(2) S. P. Cramer, W. O. Gillum, K. O. Hodgson, L. E. Mortenson, E. I. Stiefel, J. R. Chisnell, W. J. Brill, and V. K. Shah, *J. Am. Chem. Soc.*, **100,** 3814 (1978).

(3) V. K. Shah and W. J. Brill, *Proc. Natl. Acad. Sci. U.S.A.*, **74,** 3249 (1977).

(4) (a) 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); (b) T. E. Wolff, J. M. Berg, K. O. Hodgson, R. B. Frankel, and R. H. Holm, *ibid.*, **101,** 4140 (1979).

(5) (a) G. Christou, C. D. Garner, F. E. Mabbs, and T. J. King, *J. Chem. Soc., Chem. Commun.*, 740 (1978); (b) G. Christou, C. D. Garner, and F. E. Mabbs, *Inorg. Chim. Acta*, **28,** L189 (1978).

(6) G. Christou, G. D. Garner, F. E. Mabbs, and M. G. B. Drew, *J. Chem. Soc., Chem. Commun.*, 91 (1979).

(7) D. Coucouvanis, E. D. Simhon, D. Swenson, and N. C. Baenziger, *J. Chem. Soc., Chem. Commun.*, 361 (1979).

(8) D. G. Holah and D. Coucouvanis, *J. Am. Chem. Soc.*, **97,** 6917 (1975).

(9) NMR spectra (Me_2SO-d_6, 298 K) show the *m*-H resonance at 36.64 downfield and the *p*-H resonance 35.94 ppm upfield from Me_4Si in a 2:1 intensity ratio. The assignments were made on the basis of the *p*-CH_3 substituted phenyl ring derivative. The *o*-H resonance could not be detected, very likely because of extensive broadening. The magnitude of the shifts *decreases* as temperature is increased over the range 294–352 K.

(10) See for example ref 4b (Figure 7).

(11) Crystal and refinement data for $(Ph_4P)_2FeMoS_9 \cdot {}^1\!/_2DMF$: cell dimensions, $a = 11.874$ (3), $b = 22.486$ (5), $c = 10.698$ (3) Å; $\alpha = 107.3$ (1), $\beta = 79.27$ (3), $\gamma = 106.86$ (4)°; space group, $P1$; $Z = 2$; $d_{calcd} = 1.43$ g cm^{-3}, $d_{obsd} = 1.44$ g cm^{-3}; crystal dimensions, 0.2 × 0.04 × 0.3 mm; $2\theta_{max}$, 40° (Mo radiation); reflections used, $F^2 > 3\sigma(F^2)$, 3110; unique reflections, 4902; parameters, 330. Crystal and refinement data for $(Ph_4P)_2FeWS_9 \cdot {}^1\!/_2DMF$: cell dimensions $a = 11.882$ (7), $b = 22.487$ (20), $c = 10.707$ (7) Å; $\alpha = 107.0$ (1), $\beta = 78.93$ (5), $\gamma = 107.16$ (7)°; space group, $P1$, $Z = 2$; $d_{calcd} = 1.54$ g cm^{-3}, $d_{obsd} = 1.55$ g cm^{-3}; crystal dimensions, 0.1 × 0.2 × 0.04 mm; $2\theta_{max}$, 40° (Mo radiation); reflections used, $F^2 > 3\sigma(F^2)$, 3236; unique reflections, 4505; parameters, 330.

(12) D. Coucouvanis, D. Swenson, P. Stremple, and N. C. Baenziger, *J. Am. Chem. Soc.*, **101,** 3392 (1979).

(13) P. E. Jones and L. Katz, *Acta Crystallogr., Sect. B,* **25,** 745 (1969).

(14) H. Köpf, B. Block, and M. Schmidt, *Chem. Ber.*, **101,** 272 (1968).

(15) The DMF molecules of solvation are found with half occupancy at the center of symmetry, ½ ½ 0.

(16) J. T. Huneke and J. H. Enemark, *Inorg. Chem.*, **17,** 3698 (1978).

