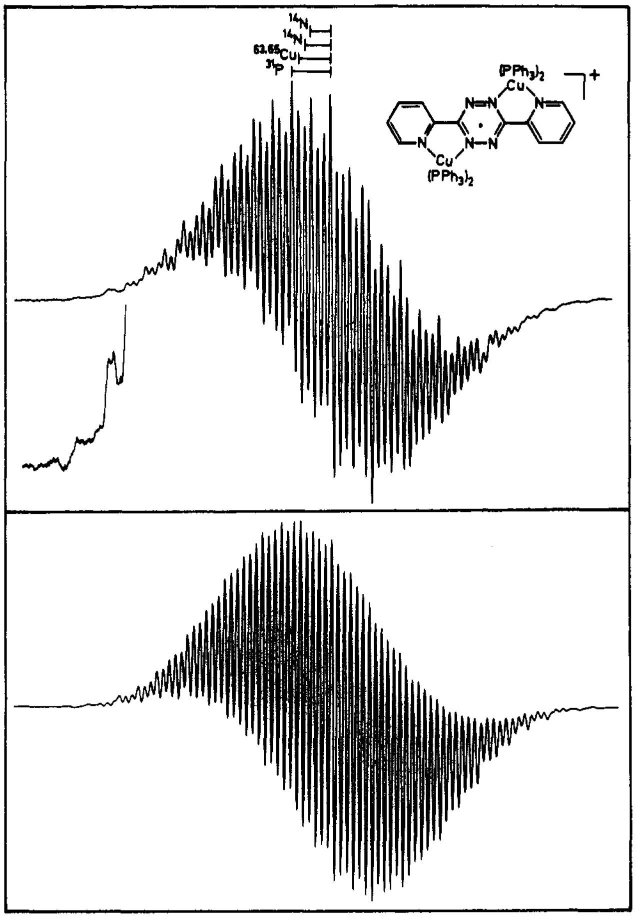
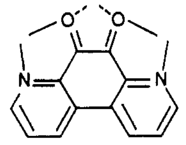


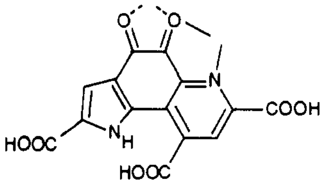
Figure 1. ESR spectrum of $[(\mu\text{-bptz})\{Cu(PPh_3)_2\}_2]^{\bullet+}$ at 300 K in dichloromethane solution with amplified low-field wing section (top) and computer simulation (bottom, 875 theoretical lines). Intensity differences at the periphery are due to selective line broadening of components with $M_N \neq 0$.[4b,c]

larization,[4c] the large ^{31}P coupling in the PPh_3 complex results from good hyperconjugative[8] overlap between Cu/P σ bonds and the π system; a smaller PCuP angle of only ~90° in the diphos complex[10] diminishes that kind of hyperconjugative interaction.[8]

In the reaction between excess[5] $Cu(PPh_3)_4{}^+BF_4{}^-$ and 4,7-phenanthroline-5,6-dione (phdo), the binuclear radical complex is the only stable product and can thus be conveniently isolated and identified (Table I).[11]



phdo



methoxatin

The phdo ligand is of particular interest because it may serve as a model[12a] for the dehydrogenase[12b] and copper-containing amine oxidase[12c] cofactor methoxatin, a potentially new vitamin,[12c] and because it can act as O,O′-chelate mononucleating ligand[12d] or as double N,O-chelating system,[12d,13,14] as in the present situation. *o*-Quinones are known to form mononuclear O,O′-coordinated copper(I) semiquinone complexes,[15] which have, however, not been isolated; the biochemical formation and conversion of *o*-quinones/catecholes is frequently catalyzed by copper-containing enzymes.[1c] Facile formation and stability of the paramagnetic complexes presented here suggest that cationic copper(I) fragments are particularly suitable in stabilizing anion radical intermediates, either through the charge effect alone or via additional contributions from σ/π hyperconjugation.

