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Structure and Properties of $[Fe(WS_4)_2]^{3-}$

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Work in our laboratories has concentrated in the area of enzymes containing both molybdenum and iron, particularly nitrogenase and its iron-molybdenum cofactor (FeMoco), and chemical models related to these entities [1–5]. Recently, we reported [4, 5] the synthesis and characterization of the new Fe–Mo–S species, $[Fe(MoS_4)_2]^{n-}$ (n = 2,3). For n = 3, a well-defined trinuclear species is obtained, while the species with n = 2 could not be isolated in a pure, crystalline form [2, 4]. The structure of the trianion, prepared by a method similar to ours, was reported independently [6]. The analogous tungsten compounds, $[Fe(WS_4)_2]^{n-}$ (n = 2,3) have also been reported [4, 7], although, with n = 3, the yield was rather poor. Of this series of compounds, only the bis (DMF) adduct of $[Fe(WS_4)_2]^{2-}$ has been structurally characterized [7]. As part of our continuing studies in this area, we now report an improved preparative method for $[Fe(WS_4)_2]^{3-}$ (*1*), together with its X-ray crystal structure and characteristic spectral features.

$[Et_4N]_3[Fe(WS_4)_2]$ is best prepared by a method similar to that of its molybdenum analog [5] except that the solvent system is 15% water in CH_2Cl_2≠. The use of this biphasic reaction medium allows yields exceeding 50%, which is at least twice that obtainable from the reported preparation involving the $[Et_4N]BH_4$ reduction of the dianion in CH_2Cl_2. The presence of water is vital, but its role is unknown. In fact, *1* precipitates in moderate-to-good yield directly from an aqueous solution containing $[NH_4]_2WS_4$, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and $[(C_6H_5)CH_2N(CH_3)_3]Cl$ after standing at room temperature for 2 hr. Solvated red-brown single crystals of the mixed cation salt of bis(triphenylphosphine)iminium (PNP) and tetraethylammonium of *1* grow in 40% yield from a saturated acetonitrile solution obtained by treating $[PNP]_2[Fe(WS_4)_2]$ with $NaBH_4$ followed by addition of excess $[Et_4N]^+$. Single crystal X-ray diffraction data§ were collected on a Syntex P2₁ four-circle diffractometer with graphite monochromatized Mo-Kα radiation (λ = 71.07 pm) and corrected for absorption by an empirical method. The structure was solved by the heavy atom method and all non-hydrogen atoms were located by subsequent structure factor calculations and difference electron density maps. Least squares refinements using anisotropic thermal parameters converged at R = 9.00% with $R_w = 8.63\%$ $[1/w = \sigma^2F + 0.00009F^2)]$ for 3586 reflections $[4° \leqslant 2\theta \leqslant 50°; I \geqslant 1.96\sigma(I)]$.

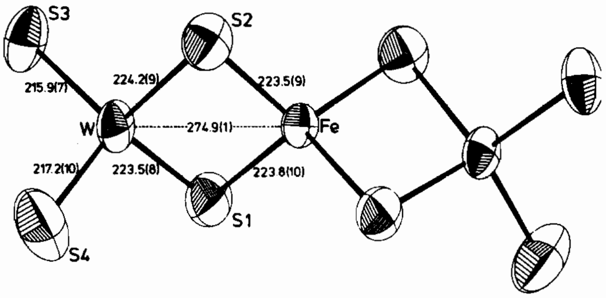

Fig. 1. ORTEP plot of *1* in crystals of the $[PNP]_2[Et_4N]$ salt.

The structure of the trianion is shown in Fig. 1 with the bond distances and angles collected in Table I, where they are compared with analogous data for $[Fe(MoS_4)_2]^{3-}$ (*2*) [6], $[(S_5)FeS_2WS_2]^{2-}$ (*3*) [8], and $[MoS_4FeCl_2)_2]^{2-}$ (*4*) [9]. All three metal atoms in *1* are approximately tetrahedrally coordinated with the two tetrathiotungstate ligands acting as bidentate chelates to the Fe atom, which lies on a two-fold crystallographic axis. The ~9° bend in W–Fe–W′ is similar to the slight bend observed in $[Fe(MoS_4)_2]^{3-}$ and contrasts with the linearity of Fe–Mo–Fe in *4*. The bend may well be a consequence of reduction because, in the series $[Co(WS_4)_2]^{n-}$ (n = 2,3), the dianion has a linear W–Co–W arrangement, which changes to ~168° in the trianion [10]. The WS_2Fe unit is similar to the MS_2Fe units in *2* and *3* and is close to planarity. The average tungsten-to-bridging (S1 and S2) sulfur ($W–S_b$) and iron to bridging sulfur ($Fe–S_b$) bond distances of 223.9 pm and 223.7 pm, respectively, in *1* are very similar to the analogous

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≠*Anal.* Calcd. $C_{24}H_{60}FeN_3S_8W_2$: C, 26.9; H, 5.65; N, 3.92; S, 23.9. Found: C, 26.6; H, 5.71; N, 3.91; S, 23.7.

