **3**, **5**, **7**, and **8**, shown in Figure 1, illustrate the effect of different ligands and donor atoms on the electrochemical behavior of the $Mo_2S_4^{2+}$ core. All complexes, with the exception of **3**, display reversible one-electron transfers. This behavior is consistent with that observed previously for complexes with the $Mo_2O_{4-x}S_x^{2+}$ (x = 0–4) core where electrochemical reversibility increases with the number of sulfide ligands.[16,18] The irreversibility observed for **3**, which contains monodentate thiophenoxide ligands, suggests that bidentate ligands may be required to stabilize the reduced $Mo_2S_4^{2+}$ complexes. The more negative reduction potentials found for the dianionic complexes **3**, **5**, and **7** relative to the neutral complexes **4**, **6**, and **8** may result from the additional electron density on the $Mo_2S_4^{2+}$ core in the dianionic complexes. In addition, electrolysis of **4**, at potentials more negative than its two irreversible waves, results in a quantitative conversion to **5**. A more detailed discussion of the electrochemical behavior will appear in a forthcoming publication.

The reduction of the disulfide complex, **1**, to give the molybdenum sulfide complexes reported here should be viewed in light of a recently reported redox reaction in which the reverse process occurs, i.e., the conversion of a molybdenum sulfide to a molybdenum disulfide complex (eq 4).[9d] Further, a recent study shows

$$2MoO_2S_2^{2-} \rightarrow Mo_2O_2S_2(S–S)_2^{2-} \qquad (4)$$

that a partial disulfide bond can be formed in the Mo^{VI} coordination sphere from two nominally noninteracting *cis*-thiolate ligands.[21] These results point to previously unrecognized intramolecular redox behavior associated with sulfur coordinated to molybdenum in its higher oxidation states.

The general procedures reported here for the preparation of a variety of $Mo_2S_4^{2+}$ complexes have allowed for the first time the isolation of this core with nonsulfur-donor and nonchelating ligands. Varying the ligand is found to have profound effects on the spectroscopic and, especially, the electrochemical properties of $Mo_2S_4^{2+}$ complexes. Further, we have found these complexes to be reactive toward a variety of divalent first-row transition-metal ions. As in the thiomolybdate series,[3,4] the terminal sulfides in $Mo_2S_4^{2+}$ complexes appear to function as donors toward the appropriate metal ions. Full characterization of the products of these reactions is under way. However, initial results indicate that $Mo_2S_4^{2+}$ complexes represent new molybdenum sulfide starting materials for the preparation of heteronuclear molybdenum sulfide containing complexes and materials.

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(17) Two infrared-active $Mo–S_t$ stretching vibrations are expected for complexes in the syn isomeric form while only one is predicted for the anti isomer. Although both stretching modes have been identified for **6**[16] it may not always be possible to observe the weaker, lower-energy absorption for the syn isomer. We attribute the $Mo–S_t$ stretching vibration observed at 522 cm^{-1} in **7** to the syn isomeric form. The shoulder observed at 510 cm^{-1} is due to either the second stretching vibrational mode of the syn isomer or the presence of small quantities of the anti isomer. The syn and anti isomers of **7** have been reported to give rise to single $Mo–S_t$ stretching vibrations of 508 and 493 cm^{-1}, respectively.[8c] The discrepancy between our finding of 522 cm^{-1} and the previously reported 508 cm^{-1} is not understood. The voltammetry of **7** is in good agreement with that reported previously[8c] for the syn isomer of **7**.

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