(17) D. Coucouvanis, D. Swenson, N. C. Baenziger, D. G. Holah, A. Kostikas, A. Simopoulos, and V. Petrouleas, *J. Am. Chem. Soc.*, **98,** 5721 (1976).

(18) J. J. Mayerle, S. E. Denmark, B. V. De Pamphilis, J. A. Ibers, and R. H. Holm, *J. Am. Chem. Soc.*, **97,** 1032 (1975).

(19) D. Coucouvanis, N. C. Baenziger, E. D. Simhon, P. Stremple, D. Swenson, A. Simopoulos, A. Kostikas, V. Petrouleas, and V. Papaefthymiou, *J. Am. Chem. Soc.*, following paper in this issue.

(20) Very recently we have obtained the crystalline $(Ph_4P)_2[(PhS)_2CoS_2MS_2]$ complexes (M = Mo, W). These complexes are X-ray isomorphous to the analogous iron complexes and show electronic spectra typical of tetrahedrally coordinated cobalt(II).

(21) W. G. Zumft, *Eur. J. Biochem.*, **91,** 354 (1978).

(22) These interactions do not survive the chromatographic procedure which results in the isolation of MoS_4^{2-}

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Synthesis and Structural Characterization of the $(Ph_4P)_2[Cl_2FeS_2MS_2FeCl_2]$ Complexes (M = Mo, W). First Example of a Doubly Bridging MoS_4 Unit and Its Possible Relevance as a Structural Feature in the Nitrogenase Active Site

Sir:

In a preceding communication[1] we reviewed the structural information available for the Mo site in nitrogenases. This information, obtained on the basis of Mo X-ray absorption fine structure (EXAFS) analyses, has led to the suggestion that a valid structural model for the Mo site of nitrogenase must involve two major features: a set of three or four Mo bound sulfur atoms at ~2.36 ± 0.02 Å and a set of two (or three?) iron atoms at a distance of 2.72 ± 0.03 Å from the Mo. Of the two distinct models, proposed for the nitrogenase Mo site[2] (Figure 1), A exists as a fragment in the recently synthesized and structurally characterized "double cubanes".[3] In this communication we report on the synthesis and structural characterization of a heteronuclear Fe–Mo–Fe linear trimer and the tungsten analogue. The former, at least partly, resembles B (Figure 1).

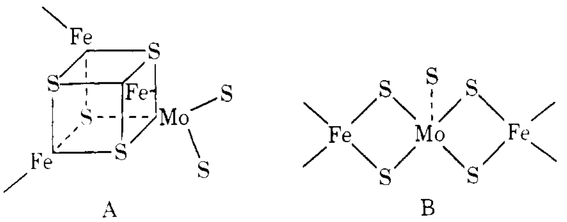

Figure 1.

The reaction of the $(Ph_4P)_2[(SPh)_2FeS_2MS_2]$ complexes[4] (M = Mo, W) with $FeCl_3 \cdot 6H_2O$ in 1:2 molar ratio in dimethylformamide (DMF) results in the oxidation of the $^-$SPh ligands to PhSSPh with the concomitant generation of Fe(II) ions. From the DMF solutions, upon the addition of ether, crystalline, X-ray isomorphous $(Ph_4P)_2[Cl_2FeS_2MS_2FeCl_2]$ complexes can be isolated [M = Mo, brown crystals 67% yield (I); M = W, orange-red crystals, 60% yield (II)]. Anal. Calcd for $Fe_2MoCl_4S_4P_2C_{48}H_{40}$: C, 49.85; H, 3.49; P, 5.36; S, 11.09; Cl, 12.26; Fe, 9.66. Found: C, 49.69; H, 3.42; P, 5.36; S, 10.94; Cl, 11.60; Fe, 9.30. Anal. Calcd for $Fe_2WCl_4S_4P_2C_{48}H_{40}$: C, 46.34; H, 3.24; S, 10.30; W, 14.77; Cl, 11.39. Found: C, 46.23; H, 3.32; S, 10.35; W, 14.45; Cl, 11.57.

