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LETTER

Synthesis and X-ray Structural Characterization of the Novel Molybdenum(V) Diethyldithiocarbamate Complex $[Mo_2(\mu\text{-}S_2)_2(S_2CNEt_2)_4](BF_4)_2\cdot 2CHBr_3$

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Two aspects of Mo chemistry are pertinent to the subject of this report. Firstly, while Mo(V) exhibits a great propensity to form dinuclear complexes with a wide variety of ligands only two types of dinuclear dithiocarbamato–Mo(V) complexes, viz. $Mo_2O_2(\mu\text{-}O)(S_2CNR_2)_4$ and $Mo_2E_2(\mu\text{-}E)_2(S_2CNR_2)_2$ (E = O, S) are known [1]; all of these complexes feature terminal chalcogenide ligands, Mo=E. Secondly, the conversion of terminal oxo ligands to terminal thio ligands, one synthetic approach to models of the oxothio–Mo(VI) centre of xanthine oxidase, is a challenging reaction which is difficult to effect in the case of Mo(VI) due to its redox interplay with sulfiding agents. Oxothiomolybdate [2] and $MoSE(R_2NO)_2$ (E = O, S) [3] complexes are rare examples of Mo(VI) species accessible by this type of reaction. Our investigation of the reaction of $[MoO(S_2CNEt_2)_3]BF_4$ [4] with boron sulfide has led to the characterization of $[Mo_2(\mu\text{-}S_2)_2(S_2CNEt_2)_4](BF_4)_2$ (**1**), the cation of which possesses a structure unprecedented in dithiocarbamato–Mo chemistry. Moreover, the fate of the redox active species in this reaction, viz. Mo(VI) and S^{2-}, has been determined.

The anaerobic reaction of $[MoO(S_2CNEt_2)_3]BF_4$ with B_2S_3 (Mo:S = 1:1.3) in dichloromethane results in the formation of **1** and $[Mo(S_2CNEt_2)_4]BF_4$ via coupled redox ($4Mo(VI) + 4S^{2-} \rightarrow 4Mo(V) + 2S_2^{2-}$) and dithiocarbamate ligand redistribution processes, as represented in eqn. (1).

$$4[MoO(S_2CNEt_2)_3]BF_4 + \tfrac{4}{3}B_2S_3 \longrightarrow \mathbf{1} + 2[Mo(S_2CNEt_2)_4]BF_4 + \tfrac{4}{3}B_2O_3 \quad (1)$$

The complex products may be fractionally crystallized, in good yield, from the filtered reaction mixture by the careful addition of diethyl ether. The spectroscopic properties of $[Mo(S_2CNEt_2)_4]BF_4$ were identical to those reported in the literature [5]. Orange, air-stable, diamagnetic **1** was characterized by elemental analysis, infrared and ^1H and ^{95}Mo NMR spectroscopy, FAB mass spectrometry and X-ray crystallography. The IR spectrum exhibits bands due to bidentate $S_2CNEt_2^-$ ligands (ν(CN) 1520 cm^{-1}) and BF_4^- (1050 cm^{-1}, br) and weak bands ascribable [6] to the S_2^{2-} ligand (600, 560, 510 cm^{-1}). At 400 MHz the ^1H NMR spectrum of **1** consists of overlapping multiplets due to four inequivalent methyl groups (δ *c.* 1.3) and four diastereotopic (H_{AB}) methylene groups; chemical shifts and coupling parameters for the methylene protons are accessible by 2-D NMR experiments**. NMR data are consistent with the maintenance of the solid state structure of the cation (below) in solution. Compound **1** exhibits a narrow ^{95}Mo NMR signal at δ −562 ($\Delta W_{1/2}$ = 90 Hz). Crystals of **1** grown from CH_2Cl_2–ether mixtures or $CHCl_3$ were unstable to loss of solvent of crystallization. Crystals suitable for an X-ray structure detemination were eventually obtained by slow evaporation of a $CHBr_3$ solution of **1**.

Crystal data for $\mathbf{1}\cdot 2CHBr_3$: $C_{11}H_{21}BBr_3F_4MoN_2S_6$, M_r = 796.1, triclinic, space group $P\bar{1}$, a = 12.560(3), b = 13.000(4), c = 8.071(4) Å, α = 94.16(4), β = 90.09(3), γ = 75.80(2)°, U = 1274.0 Å^3, D_c (Z = 1 dimer) = 2.075 Mg m^{-3}, D_m = 2.071 Mg m^{-3}. Monochromatic Mo Kα, λ = 0.7107 Å, μ = 55.92 cm^{-1}, T = 295 K, analytical absorption correction (max. and min. transmission factors 0.305 and 0.096, respectively). Total of 4187 reflections measured ($1.5° \leqslant \theta \leqslant 24.0°$) on a CAD4 diffractometer, 3893 unique and 2699 satisfied $I \geqslant 2.5\sigma(I)$ criterion. Structure solved from Patterson and refined by full-matrix least-squares procedure (SHELX). Anisotropic thermal parameters for non-H atoms and H atoms included in the model at their calculated positions. Refinement converged with R = 0.036, R_w = 0.040 for $w = 3.97/[\sigma^2(F) + 0.0008|F|^2]$.

