sonable for molecules containing a formal double bond between the metal atoms, as adjudged by the EAN criteria.[13] The bridging region of the μ-CH_2 compound **1** is planar, as required by the presence of a crystallographic twofold axis passing through atoms C_6, C_7, and O_6. As can be seen from Figure 1, the Co to μ-CH_2 carbon distance is longer than the Co to μ-CO carbon distance [1.909 (9) Å vs. 1.849 (8) Å]. The cobalt to μ-CH_2 carbon distance in **1** is slightly shorter than the cobalt to bridging alkylidene distances [1.951 (6) Å, 1.944 (7) Å] observed in $Co_2(\eta^5$-$C_5H_5)_2(CO)_2(\mu$-$CH(CO_2CH_2CH_3))$;[14] this is perhaps due to the longer formal single Co–Co bond [2.495 (1) Å] in the latter compound.

Despite the intense level of interest in alkylidene ligands in organometallic chemistry during the last several years,[15] compounds containing the simplest bridging alkylidene, μ-CH_2, are still relatively rare. Single examples have been reported in binuclear Mn,[16] Rh,[17] Ru,[18] Fe,[19] and Pt[20] systems and in a trinuclear osmium cluster.[21] The binuclear cobalt compound **1** is, however, the first such example with cobalt as the metal. Furthermore, it is the only such compound with a formal double bond between the metals and with a bridging carbonyl. These unique features may play a role in the reactions of **1** with species such as CO, H_2, and alkenes.[22]

Having established the structure of **1**, we now turn to the interesting question of the source of the μ-CH_2 and μ-CO ligands. The most reasonable source appears to be the lithium enolate of acetaldehyde ($Li^+CH_2CHO^-$, LEA) generated via the reaction of THF solvent with *n*-butyllithium. This reaction has been shown to cleanly produce ethylene and LEA,[23,24] with a $t_{1/2}$ at 35 °C of 10 min.[23] Clearly, under the conditions used to prepare **1**, some enolate would have been present with the $Li^+Me_5Cp^-$ prior to addition of $CoCl_2$. In order to test this hypothesis, several reactions were carried out. First, $Li^+Me_5Cp^-$ was generated at −78 °C via the reaction of HMe_5Cp in THF with a stoichiometric amount of *n*-BuLi/hexane solution, thus avoiding the generation of LEA. After the mixture was slowly warmed to room temperature, reaction with 0.5 equiv of anhydrous $CoCl_2$ and workup were carried out as before. Only a small amount of brown solid was obtained, tentatively identified as the dichloro bridged compound $Co_2(\eta^5$-$C_5Me_5)_2(\mu$-$Cl)_2$, **2**.[25] In contrast, when the reaction was carried out in a similar fashion, except for addition of 0.25 equiv of preformed LEA[26] in parallel with addition of the $CoCl_2$, the bridging methylene compound **1** was isolated in 10% yield. Similar experiments using acetaldehyde directly, instead of LEA, produced no identifiable product. Thus, the importance of LEA in the formation of **1** seems well established.

The exact mechanism by which LEA reacts with $CoCl_2$ and $Li^+Me_5Cp^-$ remains to be determined. While we assume the first step must involve metalation of the enolate, such metalations appear not to have been studied to date. This may in part be due to the difficulty of obtaining enolates of reactive aldehydes, since direct treatment of such aldehydes with base often leads to aldol condensation products. In the case of acetaldehyde, generation of the enolate via the *n*-BuLi/THF route[23,24] avoids such problems. Ready availability of LEA and the demonstration of its involvement in the formation of the novel μ-CH_2 compound **1** suggest that a general investigation of metalation of aldehyde enolates should be a fruitful venture.

Acknowledgments. Helpful discussions with J. W. Johnson and G. Doyle are gratefully acknowledged. We also wish to thank R. Pettit for informing us of his results on the binuclear iron μ-CH_2 compound prior to publication.

Supplementary Material Available: Tables of atomic positional and temperature parameters, bond distances, interatomic angles, and deviations of atoms from cyclopentadienyl least-squares planes, listings of observed and calculated structure factor amplitudes, and a diagram of the packing of molecules in the unit cell (16 pages). Ordering information is given on any current masthead page.

