Synthesis and Characterization of Fe–Mo–S and Fe–W–S Complexes Containing the *o*-Xylyl-α,α'-dithiolatoiron Unit

G. DELBERT FREISEN, JOHN W. McDONALD* and WILLIAM E. NEWTON

Charles F. Kettering Research Laboratory, Yellow Springs, Ohio 45387, U.S.A.

Received March 26, 1982

Since the discovery that a Fe–Mo–S cluster unit comprises the molybdenum-containing prosthetic group of the nitrogenase enzymes, a large number of complexes of this type and their tungsten analogs have been chemically synthesized [1]. Using the tetrathiometallate ions (MoS_4^{2-}, WS_4^{2-}) as starting materials, two basic types [2] of clusters have been obtained, one type contains Fe_3MoS_4 cubane-type units while the other is composed of linear arrays of Fe and Mo atoms bridged by sulfide. The first species of the latter type to be prepared was $[Et_4N]_2[(PhS)_2FeS_2MoS_2]$ (*1*), which was initially reported and structurally characterized by Coucouvanis and coworkers [3], and then further described by Teo, Averill and coworkers [4]. This latter group reported [4] that attempts to reduce *1* to its trinegative form with sodium acenaphthalenide were unsuccessful, a result consistent with the cyclic voltammogram of *1* which contains only irreversible waves [4] If stable, species of the form $[X_2FeS_2MoS_2]^{3-}$ might be expected to contain formally Fe(II) (S = 2) and Mo(V) (S = ½) which could be antiferromagnetically coupled to yield an S = 3/2 spin system analogous to that of the molybdenum–iron protein of nitrogenase [5] and its cofactor (FeMoco) [6]. Because of our interest in producing complexes characterized by this magnetic property, we have now prepared a complex analogous to *1* but with the two thiophenolate ligands substituted by the bidentate thiolate, *o*-xylyl-α,α'-dithiolate $[C_6H_4(CH_2S)_2^{2-}$ = *o*-xyl-S_2]. This report describes the synthesis and characterization of this species (*2*) and its tungsten analog (*3*), shown schematically in Fig. 1. Their electrochemical behavior indicates that their one-electron reduction products may be relatively stable. While this work was in progress, we learned that Garner and coworkers [7] had also prepared and structurally characterized the $[(o\text{-xyl-}S_2)FeS_2MoS_2]^{2-}$ ion.

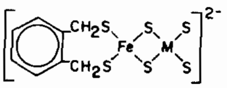

Fig. 1. Schematic representation of *2* (M = Mo) and *3* (M = W).

Reaction of $[Et_4N]_2[Fe(o\text{-xyl-}S_2)_2]$ [8] (0.54 g, 0.83 mmol) with $[Et_4N]_2[MoS_4]$ (0.40 g; 0.83 mmol) in CH_2Cl_2 (40 ml) for 1 hr at room temperature resulted in the crystallization of the product *2* which was isolated by filtration, washed with CH_2Cl_2, and dried *in vacuo*. The yield was 0.27 g, 46%. Elemental analytical data for *2* and its tungsten analog *3* indicate that the salts contain molecules of CH_2Cl_2 in their lattices. *Anal.* Calcd. for $[Et_4N]_2[(o\text{-xyl-}S_2)FeS_2MoS_2]\cdot ½CH_2Cl_2$(*2*): $C_{24.5}H_{49}N_2ClFeMoS_6$: C, 39.2; H, 6.52, N, 3.73. Found: C, 38.8; H, 6.55; N, 3.68. The complex $[Et_4N]_2[(o\text{-xyl-}S_2)FeS_2WS_2]\cdot ½CH_2Cl_2$ (*3*) was prepared analogously in 57% yield. *Anal.* Calcd for $C_{24.5}H_{49}N_2ClFeWS_6$: C, 35.1; H, 5.84; N, 3.34. Found: C, 34.9; H, 5.77; N, 3.22.