The discrete centrosymmetric dimeric $[Mo_2(\mu\text{-}S_2)_2(S_2CNEt_2)_4]^{2+}$ cation (Fig. 1) is composed of molybdenum atoms separated by a distance of 2.808(1) Å and bridged by two $\mu\text{-}S_2^{2-}$ ligands. The bridge is characterized by Mo–S(1) and Mo–S(2)

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**^1H NMR of methylene protons: H_{AB} pairs at δ 3.95 and 3.74, 4.03 and 3.69, 3.81 and 3.69, 3.81 and 3.74, $^2J_{AB}$ = 14 Hz, $^3J_{HH}$ = 7 Hz.

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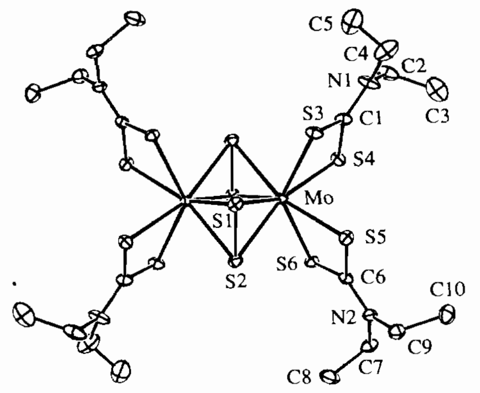

Fig. 1. Molecular structure of centrosymmetric $[Mo_2(\mu\text{-}S_2)_2(S_2CNEt_2)_4]^{2+}$ drawn with ORTEP at 15% probability ellipsoids. Selected interatomic parameters: Mo··Mo' 2.808(1), Mo–S(1) 2.443(2), Mo–S(2) 2.430(2), Mo–S(1') 2.444(2), Mo–S(2') 2.426(2), Mo–S(3) 2.491(2), Mo–S(4) 2.493(2), Mo–S(5) 2.492(2), Mo–S(6) 2.506(1), S(1)–S(2) 1.999(2) Å; S(1)–Mo–S(2) 48.4(1), S(3)–Mo–S(4) 69.7(1), S(5)–Mo–S(6) 69.6(1), S(2)–Mo–S(5) 160.2(1), S(2)–Mo–S(6) 125.7(1), S(3)–Mo–S(2') 125.2(1), S(4)–Mo–S(2') 160.4(1), Mo–S(1)–Mo' 70.1(1), Mo–S(2)–Mo' 70.6(1)°.

distances of 2.443(2) and 2.430(2) Å, respectively, and an S(1)–S(2) distance of 1.999(2). The nonbonding contact distances between the sulfur atoms of the S_2^{2-} ligands are: S(1)··S(2') = 3.443, S(1)··S(1') = 3.999(3) and S(2)··S(2') = 3.962(3) Å. The sulfur atoms of the bridge are strictly planar and both Mo atoms are 1.404(1) Å out of the plane. The atoms of the core have a distorted octahedral geometry with Mo and S atoms at the apices of the octahedron. The coordination geometry of the Mo atoms may also be described as distorted octahedral if each S_2^{2-} ligand is considered to occupy a single vertex. The Mo··Mo distance and the diamagnetism of **1** indicate the presence of a single metal–metal bond. The geometry of the $[Mo_2(S_2)_2]^{6+}$ core is similar to those previously observed in compounds such as MoS_2Cl_3 [7] and $(NH_4)_2[(S_2)_2Mo(\mu\text{-}S_2)_2Mo(S_2)_2]$ [8]. Each Mo atom is further coordinated by two bidentate dithiocarbamate ligands with Mo–S distances ranging from 2.491(2)–2.506(1) Å. The ethyl substituents of these ligands occupy chemically unique environments due to their disposition with respect to the bridging S_2^{2-} ligands. There are several intermolecular contacts in the crystal lattice involving the cations, anions and solvent of crystallization. Each F atom of the BF_4^- anions forms one contact with neighbouring entities. Thus F(1) forms a hydrogen bond to the $CHBr_3$ molecule such that F(1)··H(100) is 2.23 Å and the F(1)–H(100)–C(100) angle is 170.8°. The remaining contacts involve the bridging S_2^{2-} units such that S(1)··F(2'') is 3.094 Å, S(2)··F(3'') is 3.190 Å and S(1)··F(4) is 3.214 Å (where doubly primed atoms are related by the symmetry operation: $-x, -y, z-1$).

We are now embarking on a study of the redox behaviour and reactivity of **1** and related species.

Supplementary Material

Tables of atomic coordinates, bond lengths and angles, thermal parameters, and structure factors are available from the authors.

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