The ^{57}F Mössbauer spectrum of I at 4.2 K shows a single doublet with a quadrupole splitting (QS) of 1.99 (1) mm/s and an isomer shift (IS) of 0.58 (1) mm/s (relative to Fe metal at 298 K). These values, and particularly the isomer shift, are not very similar to those obtained[1] for the $[(SPh)_2FeS_2MS_2]^{2-}$ complexes (M = Mo, W). The IS in I, however, has a value close to that reported for the $Fe(SC_6H_5)_4^{2-}$ complex[5] (0.66 mm/s) and for the FeS_4 sites in reduced rubredoxins[6] (0.65 mm/s). These observations suggest that the two iron atoms in I are in the +2 formal oxidation state. The magnetic moment for I ($\mu_{eff}^{corr} = 6.635$ (2) μ_B at 300 K) is lower than that expected for two, noninteracting, high-spin ($S = 2$) Fe(II) ions in I. A temperature-dependence study of the magnetic susceptibility, however, shows typical antiferromagnetic behavior. Similar magnetic properties are observed with II ($\mu_{eff}^{corr} = 6.03$ (2) μ_B).

Crystal and refinement data for the structure of I are shown in Table I. Intensity data were obtained on a Picker FACS I automatic diffractometer using a step-scan technique, employing graphite monochromatized Mo Kα radiation ($\lambda = 0.7107$ Å, $2\theta_m = 12.2°$). The data were corrected for Lorentz and polarization effects and for absorption. The structure was solved by conventional Patterson and Fourier techniques and refined by full-matrix least-squares calculations. All atoms in the anion and the two phosphorus atoms were refined with anisotropic temperature factors. The carbon atoms in the cations were refined with isotropic temperature factors. The hydrogen atoms were included in the structure factor calculation at their calculated positions (C–H = 0.95 Å) but were not refined. Structural details for the complex anion are shown in Table II.

A nearly linear, Fe–Mo–Fe, array is found in the structure of the anion (Figure 2) in which the MoS_4^{2-} unit bridges two terminal $FeCl_2$ moieties. The MoS_4 and $FeCl_2S_2$ fragments show distorted tetrahedral geometry around the metal atoms. The mean value[7] for the two independent Fe–Mo distances [2.775 (6) Å] is slightly greater than the Fe–Mo distances in $[FeMoS_9]^{2-}$ [1] (III) and $[(SC_6H_5)_2FeS_2MoS_2]^{2-}$ [4] (IV), 2.731

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Table I. Crystal and Refinement Data for $[(C_6H_5)_4P]_2[Fe_2MoS_4Cl_4]$

cell dimensions, Å, deg	a = 10.197 (2) b = 13.054 (2) c = 20.164 (3) α = 100.46 (2) β = 100.61 (1) γ = 100.92 (1)
V, Å^3	2524.4
space group	$P\bar{1}$, Z = 2
d_{calcd}, g/cm^3	1.52
$d_{\text{obsd}}{}^a$	1.50 (2)
crystal dimensions, mm	0.055 × 0.08 × 0.017
μ, cm^{-1}	12.74
$2\theta_{\max}$, deg	50
unique reflections	8965
reflections used, $F^2 > 3\sigma(F^2)$	5120
parameters	310
$R_1{}^b$	0.065
$R_2{}^c$	0.081

[a] By flotation in a CCl_4-pentane mixture. [b] $R_1 = \Sigma|\Delta F|/\Sigma|F_o|$. [c] $R_2 = [\Sigma_w(\Delta F)^2/\Sigma_w|F_o|^2]^{1/2}$.

Table II. Selected Structural Parameters in the $[Fe_2MoS_4Cl_4]^{2-}$ Anion (I)

