The Preparation of Binuclear Bis-diazenido Complexes of Molybdenum. The Structure of $(HNEt_3)[Mo_2(NNC_6H_5)_4(SC_6H_5)_5]$, a Triply-thiolato-bridged Species with an Unsually Long Mo–Mo Distance

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Received December 14, 1984

Although there have been extensive studies of monomeric monodiazenido complexes [1] and a number of reports, albeit rare, of monomeric bis-diazenido complexes [2], there have been no structurally characterized instances of binuclear species exhibiting the $M_2(NNR)_4$ core. Here we describe the synthesis and structural characterization of the first binuclear bis-diazenido-complex of molybdenum. Molybdenum–diazenido complexes are of intrinsic interest as potential intermediates in the abiological reduction of dinitrogen to ammonia [3], and the incorporation of thiolate ligands into the $Mo_2(NNR)_4$ core represents a fundamental development in our continuing investigations of the properties of molybdenum–thiolates [4].

Reaction of $[Mo(NNHPh)_2(\text{butane-2,3-diolate})_2]\cdot H_2NNHPh$ with excess thiophenol in methanol in the presence of NEt_3 results in a deep purple solution. Upon addition of an equal volume of diethylether, lustrous black crystals deposit. The infrared spectrum of this material exhibits bands characteristic of ν(N–N) for the *cis* bis(diazenido)-group at 1640, 1610, and 1575 cm^{-1}. The material behaves as a 1:1 electrolyte in acetonitrile. The ^1H NMR spectrum shows resonances attributable to the $-CH_2CH_3$ groups of the $(HNEt_3)^+$ and an unresolved complex multiplet arising from the thiolato and diazenido-phenyl protons. Similar spectroscopic and physical characteristics are exhibited for the analogous complexes

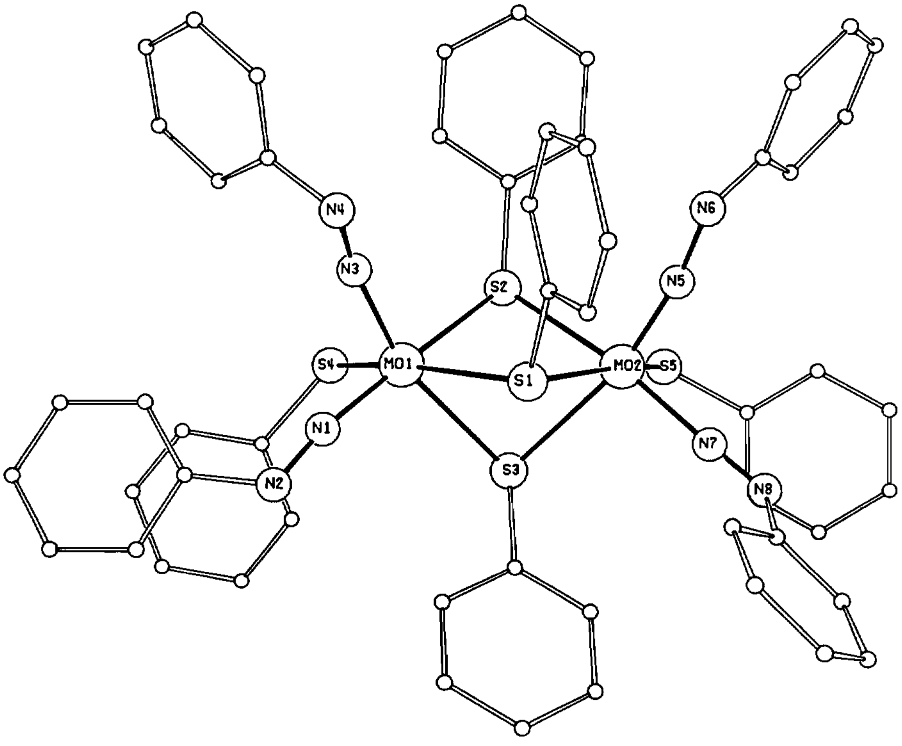

Fig. 1. ORTEP representation of $[Mo_2(NNC_6H_5)_4(SC_6H_5)_5]^-$ showing the atom-labelling scheme. Selected bond lengths (Å) and angles (°): Mo1–Mo2, 3.527(1); Mo1–S1, 2.549(5); Mo1–S2, 2.549(5); Mo1–S3, 2.635(6); Mo1–S4, 2.449(7); Mo1–N1, 1.73(1); Mo1–N3, 1.83(2); N1–N2, 1.37(2); N3–N4, 1.23(3); Mo2–S1, 2.533(5); Mo2–S2, 2.591(4); Mo2–S3, 2.653(5); Mo2–S5, 2.525(5); Mo2–N5, 1.82(1); Mo2–N7, 1.74(1); N5–N6, 1.26(2); N7–N8, 1.30(2); S1–Mo1–S4, 159.2(2); S2–Mo1–N1, 170.1(6); S3–Mo1–N3, 163.9(6); S1–Mo2–S5, 161.9(2); S2–Mo2–N7, 168.5(5); S3–Mo2–N5, 165.1(4); Mo1–N1–N2, 172.4(11); Mo1–N3–N4, 165.9(16); Mo2–N5–N6, 162.5(12); Mo2–N7–N8, 166.9(15).

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0020-1693/85/$3.30

$[Mo_2(NNR)_4(SR')_4]^-$, where $R = -C_6H_4-4\text{-}NO$ or $-C_6H_4-4\text{-}CH_3$ and $R' = -C_6H_4-4\text{-}CH_3$.