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[13] Bernal, I.; Korp, J. D.; Reisner, G. M.; Herrmann, W. A. *J. Organomet. Chem.* **1977**, *139*, 321.

[14] Herrmann, W. A.; Schweizer, I.; Creswick, M.; Bernal, I. *J. Organomet. Chem.* **1974**, *165*, C17.

[15] Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 7282, and references therein. Hains, R. J.; Leigh, G. *Chem. Soc. Rev.* **1975**, *4*, 155.

[16] Creswick, M.; Bernal, I.; Herrmann, W. *J. Organomet. Chem.* **1979**, *172*, C39.

[17] Herrmann, W. A.; Kruger, C.; Goddard, R.; Bernal, I. *Angew Chem., Int. Ed. Engl.* **1977**, *16*, 334.

[18] Anderson, R.; Jones, R. A.; Wilkinson, G.; Hursthouse, M. B.; Abdul-Malik, K. M. *J. Chem. Soc., Chem. Commun.* **1977**, 865.

[19] Sumner, C. E.; Riley, P. E.; Davis, R. E.; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 1752.

[20] Brown, M. P.; Fisher, J. R.; Franklin, S. J.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1978**, 749. Brown, M. P.; Fisher, J. R.; Puddephatt, R. J.; Seddon, K. R. *Inorg. Chem.* **1979**, *18*, 2808.

[21] Calvert, R. B.; Shapley, J. R.; Shults, A. J.; Williams, I. M.; Suib, S. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1978**, *100*, 6240.

[22] Very little is known at present about reactivity of μ-CH_2 ligands; recent work by Pettit and co-workers has uncovered what promises to be an interesting and potentially rich area (see ref 19). Compound **1** of our work reacts rapidly with CO, one major product being tentatively identified as $Co(\eta^5$-$Me_5C_5)(CO)_2$.

[23] Bates, R. B.; Kroposki, L. M.; Potter, D. E. *J. Org. Chem.* **1972**, *37*, 560; $t_{1/2}$ determined with ~10:1 ratio THF/BuLi.

[24] Jung, M. E.; Blum, R. B. *Tetrahedron Lett.* **1977**, *43*, 3791.

[25] Crystalline **2** was prepared in moderate yield (22%) by reaction of $CoCl_2$ and Li^+Me_5Cp in a 1:1 ratio, following the same procedure. Mass spectrum, *m/e* 458 (M^+, additional peaks show appropriate pattern for two chlorines), 229 (base peak, $(Me_5Cp)CoCl$).

[26] LEA was generated in situ in THF by reaction with the appropriate amount of *n*-BuLi at room temperature for 18 h. The presence of LEA was verified by NMR (see ref 23).

$Mo_2S_4^{2+}$ 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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[1] (a) F. E. Massoth, *Adv. Catal.*, **27**, 266 (1978); (b) S. C. Schuman and H. Schalit, *Catal. Rev.*, **4**, 245 (1970); (c) F. P. Daly, *J. Catal.*, **51**, 221 (1978); (d) H. C. Lee and J. B. Bult, *ibid.*, **49**, 320 (1977); (e) F. E. Massoth, *ibid.*, **47**, 316 (1977); (f) F. E. Massoth and C. L. Kibby, *ibid*, **47**, 300 (1977).

[2] (a) S. P. Cramer, K. O. Hodgson, W. O. Gillum, and L. E. Mortenson, *J. Am. Chem. Soc.*, **100**, 3398 (1978); (b) S. P. Cramer, W. O. Gillum, K. O. Hodgson, L. E. Mortenson, E. I. Stiefel, J. R. Chisnell, W. E. Brill, and V. K. Shah, *ibid.*, **100**, 3814 (1978); (c) W. G. Zumft, *Eur. J. Biochem.*, **91**, 345 (1978).

[3] (a) E. Diemann and A. Müller, *Coord. Chem. Rev.*, **10**, 79 (1973); (b) A. Müller, H. Schulze, W. Sievert, and N. Weinstock, *Z. Anorg. Allg. Chem.*, 403, 310 (1974); (c) E. Königer-Ahlborn, H. Schulze, and A. Müller, *ibid.*, **428**, 5 (1977).