I	bond lengths, Å^a	av^b values
Fe_1-Fe_2	5.551 (2)	
Mo-Fe_1	2.770 (2)	2.775 (6)
Mo-Fe_2	2.781 (2)	
Mo-S_1	2.203 (3)	2.204 (5)
Mo-S_2	2.198 (3)	
Mo-S_3	2.205 (3)	
Mo-S_4	2.211 (3)	
Fe_1-S_1	2.291 (3)	2.295 (5)
Fe_1-S_2	2.297 (3)	
Fe_2-S_3	2.290 (3)	
Fe_2-S_4	2.302 (3)	
Fe_1-Cl_1	2.241 (3)	2.225 (10)
Fe_1-Cl_2	2.216 (3)	
Fe_2-Cl_3	2.218 (3)	
Fe_2-Cl_4	2.224 (4)	

	bond angles, deg^b	range
Fe-Mo-Fe	179.38 (7)	
S-Mo-S	109.5 (1.9)	106.6 (2)-111.5 (2)
S-Fe-S	100.9 (2)	100.91 (15)-110.88 (15)
S-Fe-Cl	111.4 (2.9)	107.4 (2)-116.1 (2)
Cl-Fe-Cl	110.2 (9)	109.4 (2)-111.1 (2)
Mo-S-Fe	76.05 (1)	76.05 (9)-76.06 (9)

[a] The numbering scheme follows the one shown in Figure 2. [b] Average value, $\Sigma = [\Sigma_{i=1}^{N}(\chi_i - \bar{\chi})^2/(N-1)]^{1/2}$ where χ_i is the size of the angle and $\bar{\chi}$ is the mean value for the N equivalent bond angles.

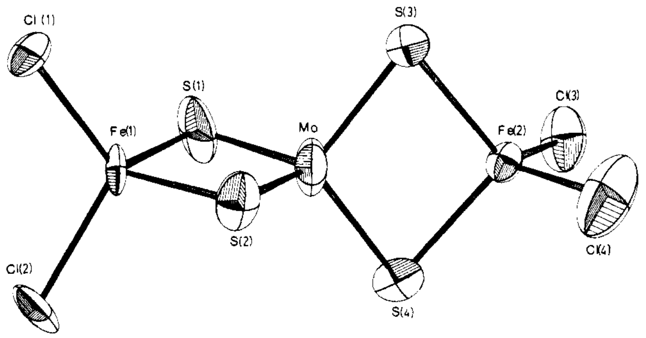

Figure 2. Structure and labeling of the $[(FeCl_2)_2MoS_4]^{2-}$ anion. Thermal ellipsoids are drawn by ORTEP (C. K. Johnson, ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965) represent the 50% probability surfaces.

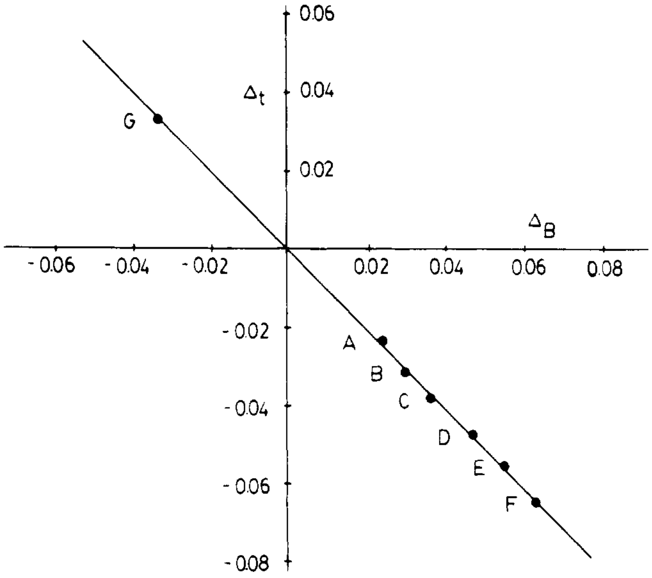

Figure 3. Bridging (b) vs. terminal (t) Fe-L bonding in μ-sulfido Fe complexes: $\Delta_t = [(\overline{\text{Fe-X}}) - (\overline{\text{Fe-X}_t})$ Å; $\Delta_B = (\overline{\text{Fe-X}}) - (\overline{\text{Fe-X}_b})$ Å; A = $[Fe_2S_2Cl_4]^{2-}$, B = $[(PhS)_2FeS_2MoS_2]^{2-}$, C = $[(S_5)FeS_2MoS_2]^{2-}$, D = $[Fe_2S_2(S_2\text{-}o\text{-xyl})_2]^{2-}$, E = $[Fe_2S_2(S\text{-}p\text{-tol})_4]^{2-}$, F = $[Fe_2S_{12}]^{2-}$, G = $[(Cl_2Fe)S_2MoS_2FeCl_2]^{2-}$