Acknowledgment. This work has been supported by the Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie, Stiftung Volkswagenwerk, and Flughafen Frankfurt/Main AG. 4,7-Phenanthroline-5,6-dione was a gift of Ciba-Geigy AG.

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Received December 16, 1986

Synthesis and Structure of the "Linear" Tetranuclear Cluster $[(MoO_2S_2)_2Fe_2S_2]^{4-}$: Implications for Aqueous Mo-Fe-S Chemistry

Sir:

Recent interest in and explorations of the chemistry of Mo, Fe, and S have been stimulated by inter alia the MoFe cofactor of nitrogenase.[1] Although the structure of this cofactor remains unsolved, the aforementioned explorations have led to several novel polynuclear Mo–Fe–S clusters of the so-called "linear" and "cubane" types.[2,3] During our explorations of aqueous and enzyme-mediated assembly of Fe–S and Mo–Fe–S clusters,[4] we noted the development of a novel absorption spectrum in aqueous mixtures containing salts of Fe(II) and $MoO_{4-x}S_x{}^{2-}$ (x = 2–4) at basic pHs. Subsequent isolation and characterization of this absorbing species showed it to be $[(MoO_2S_2)_2Fe_2S_2]^{4-}$. This cluster represents (i) the first example of a "linear" tetranuclear Mo–Fe–S

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(1) (a) Müller, A. *Polyhedron* **1986**, *5*, 323–340. (b) Newton, W. E.; Schultz, F. A.; Gheller, S. F.; Lough, S.; McDonald, J. W.; Conradson, S. D.; Hedman, B.; Hodgson, K. O. *Ibid.* **1986**, *5*, 567–572.

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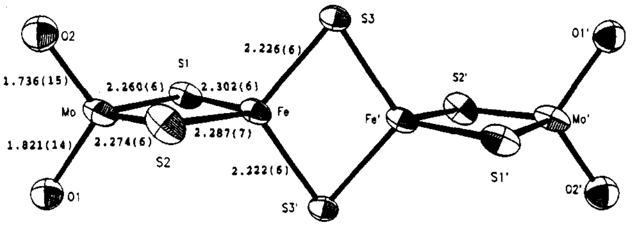

Figure 1. Perspective view of the anion in $(Ph_4P)_4[(MoO_2S_2)_2Fe_2S_2]\cdot6H_2O$. The distances Mo–Fe and Fe–Fe′ are 2.807 (4) and 2.703 (4) Å, respectively.

cluster, (ii) the first discrete, well-characterized species isolated from aqueous reaction of Fe^{2+} and MoS_4^{2-}, (iii) the first direct evidence that Fe^{2+} accelerates the hydrolyses of $MoO_{4-x}S_x^{2-}$ (x = 2–4), and (iv) trapping of the products of these hydrolyses.

The structure of $[(MoO_2S_2)_2Fe_2S_2]^{4-}$ is shown in Figure 1. $(Ph_4As)_4[(MoO_2S_2)_2Fe_2S_2]\cdot6H_2O$ can be prepared under Ar in 40% yield by adding 0.16 g (1.3 mmol) of $FeCl_2$ to 0.30 g (0.65 mmol) of Cs_2MoOS_3[9] in 80 mL of 0.2 M phosphate at pH 12. After 30 min of stirring at room temperature, the mixture is filtered anaerobically through Celite and 0.87 g (2.0 mmol) of $Ph_4AsCl\cdot H_2O$ is added to the filtrate. Overnight incubation at 4 °C results in formation of purple crystals, which are washed anaerobically with ~10 mL of H_2O and ~10 mL of THF. *Anal.* Calcd for $C_{96}H_{92}As_4Fe_2Mo_2O_{10}S_6$: C, 52.64; H, 4.21; Fe, 5.07; S, 8.74. Found: C, 52.64; H, 4.09; Fe 5.14; S, 8.20.[10] $(Ph_4P)_4[(MoO_2S_2)_2Fe_2S_2]\cdot6H_2O$ can be obtained by the analogous procedure.