[4] (a) A. Müller and S. Sarkar, *Angew. Chem., Int. Ed. Engl.*, **16**, 705 (1977); (b) T. E. Wolff, J. M. Berg, C. Warrick, K. O. Hodgson, R. H. Holm, and R. B. Frankel, *J. Am. Chem. Soc.*, **100**, 4630 (1978); (c) T. E. Wolff, J. M. Berg, P P. Power, K. O. Hodgson, R. H. Holm, and R. B. Frankel, *ibid.*, **101**, 5454 (1979); (d) T. E. Wolff, J. M. Berg, K. O. Hodgson, R. B. Frankel, and R. H. Holm, *ibid.*, **101**, 4140 (1979); (e) G. Christou, C. D. Garner, F. E. Mabbs, and M. G. B. Drew, *J. Chem. Soc. Chem. Commun.*, 91 (1979); (f) G. Christou, C. D. Garner, F. E. Mabbs, and T. T. King, *ibid.*, 740 (1978); (g) G. Christou, C. D. Garner, and F. E. Mabbs, *Inorg. Chim. Acta*, **28**, L189 (1978); (h) H. C. Silvis, R. H. Tieckelmann, and B. A. Averill, *ibid.*, **36**, L423 (1979); (i) D. Coucouvanis, E. D. Simhon, D. Swenson, and W. C. Baenziger, *J. Chem. Soc., Chem. Commun.*, 361 (1979).

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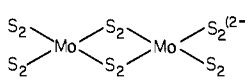
Table I. Infrared and Electrochemical Data for $Mo_2S_4{}^{2+}$ Complexes

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 solutions 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 potential for irreversible oxidation. [d] Scan rate = 0.4 V/s. [e] See ref 19.

by the lack of appropriate sulfidomolybdenum starting materials. While the thiomolybdate series $MoO_xS_{4-x}{}^{2-}$ (X = 0–3) has been useful,[3,4] the only other well-characterized complexes containing molybdenum-terminal-sulfide moieties are mononuclear sulfidomolybdenum halide complexes,[5] complexes containing cyclopentadienyl ligands,[6] and dithiolate complexes containing a $MoOS_3{}^{2+}$[7] or $Mo_2S_4{}^{2+}$ core.[8] Unfortunately, the utility of the latter series has been limited by the requirement for bidentate dithiolate ligands and by the low yields of the reactions in which these complexes are prepared.[8b,c]

Recently, Müller and co-workers have reported a series of polynuclear molybdenum complexes which contain disulfide ($S_2{}^{2-}$) ligands.[9] In this paper, we report the use of one of these complexes, $(NH_4)_2[Mo_2(S{-}S)_6]\cdot 2H_2O$ (**1**),[9a] in a general procedure for the preparation of complexes containing the $Mo_2S_4{}^{2+}$ core. This reaction involves a novel redox process whereby a Mo sulfide core, **2**, is generated via the reduction of the disulfide linkages of complex **1**. The resulting availability of $Mo_2S_4{}^{2+}$ complexes with a variety of ligand types has allowed us to investigate trends in physical and chemical properties.[10]



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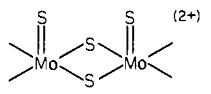

2

Reaction of **1** with 30 equiv of the sodium salt of thiophenol in CH_3CN containing $(C_2H_5)_4N^+Br^-$, for 1 h at room temperature, yields a red-orange crystalline solid upon precipitation with isopropyl alcohol. Analytical[11a] and spectroscopic properties (vide infra) indicate this complex to be $[(C_2H_5)_4N]_2[Mo_2S_4(SC_6H_5)_4]$, **3**. Similarly, reaction of **1** in ethanol with 60 equiv of *o*-aminobenzenethiol ($C_6H_4SHNH_2$) yields, depending upon the workup, two 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 thiolate.

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

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

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

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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(5) (a) M. J. Atherton and J. H. Holloway, *Adv. Inorg. Chem. Radiochem.*, **22**, 171 (1979); (b) D. A. Rice, *Coord. Chem. Rev.*, **26**, 199 (1978); (c) J. H. Holloway and D. C. Puddick, *Inorg. Nucl. Chem. Lett.*, **15**, 85 (1979).