Infrared spectra of *2* and *3* are entirely consistent with their formulations. The spectrum of *2* contains strong bands at 508 and 492 cm^{-1} assigned to terminal Mo–S vibrations and a medium intensity band at 445 cm^{-1} due to the FeS_2Mo bridge. Analogous bands for *3* are found at 488 cm^{-1} (terminal) and 435 cm^{-1} (bridge). The observation of two terminal M–S bands for *2* and only one for its tungsten analog *3* is consistent with the spectra of the species $[Cl_2FeS_2MS_2]^{2-}$ (M = Mo, W) [9]. The electronic spectra of *2* and *3* contain the following bands: *2* – 595sh(1780), 540sh(3890), 508(5040), 465(5870), 407sh(5920), 367sh(8760), 335(14190); *3* – 530sh(1960), 478(4640), 425(6480), 370(7300). No assignment of these multiple-band envelopes has been attempted, but the spectra are useful as fingerprints for identifying these complexes.

The electrochemical behavior of *2* and *3* is particularly striking when compared with that of *1* (*vide supra*). Figure 2 contains cyclic voltammograms of the two complexes indicating that both *2* and *3* undergo *pseudo-reversible* reductions at the indicated negative potentials as opposed to *1* which undergoes only an *irreversible* reduction at –1.34 V [4]. Presumably, these reversible waves are due to the 2–/3– couples of *2* and *3* although quantitative controlled-potential electrolysis experiments have yet to be completed. While the reasons for this change in electrochemical behavior on substitution of a $(SCH_2)_2C_6H_4$ moiety for two SPh groups are at present not understood, the existence of reversible couples for these complexes suggested that the

---

*Author to whom correspondence should be addressed.

0020-1693/82/0000-0000/$02.75

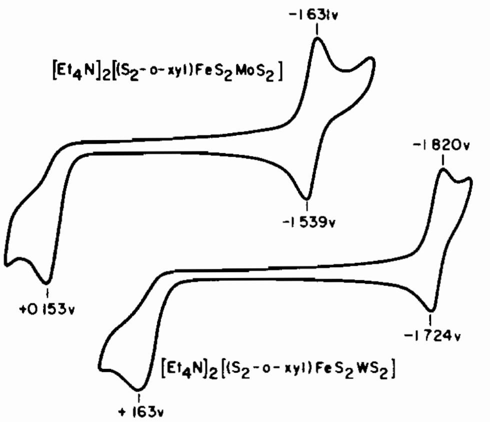

Fig. 2. Cyclic voltammograms of ~10^{-3} *M* solutions *2* and *3* in DMF containing 0.1 *M* $[Bu_4N]BF_4$ *vs* SCE. The scan rate was 0.48 V/sec.

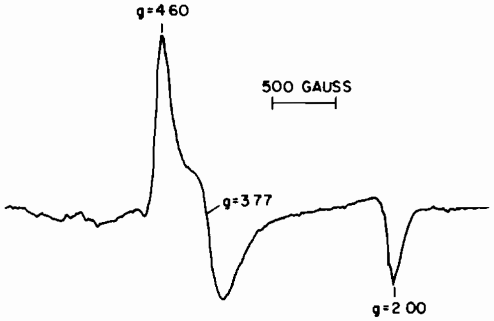

Fig. 3. EPR spectrum of a frozen 10^{-3} *M* solution of *2* in DMF containing 0.1 *M* $[Bu_4N]BF_4$ after exhaustive electrolysis of −1.75 V *vs* SCE. The temperature was ~12 K.

species $[(o\text{-xyl-}S_2)FeS_2MS_2]^{3-}$ had finite thermal stability. Therefore, a 10^{-3} *M* solution of *2* in DMF (containing 0.1 *M* $[Bu_4N]BF_4$ as supporting electrolyte) was electrolyzed at −1.75 V *vs.* SCE until the current was stable. Samples were immediately withdrawn for EPR spectral studies with the result shown in Fig. 3. The EPR spectrum of the electrolyzed solution run at ~12 °K is indicative of an S = 3/2 spin system. While we have thus far not isolated any complex, it would seem reasonable to attribute the signal to the $[(o\text{-xyl-}S_2)FeS_2MoS_2]^{3-}$ ion, since the antiferromagnetic coupling described above between Fe(II) and Mo(V) would be expected to produce a magnetic state characterized by three unpaired electrons. We cannot be certain the observed EPR signal represents complete conversion of *2* into its reduced EPR-active form until this signal is quantitated by double integration. The preparation of salts of $[(o\text{-xyl-}S_2)FeS_2MoS_2]^{3-}$ by chemical reduction of *2* are now in progress as are similar studies on the analogous tungsten system.