§Crystal and refinement data for $[(Ph_3P)_2N]_2[Et_4N][Fe(WS_4)_2] \cdot 2CH_3CN$: orthorhombic with a = 1257.1(3) pm, b = 3394.6(13) pm, c = 1079.8(3) pm and $\alpha = \beta = \gamma$ = 90.00(3)°; space group $P2_12_12$; Z = 2; d_{calc} = 1.42 g/cm³; crystal dimensions, 0.7 × 0.5 × 0.45 mm.

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TABLE I. Interatomic Distances (pm), Bond Angles (Degrees) and Standard Deviations in $[Fe(WS_4)_2]^{3-}$ (*1*), $[Fe(MoS_4)_2]^{3-}$ (*2*)[a], $[(S_5)FeS_2WS_2]^{2-}$ (*3*)[b], and $[MoS_4FeCl_2)_2]^{2-}$ (*4*)[c].

	1 (M = W)	*2* (M = Mo)	*3* (M = W)	*4* (M = Mo)[d]
M–Fe	274.9(1)	274.0(1)	275.3(3)	277.5(6)
M–S1	223.5(8)	226.0(4)	224.0(6)	220.4(5)
M–S2	224.2(9)	225.1(5)	226.9(7)	
M–S3	215.9(7)	216.9(5)	214.2(6)	
M–S4	217.2(10)	217.3(5)	217.2(8)	
Fe–S1	223.8(10)	224.5(4)	226.0(7)	229.5(5)
Fe–S2	223.5(9)	226.8(4)	228.0(7)	
M–Fe–M^1	171.2(3)	172.64(6)		179.38(7)[e]
S1–Fe–S2	103.9(3)	104.9(2)		100.9(2.0)
S1–M–S2	104.0(3)	105.0(2)	105.4(2)	109.5(1.9)
M–S1–Fe	75.8(3)	74.90(12)	74.9(6)[d]	76.05(9)
M–S2–Fe	75.8(3)	74.64(13)		

[a] From ref. 6. [b] From ref. 10. [c] From ref. 11. [d] Mean values with standard deviation from the mean in parenthesis. [e] Angle for Fe–Mo–Fe.

distances of *2* (225.6 pm and 225.7 pm) and *3* (225.5 pm and 227.0 pm). The tungsten-to-terminal (S3 and S4) sulfur (W–S$_t$) distance in *1* is distinctly shorter (216.6 pm) than W–S$_b$ but similar to M–S$_t$ in *2* (217.1 pm), *3* (215.7 pm) and WS_4^{2-} (217.7 pm [11]). The tungsten–iron distance of 274.9 pm in *1* is also similar to the corresponding distances in *2* (Mo–Fe = 274.0 pm [6]) and *3* (W–Fe = 275.3 pm [8]) and not much different from the Mo–Fe distance (277.5 pm) in *4*, where ^{57}Fe Mössbauer and magnetic data [9] indicate a Fe(II) and, thus, Mo(VI) formulation. For *1–4*, the M–S$_b$–Fe angles are all between 74.6° and 76.1°, a variation of only 1.5°. This small variation may indicate a controlling influence for this angle on the M–Fe separation because the S$_b$–M–S$_b$ and S$_b$–Fe–S$_b$ angles vary more, from 103.7°-to-109.5° and 101°-to-104.9°, respectively. However, these structural data are not very definitive in gaining insight into the distribution of electron density over the three metal atoms in these complex anions.

