Inorganica Chimica Acta, 53 (1981) L135–L137

Synthesis and Structural Characterization of $[(NO)_2FeS_2MoS_2]^{2-}$ a Dinitrosyl Complex Containing the FeS_2MoS_2 Core

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Received October 8, 1980

Two important features of the Mo site in nitrogenase which have been revealed by Mo- X-ray absorption fine structure (EXAFS) analyses [1] are: a) a set of three or four Mo bound sulfur atoms at 2.36 ± 0.02 Å and b) a set of two iron atoms at a distance of 2.72 ± 0.03 Å from the Mo atom. This information has stimulated research aimed toward the synthesis of Mo–Fe–S aggregates, and has defined certain minimal structural constraints which should be adhered to by any structurally relevant synthetic analogues for the nitrogenase active site.

Various Mo–Fe–S complexes have been reported which, at least partially, seem to be within the structural limitations imposed by the EXAFS studies. Two major classes of these complexes are a) the oligonuclear Fe–Mo complexes derived from MoS_4^{2-}; $[(SPh)_2FeS_2MoS_2]^{2-}$, (II) [2], $[(S_5)FeS_2MoS_2]^{2-}$, (III) [3], $[Cl_2FeS_2MoS_2FeCl_2]^{2-}$, (IV) [4], $[(MoS_4)_2Fe]^{3-}$, (V) [5], $[Cl_2FeS_2MoS_2]^{2-}$ [4, 2b], and $[(SPh)_2FeS_2FeS_2MoS_2]^{3-}$ [6]; and b) the 'double cubane' cluster complexes $[Mo_2Fe_6S_9(SEt)_8]^{3-}$ [7]; $[Mo_2Fe_6S_8(SR)_9]^{3-}$ (R = Et [7], R = Ph [8], R = SCH_2CH_2OH [9]) and $[Mo_2Fe_7S_8(SR)_{12}]^{3-/4-}$, (R = Et, CH_2Ph) [10].

As a continuation of our studies on the coordination chemistry of the tetrathiometallate, MS_4^{2-}, (M = Mo, W) anions, we report herein the synthesis and structural characterization of the new $[(NO)_2FeS_2MS_2]^{2-}$ complexes (M = Mo, W).

Preparation of $(Ph_3PNPPh_3)_2[(NO)_2FeS_2MS_2]$ (M = Mo, W)

A solution of 0.5 g of $[(Et_4N)(Ph_3PNPPh_2)_2]$ $[Fe(MoS_4)_2]$ in 15 ml of dimethylformamide, DMF, was allowed to react with pure NO gas by bubbling the gas through the solution for *ca.* 1 min. The initially deep violet DMF solution turned to a red brown color. Upon filtration and addition of diethyl ether to the filtrate single crystals formed on standing which were isolated and washed with several portions of diethyl ether, 0.2 g; 50% yield. All operations were performed under a dinitrogen atmosphere using degassed solvents. *Anal.* Calcd. for $FeMoS_4C_{72}H_{60}P_4N_4O_2$ (MW, 1417.2) C, 61.01; H, 4.28; N, 3.95; P, 8.74; S, 9.05; Mo, 6.77; Fe, 3.94. Found: C, 59.55; H, 4.21; N, 3.75; P, 8.65; S, 10.01; Mo, 7.10; Fe, 3.08%. *Visible–UV Spectra* in DMF solution (Fig. 1); nm (ϵ), 530 (2075); 467 (7512); 346 (11872); 295 (17315). *Infrared Spectra* in Kbr pellet, ν(N–O), 1667, 1631 cm^{-1}.