(3) and 2.750 (4) Å, respectively. The $\overline{\text{Mo-S}}$ bond length in I, at 2.204 (5) Å, is shorter than the $\overline{\text{Mo-S}}$ "bridge" bonds of 2.253 (9) and 2.246 (6) Å found in the structures of III and IV, respectively. The mean value for the Fe-S bond lengths in I [2.295 (5) Å], is longer than corresponding values of 2.244 (8) Å in III and 2.243 (7) Å in IV. The Fe-Cl bond length [$\overline{\text{Fe-Cl}}$ = 2.225 (10) Å] in I is shorter than values reported for the tetrahedral $FeCl_4{}^{2-}$ anion, 2.302 (18)[8] and 2.292 (2) Å,[9] but still longer than values reported for the $FeCl_4{}^{-}$ anion, 2.185 (2)[10] and 2.182 (1) Å.[11] It is however, similar (within 3σ) to the mean Fe-Cl bond found in the dimeric $[Fe_2S_2Cl_4]^{2-}$ anion (in which the formal oxidation state of iron is +3) at 2.251 (7) Å.[12] The rather short Fe-Cl bonds in I seem to represent another example of an anomaly which has been noted[12] in the structures of the ferredoxin active site analogues. Thus, the terminal Fe-X bond lengths in the $[Fe_2S_2X_4]^{2-}$ dimers [which formally contain Fe(III)] are *longer* than the terminal Fe-X bond lengths in the $[Fe_4S_4X_4]^{2-}$ tetramers (in which the *formal* oxidation state of the Fe atoms is +2.5). A useful ordering of the homo- or heterometallic S-bridged dimers, and of I, is obtained when the $\overline{\text{Fe-X}}$ terminal and bridge distances are compared with the mean value of the Fe-X bonds in each of the FeX_4 units (X = S or Cl). The differences (Δ_B) of the $\overline{\text{Fe-X}}$ *bridge* distances from $\overline{\text{Fe-X}}$ were found positive for all dimers. By contrast, Δ_B in I is negative. A plot of Δ_B vs. the difference (Δ_T) of the $\overline{\text{Fe-X}}$ *terminal* distances from the mean was constructed for eight molecules: I, III, IV, $[FeWS_9]^{2-}$,[1] $[Fe_2S_{12}]^{2-}$,[13] $[Fe_2S_2Cl_4]^{2-}$,[12] $[Fe_2S_2(S_2\text{-}o\text{-xyl})_2]^{2-}$,[14] and $[Fe_2S_2(S\text{-}p\text{-tol})_4]^{2-}$.[14] The points were well separated on a straight line with the $[Fe_2S_2X_4]^{2-}$ dimers showing large positive values for Δ_B, the $[FeMoS_2X_4]^{2-}$ dimers showing smaller but still positive values for Δ_B and the Fe_2Mo trimer (I), showing a *negative* value for Δ_B. By construction of this plot (Figure 3), we suggest that as the M-X bonds in the bridge lengthen the terminal bond lengths become shorter in an apparent shift of the bonding strength in the FeX_4 units.[15] Qualitatively, the same ordering for the eight molecules is obtained, when the ^{57}Fe isomer shifts are considered.

