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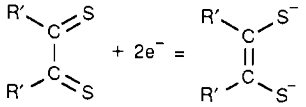
Communications

Molybdenum Dithiooxamide Complexes: Is the Ligand Oxidized or Reduced?

The possibility[1,2] that a 1,2-dithiolene ligand bound to a reduced pterin nucleus exists in the molybdenum cofactor of the oxomolybdenum enzymes[3] would, if confirmed, represent a unique structural unit in biology. Synthetic modeling has established the feasibility of oxo and dithiolene ligands coexisting on the same molybdenum center[4-6] as well as the possibility of direct metal–pterin linkages.[7-9]

The possible interplay of formal oxidation levels of the pterin ring, the dithio unit, and the molybdenum atom (VI, V, and IV in the enzymes) in terms of catalytic electron-transfer properties makes for fascinating speculation. In particular, unsaturated 1,2-dithio moieties can exist in dithione and dithiolene oxidation levels:



Free dithiones are unstable in general, but dithiooxamides, $R'_2NC(S)-C(S)NR'_2$, are stabilized by the thioamide fragments.[10,11] Coordinated dithiooxamides normally feature nonplanar MS_2C_2 chelate rings,[12] although monodeprotonation of sterically uncrowded N,N′-disubstituted ligands can stabilize conformations close to planarity via intramolecular hydrogen bonding between amide nitrogen atoms.

tom Dieck[10,13] has studied the reactions of tetraalkyl dithiooxamides with various $[Mo(CO)_{4-x}(PR_3)_x]$ fragments. Trends in CO stretching frequencies led him to an interesting assertion: $[Mo(CO)_4(R'_4N_2C_2S_2)]$ and $[Mo(CO)_3(PR_3)(R'_4N_2C_2S_2)]$ species are Mo^0–dithione complexes whereas $[Mo(CO)_2(PR_3)_2(R'_4N_2C_2S_2)]$ are Mo^{II}–dithiolene complexes. Initial ^1H NMR data on these rather insoluble species supported the formulation, but definitive structural characterization was lacking. The present communication presents NMR and X-ray crystallographic evidence to support the proposals.

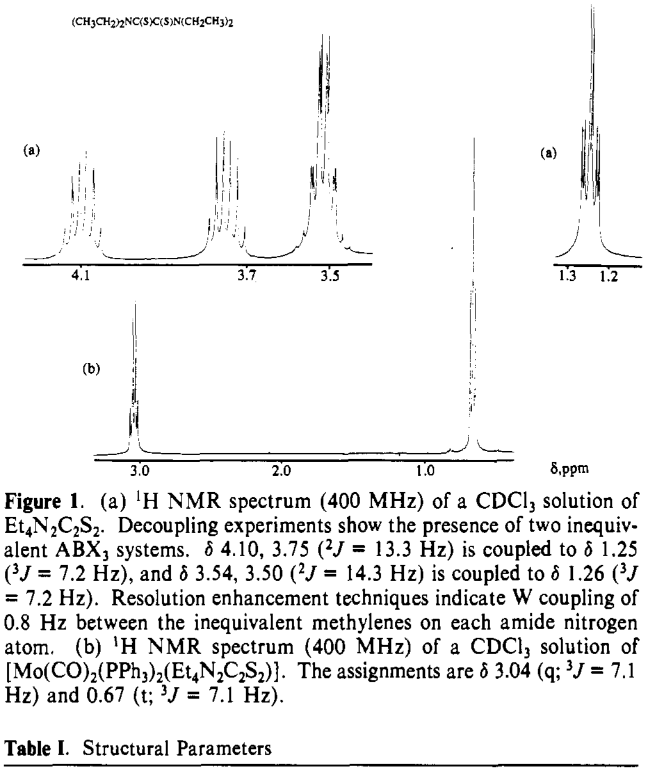


Figure 1. (a) ^1H NMR spectrum (400 MHz) of a $CDCl_3$ solution of $Et_4N_2C_2S_2$. Decoupling experiments show the presence of two inequivalent ABX_3 systems. δ 4.10, 3.75 ($^2J = 13.3$ Hz) is coupled to δ 1.25 ($^3J = 7.2$ Hz), and δ 3.54, 3.50 ($^2J = 14.3$ Hz) is coupled to δ 1.26 ($^3J = 7.2$ Hz). Resolution enhancement techniques indicate W coupling of 0.8 Hz between the inequivalent methylenes on each amide nitrogen atom. (b) ^1H NMR spectrum (400 MHz) of a $CDCl_3$ solution of $[Mo(CO)_2(PPh_3)_2(Et_4N_2C_2S_2)]$. The assignments are δ 3.04 (q; $^3J = 7.1$ Hz) and 0.67 (t; $^3J = 7.1$ Hz).