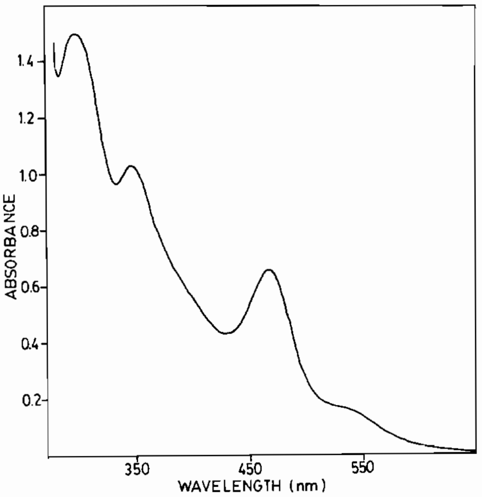

Fig. 1. Spectrum of $[(NO)_2FeS_2MoS_2]^{2-}$ in Dimethylformamide Solution (8.33 × 10^{-4} *M*).

The tungsten analog is obtained by a similar procedure, passing NO through a DMF solution of $Fe(ClO_4)_2 \cdot 6H_2O$, $(NH_4)_2WS_4$ and Ph_3PNPPh_3Cl in a 1:1:2 molar ratio. On a millimolar scale the product is obtained in 46% yield. *Anal.* Calcd. for $FeWS_4C_{72}H_{60}P_4N_4O_2$ (MW, 1504.52), C, 57.5; H, 4.01; N, 3.72. Found: C, 56.88; H, 3.92; N, 3.60%. The complex is X-ray isomorphous and very likely isostructural to the Mo analogue. Visible UV spectra in CH_2Cl_2 solution: nm (ϵ), 612 (200); 442 (sh); 386 (8700); 336 (7400).

Structure Determination

Single crystals of $(Ph_3PNPPh_3)_2[(NO)_2FeS_2MoS_2]$, (I), were obtained by the slow diffusion of ether into a DMF solution of the complex. The compound crystallizes in the monoclinic space group $P2_1/n$ with a = 23.950(8) Å, b = 13.260(5) Å, c = 21.800(8) Å, β = 103.00(4)°, V = 6,745.7 Å^3, Z = 4, d(calcd) = 1.39 g cm^3 (Found by flotation in a CCl_4/pentane mixture, 1.41(1) g cm^3). A complete data set was collected to a 2θ max of 50° (MoK_α radiation, λ = 0.7107 Å) on a Picker FACS I automatic diffractometer using a step-scan technique, and employing graphite monochromatized MoK_α radiation ($2\theta_m$ = 12.2°). The data was averaged, corrected for Lorentz and polarization effects and

TABLE I. Selected Structural Parameters in the $[(NO)_2FeS_2MoS_2]^{2-}$, (I); $[(SPh)_2FeS_2MoS_2]^{2-}$, (II) [2] $[(S_5)FeS_2MoS_2]^{2-}$, (III) [3]; $Cl_2FeS_2MoS_2FeCl_2)^{2-}$, (IV) [4] and $[(MoS_4)_2Fe]^{3-}$, (V) [5].

	(I)	(II)	(III)	(IV)	(V)
	Bond Lengths[a], *Angstroms*				
Fe–Mo	2.835(13)[b]	2.731(3)	2.775(6)	2.740(6)	2.740(1)
Mo–S_b	2.259(8)[c]	2.246(6)	2.253(8)	2.204(5)	2.255(5)
Mo–S_t	2.182(8)[d]	2.153(6)	2.145(7)		2.171(5)
Fe–S_b	2.257(8)	2.250(8)	2.245(8)	2.295(5)	2.256(12)
S_b–S_b		3.571(8)	3.568(8)	3.543(6)	3.579(5)
Fe(Mo)–N	1.9(2)[e]				
Fe(Mo)–O	2.66(5)				
	Bond Angles[a], *Degrees*				
M–S_b–M′	77.7(4)	75.5(2)	74.9	76.05(9)	74.6(1)
S_b–Fe–S_b	104.5(3)	102.9(3)		101.0(1)	104.9(2)
S_b–Mo–S_b		104.5(3)		107.1(1)	105.0(2)
Fe–N–O	162(4)[f]				
O–Fe(Mo)–O	105(2)				
N–Fe(Mo)–N	113(2)				

[a] Mean values for the chemically equivalent bonds or angles. The standard deviations of the averages were taken as the larger of the individual standard deviations or the standard deviation of the mean. [b] Independent values of 2.822(2) and 2.849(2) A. [c] Range 2.271(3) to 2.248(3) A. [d] Range 2.175(3) to 2.195(3) A. [e] Range 2.10(1) to 1.67(2) A. [f] Range 166(1) to 155(1)°.