Evidence that the $MoS_4{}^{2-}$ as a bridging unit in I is a weaker

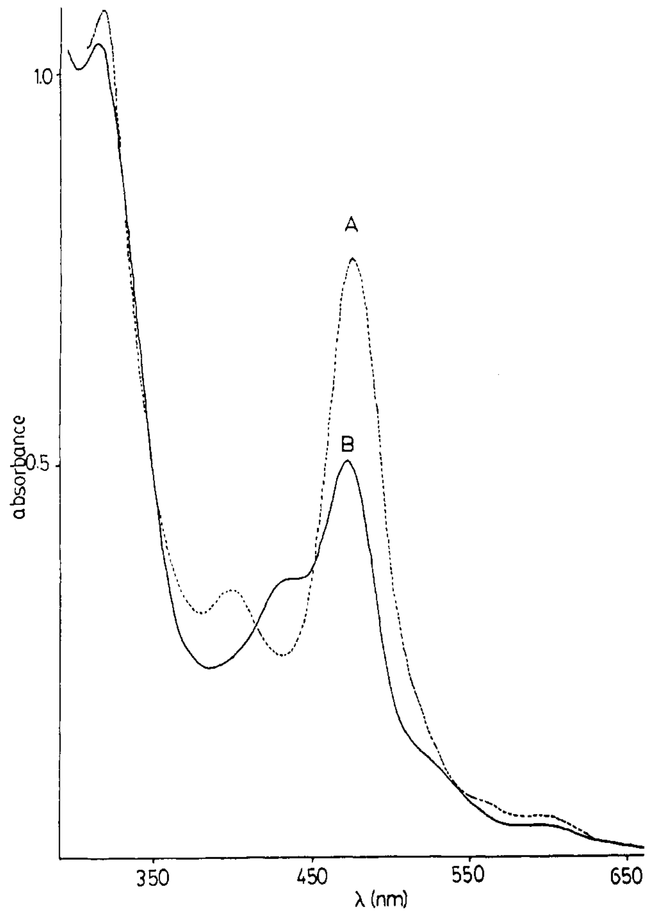

Figure 4. The visible spectra of $(Ph_4P)_2[(FeCl_2)_2MoS_4]^{2-}$ in the same concentration (9×10^{-4} M) in (A) CH_2Cl_2 and (B) DMF.

ligand than as a terminal bidentate chelate in III or IV is found in the solution behavior of I.

The visible spectrum of I varies with the polarity of the solvent, and spectra obtained in DMF [600 nm (sh), 522 (sh), 472 (ϵ 5849), 432 (4070), 314 (12 250)] are different from those obtained in CH_2Cl_2 [600 nm (ϵ 580), 566 (sh), 475 (9892), 398 (4369), 319 (13 870)] (Figure 4). Following the addition of 1 equiv of MoS_4^{2-}, the spectrum of I in CH_2Cl_2 changes and becomes virtually identical with that obtained in DMF. Alternatively, the visible spectrum of I in DMF and in the presence of an excess of anhydrous $FeCl_2$ is very similar to that obtained for I alone in CH_2Cl_2.

These observations suggest that, in polar solvents, I dissociates according to the equilibrium $[Cl_2FeS_2MoS_2FeCl_2]^{2-} \rightleftarrows [Cl_2FeS_2MoS_2]^{2-} + FeCl_2$. The same behavior is found with the tungsten analogue (II) for which the spectra are as follows: in CH_2Cl_2, 502 nm (ϵ 930), 418 (7100), 360 (5400), 294 (14 200); in DMF, 524 nm (ϵ 530), 417 (6300), 373 (7110). The $(Ph_4P)_2[Cl_2FeS_2MS_2]$ complexes (M = Mo, brown-red crystals; M = W, red orange crystals, V and VI, respectively) form by the reactions I or II with equimolar amounts of $(Ph_4P)_2MoS_4$ or $(Ph_4P)_2WS_4$ in DMF. They are isolated in crystalline form, and in excellent yields, upon the addition of ether to the DMF solutions.[16]

In conclusion, the structure of I demonstrates for the first time the ability of MoS_4^{2-} to serve as a doubly bridging ligand.[17] Clearly, the Mo-S bond lengths in I are shorter than those reported for the Mo site in nitrogenase which probably contains Mo in a lower formal oxidation state. In its entirety, I cannot be considered as a model; however, it contains gross structural features in common with one of the minimal models (Figure 1, B) proposed for the Mo site in nitrogenase on the basis of the EXAFS studies. At present we are investigating the coordination chemistry of the bridging MoS_4^{2-} ligand.