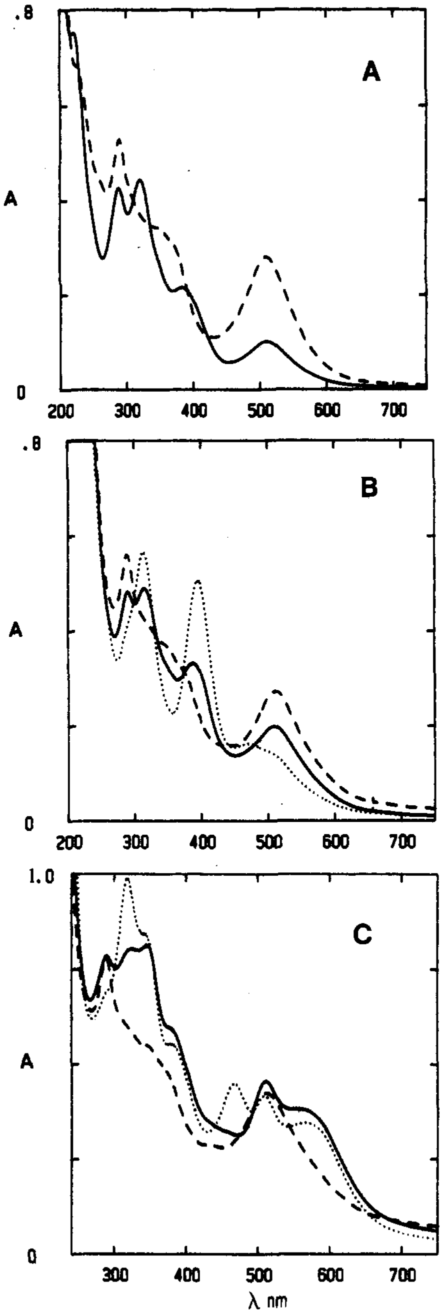

Figure 3. Absorption spectra of 15.6 mM $FeCl_2$ + 7.8 mM $(NH_4)_2MoO_2S_2$ (A), Cs_2MoOS_3 (B), or NH_4MoS_4 (C) in anaerobic 0.2 M sodium phosphate pH 12. Cell pathlength = 0.01 cm. Spectra recorded after reaction at room temperature for 1.5 (—) and 7 (- -) min in part A, 2 (···), 7 (—), and 23 (- -) min in part B, and 6 (···), 16 (—), and 62 (- -) min in part C.

The structures of both Ph_4P^+ and Ph_4As^+ salts were solved. Since differences between the two structures are trivial, data are reported only for the Ph_4P^+ salt (Figure 1).[5] The symmetry of the anion approaches D_{2h} but is reduced to C_i most prominently by inequivalent Mo–O distances and to a lesser extent by a Mo–Fe–Fe′ angle of 176°. All metal atoms have an approximately tetrahedral coordination geometry consisting of bridging sulfur and/or terminal oxygen atoms. The distances (shown in Figure 1) and angles (supplementary material) of the anion are within ranges known for clusters containing either Fe_2S_2 or MoS_2Fe cores and approximately tetrahedral coordination geometry.[2,11,12] The