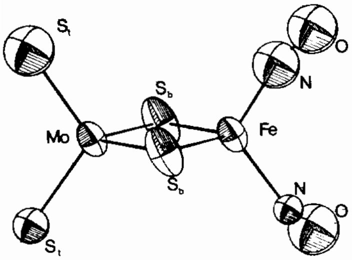

Fig. 2. Structure of the $[(NO)_2FeS_2MoS_2]^{2-}$ anion. Thermal ellipsoids as drawn by ORTEP (Ref. 15) represent the 50% probability surfaces.

the structure was solved by conventional Patterson and Fourier techniques. Refinement was carried out by full matrix least-squares calculations. The Fe, bridging S and Mo atoms in the anion and the P and N atoms in the cations were refined with anisotropic temperature factors, all other non-hydrogen atoms were refined by 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. Refinement of all parameters on 7275 data ($F_o^2 \geqslant 3\sigma(F_o^2)$) converged to a conventional R factor of 7.4%.

Structure and Properties of $[(NO)_2FeS_2MoS_2]^{2-}$

The unit cell contains two pairs of crystallographically independent centrosymmetric dimers and eight $(Ph_3P)_2N^+$ cations. The position of the dimers on inversion centers ($\bar{1}$) reflects a two fold disorder in the location of the $(NO)_2Fe$ and MoS_2 terminal units. The anions were refined successfully using an equal admixture of Fe and Mo for the metal sites and half occuppancy for each of the terminal sulfur, nitrogen and oxygen atoms. Refinement of the N and O atoms of the NO groups was not entirely satisfactory primarily because of the small scattering power of the half atoms and the close proximity of these atoms to the terminal sulfur atoms*. The structure of the anion** (Fig. 2) contains the S_2MoS_2Fe unit already structurally characterized in various other Mo–Fe–S complexes [5–8]. The structural details of this unit in (I), are comparable to those reported earlier for other Mo–Fe–S complexes (Table I). The rather long terminal Mo–S bonds in (I) may reflect charge delocalization to the MoS_2^{4-} ligand which results in a weakening of the $Mo–S_4$ π bonds and a higher electron density at the terminal sulfur atoms.

As a $L_2M(NO)_2$ complex, (I) can be described by the $M(NO)_2$ [10] formalism [11] and its struc-

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*A model allowing positional and thermal parameters of both terminal S and NO to vary could not resolve N, O and S. A model holding terminal S atoms fixed and varying the N and O positional coordinates gave consistant M–O distances for the four independent cases, but large variations in the N atom positions which more nearly overlap the S atom positions.

**The structure of the $(Ph_3P)_2N^+$ cation is normal with $\overline{P–N}$ = 1.581(10) A $\overline{P–C}$ = 1.804(15) and P–N–P = 140(1)°.

tural characteristics (particularly the N–M–N, O–M–O and M–N–O angles) are consistent with a molecular orbital, M.O., scheme for pseudotetrahedral (C_{2v}) geometry. Accordings to this scheme [11], and considering the N–M–N and O–Mo–O angles, the highest occupied M.O. ($1b_1$) must be composed primarily of d_{xz} of the metal.

The only other, structurally characterized $(NO)_2$-FeS_2 unit exists in the dimeric $[Fe(NO)_2SC_6H_5]_2$ complex [12], and shows N–M–N, 117.4(2)°; O–M–O, 106.6(2); M–N–O, 167(4)° and M–N, 1.67(1) Å. These values are comparable to those observed in (I) within the accuracy of the structural determinations.

Acknowledgements

This work has been supported by grants from the National Science Foundation (CHE-79-0389) and the National Institute of Health (GM-26671-01). The computing expenses have been covered by grants from the University of Iowa Graduate College.

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