(6) (a) J. C. Daran, K. Prout, G. J. S. Adam, M. L. H. Green, and J. Sala-Pala, *J. Organomet. Chem.*, **131**, C40 (1977); (b) W. Beck, W. Danzer, and G. Thiel, *Angew. Chem.*, **14**, 625 (1973).

(7) W. E. Newton, J. W. McDonald, K. Yamanouchi, and J. H. Enemark, *Inorg. Chem.*, **18**, 1621 (1979).

(8) (a) T. Sakurai, H. Okabe, and H. Isoyama, *Bull. Jpn. Pet. Inst.*, **13**, 243 (1971); (b) W. E. Newton, G. J.-J. Chen, and J. W. McDonald, *J. Am. Chem. Soc.*, **98**, 5387 (1976); (c) G. Bunzey, J. H. Enemark, J. K. Howie, and D. T. Sawyer, *ibid.*, **99**, 4168 (1977).

(9) A. Müller, W. O. Nolte, and B. Krebs, *Angew. Chem., Int. Ed. Engl.*, **17**, 279 (1978); (b) A. Müller, S. Sarkar, R. G. Bhattacharyya, S. Pohl, and M. Dartmann, *ibid.*, **17**, 535 (1978); (c) A. Müller, W. Eltzner, and W. Mohan, *ibid.*, **18**, 168 (1979); (d) W. Rittner, A. Müller, A. Newman, W. Bäther, and R. C. Sharma, *ibid.*, **18**, 530 (1979).

(10) Preliminary results have been reported by K. F. Miller, A. E. Bruce, J. L. Corbin, and E. I. Stiefel, Midwest Regional Meeting of the American Chemical Society, Columbus, Ohio, May 1979; 178th National Meeting of the American Chemical Society, Washington, D.C., September 1979.

(11) Anal. (a) Calcd for $[(C_2H_5)_4N]_2[Mo_2S_4(SC_6H_5)_4]$: C, 47.23; H, 5.94; N, 2.75. Found: C, 47.18; H, 6.05; N, 2.66. (b) Calcd for $Mo_2S_4(C_6H_4SNH_2)_2$: C, 25.35; H, 2.13; N, 4.93. Found: C, 25.62; H, 2.31; N, 4.80. (c) Calcd for $[(C_2H_5)_4N]_2[Mo_2S_4(C_6H_4SNH)_2]$: C, 40.67; H, 6.09; N, 6.78. Found: C, 40.88; H, 6.43; N, 6.68. (d) Calcd for $Mo_2S_4[S_2CN(C_2H_5)_2]_2$: C, 19.48; H, 3.28; N, 4.54. Found: C, 19.20; H, 3.35; N, 4.47. (e) Calcd for $[(C_2H_5)_4N]_2[Mo_2S_4(SCH_2CH_2S)_2]$: C, 31.40; H, 6.32; N, 3.66. Found: C, 31.49; H, 6.36; N, 3.79. (f) Calcd for $Mo_2S_4[CH_3NHCH_2C(CH_3)_2S]_2$: C, 21.58; H, 4.35; N, 5.03. Found: C, 21.78; H, 4.41; N, 5.08.

(12) J. K. Gardner, N. Pariyadath, J. L. Corbin, and E. I. Stiefel, *Inorg. Chem.*, **17**, 897 (1978).

(13) R. Luhowy and F. Meneghini, *J. Org. Chem.*, **38**, 2405 (1973).

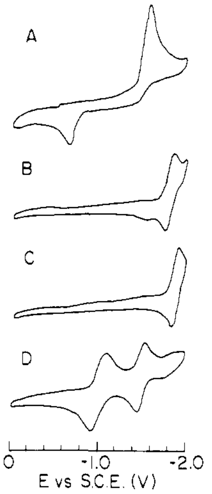

Figure 1. Cyclic voltammograms of 3-mM solutions in 0.1 M $(C_2H_5)_4NClO_4$ vs. SCE in DMF at a platinum button electrode, scan rate 0.4 V/s. (A) $[(C_2H_5)_4N]_2[Mo_2S_4(SC_6H_5)_4]$, (B) $[(C_2H_5)_4N]_2[Mo_2S_4(C_6H_4SNH)_2]$, (C) $[(C_2H_5)_4N]_2[Mo_2S_4(SCH_2CH_2S)_2]$, (D) $Mo_2S_4(CH_3NHCH_2C(CH_3)_2S)_2$.