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Supplementary Material Available: Structure factors and positional coordinates for $(Ph_4P)_2[Cl_2FeS_2MoS_2FeCl_2]$ (27 pages). Ordering information is given on any current masthead page.

References and Notes

(1) D. Coucouvanis, N. C. Baenziger, E. D. Simhon, P. Stremple, D. Swenson, A. Kostikas, A. Simopoulos, V. Petrouleas, and V. Papaefthymiou, *J. Am. Chem. Soc.*, preceding paper in this issue.
(2) S. P. Cramer, K. O. Hodgson, W. O. Gillum, and L. E. Mortenson, *J. Am. Chem. Soc.*, **100**, 3398 (1978).
(3) T. E. Wolff, J. M. Berg, K. O. Hodgson, R. B. Frankel, and R. H. Holm, *J. Am. Chem. Soc.*, **101**, 4140 (1979).
(4) D. Coucouvanis, E. D. Simhon, D. Swenson, and N. C. Baenziger, *J. Chem. Soc., Chem. Commun.*, 361 (1979).
(5) A. Kostikas, V. Petrouleas, A. Simopoulos, D. Coucouvanis, and D. G. Holah, *Chem. Phys. Lett.*, **38**, 582 (1976).
(6) P. G. Debrunner, E. Münck, L. Que, and C. E. Schulz in "Iron–Sulfur Proteins", Vol. III, W. Lovenberg, Ed., Academic Press, New York, 1977, Chapter 10 and references therein.
(7) For the reported mean values, the larger of the standard deviations from the mean $(\Sigma_{i=1}^{N}[(\chi_i - \bar{\chi})^2/(N-1)]^{1/2})$ or the standard deviations (as derived from the inverse matrix) are reported.
(8) Trinh-Toan and L. F. Dahl, *J. Am. Chem. Soc.*, **93**, 2654 (1971).
(9) J. W. Lauher and J. A. Ibers, *Inorg. Chem.*, **14**, 348 (1975).
(10) T. J. Kistenmacher and G. D. Stucky, *Inorg. Chem.*, **7**, 2150 (1968).
(11) F. A. Cotton and C. A. Murrillo, *Inorg. Chem.*, **14**, 2467 (1975).
(12) M. A. Bobrik, K. O. Hodgson and R. H. Holm, *Inorg. Chem.*, **16**, 1851 (1977).
(13) D. Coucouvanis, D. Swenson, P. Stremple, and N. C. Baenziger, *J. Am. Chem. Soc.*, **101**, 3392 (1979).
(14) J. J. Mayerle, S. E. Denmark, B. V. DePamphilis, J. A. Ibers, and R. H. Holm, *J. Am. Chem. Soc.*, **97**, 1032 (1975).
(15) The ability of the terminal ligands to undergo this change may well affect the ease by which the Fe–L bridge can be lengthened. Such lengthening is expected to occur on reduction of the Fe(III)-containing dimers, $[Fe_2S_2L_4]^{2-}$.
(16) The $[Cl_2FeS_2MoS_2]^{2-}$ complex anion has been synthesized via an alternate route and the crystal and molecular structures of the Et_4N^+ salt of this complex have been determined: B. Averill and B. Teo, private communication.
(17) A triply bridging MoS_4^{2-} unit has been observed recently in the structure of the very interesting $[Mo_2S_8Ag_4](PPh_3)_4$ molecule: A. Müller, H. Bögge, E. Königer-Ahlborn, and W. Hellman, *Inorg. Chem.*, **18**, 2301 (1979).

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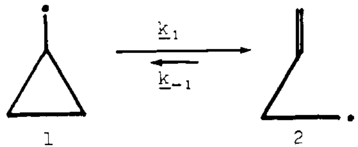
Allylcarbinyl-Cyclopropylcarbinyl Rearrangement[1]

Sir:

The *ring opening* of cyclopropylcarbinyl (**1**) to the 3-butenyl radical (**2**) has been extensively investigated in recent years, as have a number of related reactions.[2] This reaction is extremely rapid but its rate has, nevertheless, been measured by kinetic EPR spectroscopy.[3] The Arrhenius equation for ring opening was found to be[3,4]



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