Table I. Structural Parameters

	C–S, Å	C–C, Å	dihedral angle,[a] deg
$[Mo(CO)_2(PBu^n{}_3)_2((C_5H_{10}N)_2C_2S_2)]$	1.74 (2)	1.37 (4)	0
$[ZnCl_2(H_2Me_2N_2C_2S_2)]$[12]	1.69 (1)	1.52 (1)	38.4
$[Cu(H_2(PhCH_2)_2N_2C_2S_2)](ClO_4)_2$[12]	1.67 (1)	1.50 (2)	35.0
dithiolene complexes[18]	1.69–1.75	1.31–1.39	0

[a] Between the two NCS fragments.

The ^{13}C and ^1H NMR spectra of $Et_4N_2C_2S_2$[14] in $CDCl_3$ indicate the presence of five carbon environments[15] and *two* inequivalent

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(15) ^{13}C NMR [100 MHz; δ, ppm (assignment)]: $Et_4N_2C_2S_2$, 193.02 (CS), 47.53 and 44.07 (CH_2), 12.65 and 10.61 (CH_3); $[Mo(CO)_2(PPh_3)_2(Et_4N_2C_2S_2)]$, 162.75 (CS), 48.68 ($CH_2$), 12.60 ($CH_3$).

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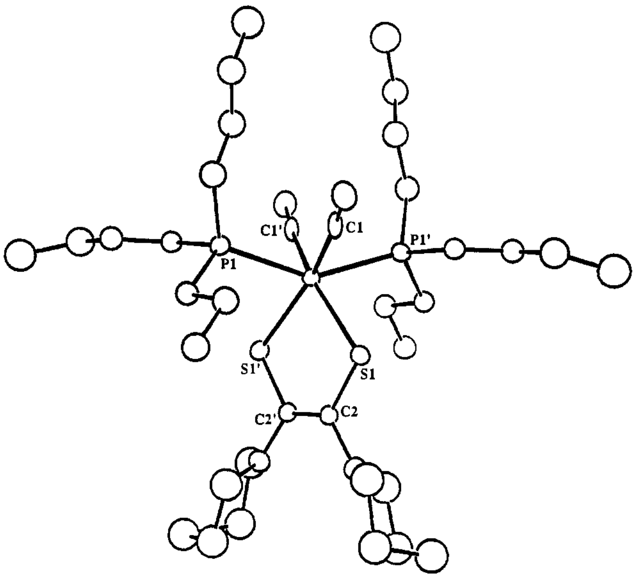

Figure 2. Molecular structure of *cis,trans*-$[Mo(CO)_2(PBu^n_3)_2((C_5H_{10}N)_2C_2S_2)]$. Primed atoms are related by a crystallographic 2-fold axis. Selected bond distances (Å) and angles (deg): Mo–S(1) = 2.384 (7), Mo–P(1) = 2.472 (6), Mo–C(1) = 2.00 (3), S(1)–C(2) = 1.74(2), C(2)–C(2)′ = 1.37 (4); S(1)–Mo–P(1) = 125.1 (2), S(1)–Mo–C(1) = 91.8 (7), S(1)–Mo–S(1)′ = 80.8 (3), S(1)–Mo–P(1)′ = 81.9 (2), S(1)–Mo–C(1)′ = 152.1 (7), P(1)–Mo–C(1) = 80.6 (7), P(1)–Mo–P(1)′ = 146.8 (2), P(1)–Mo–C(1)′ = 79.7 (7), C(1)–Mo–C(1)′ = 106 (1), Mo–S(1)–C(2) = 109.9 (7), S(1)–C(2)–C(2)′ = 120 (1), Mo–C(1)′–O(1) = 177 (2).

ABX_3 proton spin systems (Figure 1a). The diastereotopic nature of this molecule follows from the effective C_2 symmetry imposed by the inequivalence of the two ethyl substituents on a given amide nitrogen. The dihedral angle between the planar thioamide groups and the detailed conformation cannot be derived from the present data.