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 ν(Mo–S$_t$) occurs at 542 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

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

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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(14) (a) B. Spivack, Z. Dori, and E. I. Stiefel, *Inorg. Nucl. Chem. Lett.*, **11**, 501 (1975); (b) J. T. Huneke and T. H. Enemark, *Inorg. Chem.*, **17**, 3698 (1978); (c) A. Müller, R. G. Bhattacharyya, N. Mohan, and B. Pfefferkorn, *Z. Anorg. Allg. Chem.*, **454**, 118 (1979).

(15) G. Bunzey and J. H. Enemark, *Inorg. Chem.*, **17**, 682 (1978).

(16) F. A. Schultz, V. R. Ott, D. S. Rolison, D. C. Bravard, J. W. McDonald, and W. E. Newton, *Inorg. Chem.*, **17**, 1758 (1978).

(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**.

(18) V. R. Ott, D. S. Swieter, and F. A. Schultz, *Inorg. Chem.*, 16, 2538 (1977).

(19) Schultz et al. report waves at −0.84 and −1.27 V vs. SCE in Me$_2$SO with 0.1 M $(C_2H_5)_4NClO_4$.[16] Faulkner reports waves at −0.86 and −1.48 V vs. SCE in DMF with $(C_2H_5)_4NClO_4$ for $Mo_2S_4(S_2CN(n\text{-}C_4H_9)_2)_2$.[20]

(20) H. D. Faulkner, *J. Electrochem. Soc.*, **125**, 287C (1978).

(21) E. I. Stiefel, K. F. Miller, A. E. Bruce, J. L. Corbin, J. M. Berg, and K. O. Hodgson, *J. Am. Chem. Soc.*, **102**, 3624 (1980).

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A Quintet-State Triplet–Triplet Radical Pair

Sir:

Radical pairs having triplet multiplicity–and only triplet multiplicity–have been detected in many chemical reactions in the past decade and a half by using ESR spectroscopy.[1,2] Even among stabilized organic radicals, multiplicities higher than triplet are scarce. Trozzolo, Wasserman, and co-workers[3] observed complex ESR spectra in the low-temperature matrix photolysate of 1,3-bis(α-diazobenzyl)benzene and 1,3-diazidobenzene and assigned them to the quintet ground states of *m*-dicarbene and *m*-dinitrene, respectively. Itoh[4] also succeeded in stabilizing the quintet state of *m*-dicarbene in the precursor single crystal. There are also reports on the detection of septet-state organic radicals

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(1) Kurita, Y. *J. Chem. Phys.* **1964**, *41*, 3926. Wiersma, D. A.; Kommandeur, J. *Mol. Phys.* **1967**, *13*, 241. Ohigashi, H.; Kurita, Y. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 704. Symons, M. C. R. *Nature* (*London*) **1967**, *231*, 1226. Geoffroy, M.; Lucken, E. A. C. *Helv. Chim. Acta* **1970**, *53*, 813.

(2) Gordy, W.; Morehouse, R. *Phys. Rev.* **1966**, *151*, 207. Niizuma, S.; Kokubun, H.; Koizumi, M. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 335. Arimitsu, S.; Tsubomura, H. *Ibid.* **1972**, *45*, 1357.

(3) Trozzolo, A. M.; Murray, R. W.; Smolinsky, G.; Yager, W. A.; Wasserman, E. *J. Am. Chem. Soc.* **1963**, *85*, 2526. Wasserman, E.; Murray, R. W.; Yager, W. A.; Trozzolo, A. M.; Smolinsky, G. *Ibid.* **1967**, *89*, 5076.

(4) Itoh, K. *Chem. Phys. Lett.* **1967**, *1*, 235.

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