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(5) Crystal data: $4PPh_4^+[FeMoS_3O_2]_2^{4-}\cdot6H_2O$, monoclinic $P2_1/a$, $Z = 2$, $\rho_{calcd} = 1.46$ g/cm³, $a = 15.808$ (6) Å, $b = 19.996$ (8) Å, $c = 14.796$ (5) Å, $\beta = 101.75$ (9)°, $V = 4579.0$ (15) Å³, $\mu = 8.27$ cm⁻¹ for Mo $K\alpha$ ($\lambda = 0.79066$ Å, graphite monochromated). All the data (7241 reflections) in hkl and $h\bar{k}l$ octants within $2\theta \leq 45°$ (a weakly diffracting platelike crystal) were collected on a DATEX diffractometer at ambient temperature by using an ω-step scan mode (0.5 s/0.01° for a 1.2° scan range). The general procedures for data collection and reduction have been published elsewhere.[6,7] After an empirical absorption correction and data reduction, 2188 reflections were observed ($I \geq 2\sigma_I$) and averaged into 1816 reflections ($R_I = 0.04$). In the final refinement, 1607 reflections with $F \geq 6\sigma_F$ were used. A unique determination of the space group was not possible due to ambiguities in $0k0$ and $h0l$ reflections related to weak diffracting characteristics and possible pseudosymmetry effects. Patterson superposition analysis (ALCAMPS) using a Mo–P interaction as a shift vector readily gave rise to the structural solution. This result strongly suggested $P2_1/a$ as the correct space group, which was confirmed later on via successful refinements. From the positions of the metal and sulfur atoms thus obtained, subsequent structure factor and electron density map calculations revealed the remaining atoms of the compound. Three strong residual densities outside the molecular boundaries were assigned as oxygen atoms of water of crystallization molecules, as based on the peak heights and occupancy factors refinements. Hydrogen atoms were included and fixed at calculated positions with C–H distance set to 1.0 Å. The least-squares refinement was carried out by using a blocked full-matrix method, minimizing $\sum w(|F_o| - |F_c|)^2$. The final residual indices were $R = \sum ||F_o - F_c|| / \sum |F_o| = 7.00\%$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 8.01\%$.

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dimensions of the analogous cores in isostructural $[(WS_4)_2Fe_2S_2]^{4-}$ are very similar to those in $[(MoO_2S_2)_2Fe_2S_2]^{4-}$.[13] The average of the terminal Mo–O distances shown in Figure 1 (1.78 Å) is the same as the Mo–O distance in Cs_2MoOS_3.[14] The unit cell of $(Ph_4P)_4[(MoO_2S_2)_2Fe_2S_2]\cdot 6H_2O$ contains chains of anions (cf. Figure 2 (supplementary material)). These chains are linked by water molecules which are hydrogen-bonded to terminal oxygen atoms, O1 and O2 of the anion. The longer Mo–O1 distance could be the result of an extra water molecule that is within hydrogen-bonding distance of O1. This pattern of hydrogen bonding suggests that solvation of the terminal oxygen atoms may help stabilize $[(MoO_2S_2)_2Fe_2S_2]^{4-}$ in water.

The electronic absorption spectrum of $(Ph_4As)_4[(MoO_2S_2)_2Fe_2S_2]\cdot 6H_2O$ in acetonitrile shows three principal bands [λ_{max}, nm (ϵ, $mM^{-1}\ cm^{-1}$): 290 (23.1), 372 (14.6), 526 (12.2). Absorption and resonance Raman spectra of the analogous "linear" cluster $[(WS_4)_2Fe_2S_2]^{4-}$ suggest that the lowest energy absorption band involves transitions within the Fe_2S_6 portion of the anion.[1a,15] The ^{57}Fe Mössbauer spectrum of a frozen solution of $(Ph_4As)_4[(MoO_2S_2)_2Fe_2S_2]\cdot 6H_2O$ in acetonitrile shows a single quadrupole doublet at both 200 and 4.2 K. Parameters of the doublet at 4.2 K are $\delta = 0.42$ mm/s and $\Delta E_Q = 1.04$ mm/s vs. metallic iron at 300 K. No significant changes in these parameters occur upon application of a 2.2-kG magnetic field. These data are consistent with the expected antiferromagnetic coupling between iron atoms.[2c,11,12] Using the empirical relationship between Mössbauer isomer shift and mean oxidation state, s, developed by Christou et al.[16] for clusters containing tetrahedral FeS_4 sites gives $s = 2.4$ for each iron atom in $[(MoO_2S_2)_2Fe_2S_2]^{4-}$. Thus, while the anion formally contains Fe(II) and Mo(VI), this calculation indicates considerable delocalization of electron density from Fe onto Mo, and a mean oxidation state of Fe approximately midway between Fe(II) and Fe(III). $[(MoO_2S_2)_2Fe_2S_2]^{4-}$ appears to be the first example of a cluster containing an $[Fe_2S_2]^{1+}$ core without trapped valence Fe(II) and Fe(III).