The electronic absorption spectra of $[Fe(WS_4)_2]^{n-}$ (n = 2,3) in CH_3CN solution are presented in Fig. 2. A comparison of the two spectra shows that the formation of *1* from $[Fe(WS_4)_2]^{2-}$ (*5*) cannot be interpreted as a reduction of only the Fe center ($Fe^{II} \rightarrow Fe^{I}$). Not only is there a shift of the L → d(Fe) type [10] absorption band from 16.2 kK to 18.0 kK, but a second intense band appears at these lower energies (20.3 kK) on reduction and a pronounced change in the $L \rightarrow L^*$ bands occurs (from 23.4 and 26.7 kK in *5* to 22.9 and 27.6 kK in *1*). The spectrum of *1* shows a very similar pattern to that of its molybdenum analog *2* [5, 6]. The infrared spectrum of *1* contains a strong band at 470 cm^{-1} (ν_{as}W–S$_t$) and a medium intensity band at 431 cm^{-1} ('νW–S$_b$'). The strong W–S bands in the infrared appear as only weak shoulders in the Raman spectrum (excitation frequency of 647.1 nm) as shown in Fig. 3, where the strongest bands are observed at 422, 475 and 496 cm^{-1}. The symmetric νW–S$_t$ and the νW–S$_b$ vibrations are much less characteristic for *1* than for *5* (see ref. 10 for a short discussion of this topic). The 475 cm^{-1} band shows a strong enhancement in the resonance Raman spectrum [12] using the 514.5 or 488.0 nm lines of an Ar laser. The latter spectrum also shows a remarkable combination (ν_sFe–S + ν_sW–S$_t$) band and two overtones of ν_sW–S$_t$. The ^{57}Fe Mössbauer spectrum of *1* at room temperature exhibits a value of 0.45(2) mm/s for the isomer (IS) with a quadruple splitting (QS) of 1.03(2) mm/s. These values are similar to *2* (IS = 0.42 and QS = 1.04 mm/s at 77 K) [15] and comparable to those for *5* (IS = 0.44 and QS = 2.65 mm/s). These isomer shift data indicate extensive charge delocalization from Fe to the two bidentate MS_4^{2-} ligands producing similar electron density at Fe for all three complexes. The magnetic moment and EPR spectral data for *1* are

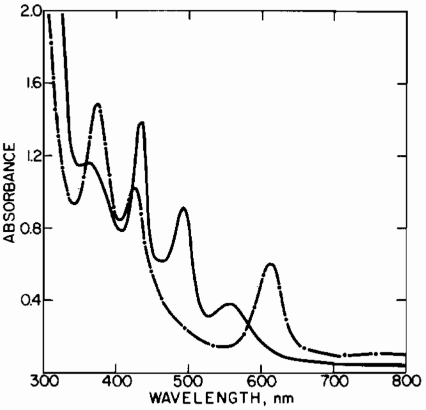

Fig. 2. Electronic absorption spectrum of $[Et_4N]_3$-$[Fe(WS_4)_2]$ (———) and $[Et_4N]_2[Fe(WS_4)_2]$ (–·–·–) in acetonitrile solution.

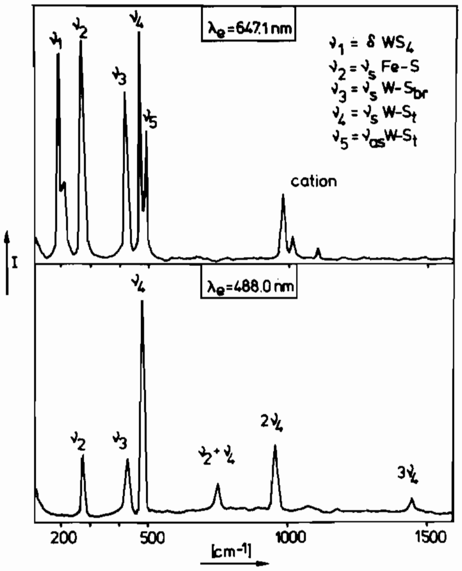

Fig. 3. Raman and Resonance Raman spectra of solid $[PNP]_2[Et_4N][Fe(WS_4)_2]$.

consistent with the presence of a S = 3/2 spin system and a detailed analysis of these data has been submitted [16].

The interpretation of the electronic absorption and Mössbauer data as indicating only minor changes in the relative charge (or electron density) at Fe on reduction of *5* to give *1* is supported by EH-SCCC-MO calculations on the complexes $[M^1(WS_4)_2]^{n-}$ (M^1 = Fe, Co; n = 2,3), which show a high electron delocalization ($M^1 \rightarrow WS_4^{2-}$) as inferred from the MO's with predominant $3d(M^1)$ character [2]. These studies show that, upon reduction: (i) the net charge on each of the three metal centers remains almost unchanged with the additional charge located mainly at the terminal S atoms (for more details, see ref. 10); and (ii) the W–S$_t$ overlap population and, thus, bond order decreases (see structural data on the related Co complexes [10]) which is exemplified by the shift of ν_{as}W–S$_t$ from 493/484 cm^{-1} in *5* to 470 cm^{-1} in *1*.

$[Fe(WS_4)_2]^{3-}$ and its molybdenum analog provide good, simple prototypes with which to initiate studies of the charge delocalization in clusters of Mo(W)–Fe–S atoms. It is of special interest to compare these effects, together with structural data, in two species differing only in their electron populations. Unfortunately, the appropriate pairs of Mo(W)–Fe–S complexes have, so far, eluded isolation and/or crystallization. However, we have been able to obtain single crystals of $[Co(WS_4)_2]^{n-}$ (n = 2,3) and such studies in this series are ongoing [10]. These complexes continue to be important in our efforts to understand the properties of, and indeed even identify, multimetal clusters in protein and enzymes.

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