The S = 3/2 EPR spectrum from reduced solutions of *2* represents the third example of a signal of this type from Fe–Mo–S complexes. Previously, the ion $[Fe(MoS_4)_2]^{3-}$ [10, 11] was shown to be characterized by this magnetic state [10], which is likely to arise from antiferromagnetic coupling between two Mo(V) and one high spin Fe(III) atoms. More recently, the cubane-type ion $[MoFe_3S_4(SR)_3\text{-}(Pr_2cat)(DMSO)]^{2-}$ (Pr_2cat = 3,6-di-n-propyl-catecholate) has also been shown [12] to exhibit an S = 3/2 EPR signal. Although EXAFS data on complexes of the cubane-type have been found [13] to be more similar to those of the molybdenum–iron protein of nitrogenase and FeMoco than analogous data from the linear-type species [1], the details of the metal configuration at the molybdenum-containing prosthetic group of nitrogenase are still unknown. Thus, any Fe–Mo–S species which simulates its magnetic properties is important in efforts to elucidate the nature of this enzymic site.

Acknowledgement

This research was supported by a grant from the USDA/SEA Competitive Research Grants Office (59-2394-1-1-675-0). This manuscript constitutes Contribution Number 759 from the Charles F. Kettering Research Laboratory.

References

1 V. K. Shah and W. J. Brill, *Proc. Nat. Acad. Sci. U.S.A.*, *74*, 3249 (1977);
S. P. Cramer, W. P. 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). Also see E. I. Stiefel, 'Molybdenum and Molybdenum Containing Enzymes', (M. P. Coughlan, ed.), Pergamon Press, New York and Oxford, 1980, p. 41 and W. E. Newton *et al.*, 'Current Perspectives in Nitrogen Fixation', (A. H. Gibson and W. E. Newton, eds.), Elsevier/North Holland, New York, 1981, p. 30 and references therein.

2 B. A. Averill, 'Structure and Bonding', in press.

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

4 R. H. Tieckelmann, H. C. Silvis, T. A. Kent, B. H. Huynh, J. V. Wasyczak, B.-K. Teo and B. A. Averill, *J. Am. Chem. Soc*, *102*, 5550 (1980).

5 G. Palmer, J. S. Multani, W. D. Cretney, W. G. Zumft and L. E. Mortenson, *Arch Biochem Biophys*, *153*, 325 (1972),
B E. Smith, D. J. Lowe and R. C. Bray, *Biochem. J.*, *135*, 331 (1973),
E Munck, H. Rhodes, W. H. Orme-Johnson, L. C. Davis, W. J. Brill and V. K. Shah, *Biochim. Biophys. Acta*, *400*, 32 (1975).

6 J. Rawlings, V. K. Shah, J. R. Chisnell, W. J. Brill, R. Zimmerman, E. Munck and W. H. Orme-Johnson, *J. Biol. Chem.*, *253*, 1001 (1978),
B. K. Burgess, E I. Stiefel and W. E. Newton, *J. Biol. Chem*, *255*, 353 (1980).

7 C. D. Garner, S. R. Acott, G. Cristou, G. Collison, F. E. Mabbs, V. Petrouleas and C. J. Pickett, 'Nitrogen

Fixation: The Chemical/Biochemical/Genetical Interface', (A. Muller and W. E. Newton, eds.), Plenum Press, New York, in press.
8 R. W. Lane, J. A. Ibers, R. B. Frankel, G. C. Papaefthmiou and R. H. Holm, *J Am. Chem. Soc.*, *99*, 84 (1977)
9 J. W. McDonald and W. E. Newton, unpublished observations.
10 J. W. McDonald, G. D. Friesen and W. E. Newton, *Inorg. Chim. Acta*, *46*, L79 (1980).
11 D. Coucouvanis, E. D. Simhon and N. C. Baenziger, *J Am. Chem. Soc.*, *102*, 6644 (1980).
12 W. H. Armstrong and R. H. Holm, *J. Am. Chem. Soc.*, *103*, 6246 (1981).
13 T. E. Wolff, J. M. Berg, K. O. Hodgson, R. B. Frankel and R H. Holm, *J. Am. Chem. Soc.*, *101*, 6246 (1979)