The spectral time courses for reactions of Fe^{2+} with $MoO_{4-x}S_x^{2-}$ (x = 2–4) at pH 12 shown in Figure 3 demonstrate that the same product, namely $[(MoO_2S_2)_2Fe_2S_2]^{4-}$ (indicated by the dashed spectra with λ_{max} at 510, ~350 sh, and 290 nm), is obtained in each case.[17] However, the rate of formation of this product decreases monotonically with increasing numbers of sulfido vs. oxo ligands in the starting $MoO_{4-x}S_x^{2-}$. This trend in rates is the same as that observed for hydrolyses of $MoO_{4-x}S_x^{2-}$ at basic pHs.[18] In the absence of Fe^{2+} the half-time for hydrolysis of MoS_4^{2-} under these conditions is ~170 h at 25 °C. Thus, Figure 3C shows that Fe^{2+} accelerates the hydrolysis of MoS_4^{2-} by at least a factor of 100. Similar acceleration is observed for $MoOS_3^{2-}$ in Figure 3B. The even more rapid reaction of $MoO_2S_2^{2-}$ shown in Figure 3A together with the trend in rates discussed above strongly suggests that some complete hydrolysis to MoO_4^{2-} occurs in all cases during formation of $[(MoO_2S_2)_2Fe_2S_2]^{4-}$.

Our results imply that the MoFe cofactor of nitrogenase is *not* constructed by a combination of "free" Fe^{2+} and performed MoS_4^{2-} in an aqueous environment, since this combination would likely result ultimately in MoO_4^{2-} and FeS. This statement applies only in the absence of thiol. In the presence of 2-mercaptoethanol at pH 9, the combination of MoS_4^{2-} and Fe^{2+} in water results in assembly of the "double-cubane" cluster $[Fe_6S_8Mo_2(SCH_2CH_2OH)_9]^{3-}$,[19] which we have isolated in 60% yield as its n-Bu_4N^+ salt.[20]

Acknowledgment. We thank J. T. Sage and P. G. Debrunner of the Department of Physics, University of Illinois, for obtaining the Mössbauer spectra. This research was supported by the National Science Foundation (D.M.K., Grant DMB-8216447) and by the Office of Basic Energy Sciences Division of the U.S. Department of Energy. Ames Laboratory is operated for the USDOE by Iowa State University under Contact No. W-7405-ENG-82.

Supplementary Material Available: Figure 2 (which contains a view of the unit cell) and listings of atomic positional and thermal parameters and bond and dihedral angles for the anion (9 pages); a listing of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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(17) As determined spectrophotometrically, the same product can be obtained at pH 9 by using borate but not tris(hydroxymethyl)aminomethane buffers. The dashed spectra of Figure 3 gradually decay over the course of several hours, yielding a clear solution plus an insoluble black solid that liberates H_2S upon acidification. Lower pHs of reaction result in increased formation of this solid.

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Received October 28, 1986

Synthesis, Molecular Structure, and Physicochemical Properties of $M_2(form)_4$ (M = Ni, Pd; form = *N,N'*-Di-*p*-tolylformamidinato). Attempts To Generate a Palladium(III) Dimer

Sir:

Many dinuclear compounds of platinum(III) containing four bidentate bridging ligands and a metal–metal interaction through an electron-rich single bond of electronic configuration $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$ are known.[1,2] A few dinuclear compounds with the Pt atoms in the 2.5 average oxidation state and a formal bond order of 0.5 between the two metals have also been prepared.[3,4] On the other hand, analogous compounds for nickel and palladium have never been reported. Only one Ni_2^{5+} compound, $Ni_2(S_2CCH_3)_4I$, has been described.[5]

Since many dinuclear, quadruply bridged compounds of nickel(II) and palladium(II) are known, we thought that we might have a chance to generate oxidized species from these provided we could find the right combination of ligands and oxidizing material. We decided to test the *N,N'*-di-*p*-tolylformamidinato (form) ligand for the following reasons. First, the nitrogen donors are expected to increase the electronic charge on the metal atoms as compared, for example, to that obtained with carboxylato ligands, thereby decreasing the oxidation potential. Such a trend has been well established for compounds of the Rh_2^{4+} core.[6]

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