$[Mo(CO)_2(PPh_3)_2(Et_4N_2C_2S_2)]$ is synthesized from $[Mo(CO)_2(PPh_3)_2(MeCN)_2]$ and $Et_4N_2C_2S_2$.[13] The ^{13}C and ^1H NMR spectra indicate, for the dithiooxamide ligand, the presence of three carbon environments[15] and equivalent methylene and methyl protons (Figure 1b). This simplicity contrasts starkly with the free ligand behavior, where all four methylene protons associated with half of the molecule were inequivalent (Figure 1a). The total NMR and IR data are consistent with the presence of a *cis,trans*-$[Mo(CO)_2(PPh_3)_2(Et_4N_2C_2S_2)]$ isomer of effective C_{2v} point symmetry.

Equivalent conclusions can be drawn for $CDCl_3$ solutions of $[Mo(CO)_2(PBu^n_3)_2((C_5H_{10}N)_2C_2S_2)]$, which features piperidine substitutents. Crystalline samples of this species can be grown,[16] and X-ray analysis[17] shows the presence in the solid state of the cis, trans isomer suggested from the solution data (Figure 2). Although the crystal structure analysis is of limited accuracy (owing to the paucity of observable data and high thermal motion associated with the organic residues), the molecular geometry is established unequivocably with the Mo atom lying on a crystallographic 2-fold axis.

Table I compares the coordination geometry of the chelate ring Mo–S(1)–C(2)–C(2′)–S(2) with those observed for an extensive range of dithiolene complexes[18] and with those present in $[ZnCl_2(H_2Me_2N_2C_2S_2)]$ and $[Cu(H_2(PhCH_2)_2N_2C_2S_2)_2](ClO_4)_2$, which contain neutral dithiooxamide ligands unaffected by intraligand hydrogen bonding.

The short C–C bond length and planar chelate ring observed in the present compound provide substantive evidence that the dithiooxamide ligand is present in its reduced ditholene form, confirming the previous assignments.[10,13]

Variation of phosphine and dithiooxamide substituents to improve solubility and stability of other members of the $[Mo(CO)_{4-x}(PR_3)_x(R'_4N_2C_2S_2)]$ series is underway. The present results are interesting in the context of the suggested role of the molybdenum cofactor in modulating internal electron transfer in oxomolybdenum enzymes.

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Registry No. *cis,trans*-$[Mo(CO)_2(PBu^n_3)_2((C_5H_{10}N)_2C_2S_2)]$, 124687-45-2.

Supplementary Material Available: Tables S1 and S2, listing thermal parameters and all bond distances and angles (2 pages); Table S3, listing calculated and observed structure factors (5 pages). Ordering information is given on any current masthead page.

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(16) $[Mo(CO)_2(PBu^n_3)_2((C_5H_{10}N)_2C_2S_2)]$ (0.36 g) was dissolved in acetone (3.3 cm^3) at 42 °C. The solution was allowed to cool slowly to room temperature and was then placed at −20 °C overnight. Rhombic crystals (0.28 g) were filtered off, washed with MeOH (2 × 5 cm^3), and dried in vacuum.

(17) X-ray data were collected on an Enraf-Nonius CAD4 diffractometer fitted with Mo Kα radiation (λ = 0.71073 Å) at room temperature. The ω–2θ scan technique was employed to measure 4533 reflections (θ_{max} = 25.0°) on a dark purple crystal with face dimensions as follows: 0.48 mm, ±($1\bar{1}0$); 0.32 mm, ±(110); 0.94 mm, ±(001). A total of 4043 unique reflections were collected of which 1764 satisfied the $I > 2.5\sigma(I)$ criterion. X-ray data for $C_{38}H_{74}MoN_2O_2P_2S_2$, M_r = 813.0: monoclinic, space group $C2/c$, a = 18.558 (5) Å, b = 15.729 (1) Å, c = 16.71 (1) Å, β = 110.16 (3)°, V = 4578.8 Å^3, Z = 4, d_{calcd} = 1.179 g cm^{-3}, $F(000)$ = 1644, μ = 4.35 cm^{-1}. The structure was solved from the Patteron map and refined by a full-matrix least-squares procedure based on F (SHELX-76). Butyl groups were refined with constrained C–C bond lengths (1.54 (2) Å), and the piperidine ring was refined with constrained N–C and C–C bond lengths (1.42 (2) and 1.54 (2) Å, respectively). Anisotropic thermal parameters were used for Mo, S, P, O, N, C(1), and C(2); hydrogen atoms were not included. Refinement converged to R = 0.097 with unit weights (no improvement in the Cc model).

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