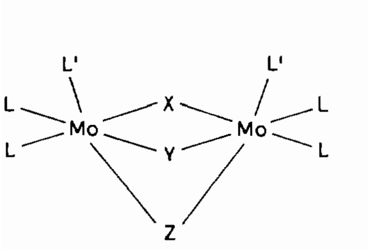
X-ray quality crystals were grown from methanol/ether solution. Crystal data: triclinic space group $P1$ with a = 10.994(2) Å, b = 12.173(2) Å, c = 24.179(4) Å, α = 91.03(1)°, β = 91.45°, γ = 109.78(1)°, V = 3042.9(12) A^3, Z = 2, D_c = 1.38 g/cm^3. The structure solution and refinement was based on 4763 reflections with $I_o \geqslant 3\sigma(I_o)$ to give a final R = 0.051. The structure of one of two crystallographically unique anions is shown in Fig. 1, together with relevant bond lengths and angles.

The complex monoanion is binuclear with equivalent pseudo-octahedral molybdenum atoms sharing a common face defined by three bridging thiolate donors. The coordination about each molybdenum atom is completed by the thiolate sulfur atom of the terminal thiophenolate groups and by the nitrogen donors of two σ-diazenido ligands.

A unique feature of the structure is absence of strong Mo–Mo interaction as suggested by the Mo–Mo distance of 3.527(1) Å. All other triply-bridged binuclear molybdenum complexes reported to date exhibit Mo–Mo distances in the range of 2.628(2) Å to 2.915(1) Å, consistent with a degree of direct metal–metal interaction [5–10]. This significant lengthening of the Mo–Mo distance is attributable to the ligation of two terminal diazenido-groups, strongly π-bonding ligands that effectively drain all the electron density which might otherwise be available for metal–metal bonding.

A further consequence of the lengthening of the Mo–Mo distance is a dramatic increase in the molybdenum-bridging thilate bond lengths and an increase in the valence angles at the bridging sulfurs, Mo1–S_b–Mo2. The comparison of bonding parameters for $[Mo_2(NNC_6H_5)_4(SC_6H_5)_5]^-$ to those reported for $[Mo_2(NNPh)(NNHPh)(SCH_2CH_2S)_3(SCH_2CH_2SH)]^{2-}$, a more typical example of a triply-bridged binuclear molybdenum complex, in Table I illustrates these points.

Concomitant to the lengthening of the Mo–Mo and Mo–S_b distances and to the expansion of the valence angles at the bridging thiolates is a significant distortion of the gross geometrical features of the $Mo_2(SR)_3$ bridge moiety. The schematic illustrates the coordination geometry of the pseudo-octahedral triply-bridged binuclear unit. A common feature



$[Mo_2O_2(SPh)_2Cl(S_2CNEt_2)_2]^+$, Z = Cl^-

TABLE I. Comparison of Structural Features of the Bridge Geometry of Triply-bridged binuclear Molybdenum-Thiolates.

Complex[a]	Mo–Mo	Mo–X	Mo–Y	Mo–Z	Mo–X–Mo	Mo–Y–Mo	Mo–Z–Mo	X–Mo–Y	Mo_2S_2 Dihedral Angle	Mo Displacement	Ref.
$[Mo_2(N_2C_6H_5)_4(SC_6H_5)_5]^-$	3.527(1)	2.570(6)	2.644(6)	2.487(6)	86.7(1)	83.7(1)	87.9(2)	108.6(2)	113.5	0.04	This work
$[Mo_2(NNHPh)(NNPh)(SCH_2CH_2S)_3(SCH_2CH_2SH)]^{2-}$	2.837(2)	2.424(6)	2.431(6)	2.577(6)	71.0(1)	71.7(1)	66.9(1)	79.5(1)	172.7	0.45	4
$[Mo_2O_2(SPh)_2Cl(S_2CNEt_2)_2]^+$	2.822(2)	2.455(2)	2.460(3)	2.613(3)	70.0	70.2	65.4	109.9(1)	177.7	0.40	6

[a] Abbreviations: X, Y, Z are the bridging donor groups as defined in the schematic diagram for $[Mo_2O_2(SPh)_2Cl(S_2CNEt_2)_2]^+$, Z = Cl^-.

of structures of this type is the planarity of the Mo_2S_2 fragment, involving the thiolate donors occupying two positions on the equatorial plane about each Mo defined by X, Y and the two terminal ligands L. The axial position L′ is invariably occupied in these structures by a strongly π-bonding ligand, such as oxo- or diazenido-donors. The second axial site, bridging and *trans* to the π-bonding group, exhibits a significant *trans* influence, presenting an unusually long Mo–Z distance. In contrast, the Mo_2S_2 rhombus in $[Mo_2(NNC_6H_5)_4(SC_6H_5)_5]^-$ is distinctly non-planar, with a dihedral angle of 113.5°. Furthermore, the π-bonding diazenido-groups occupy the equatorial plane approximately *trans* to the bridging thiolato donors S2 and S3.

The structure illustrates the remarkable flexibility of the triply-bridged geometry in stabilizing binuclear molybdenum complexes. Furthermore, the persistence of the bis-diazenido molybdenum unit suggests that this represents a robust structural fragment that should prove useful in probing the chemistry of molybdenum–thiolate systems. Unlike the *cis*-oxomolybdenum unit MoO_2^{2+}, the $[Mo(NNR)_2]$ moiety undergoes considerable chemistry of its own such as protonation, alkylation, and N–N bond cleavage and, furthermore, appears to allow *trans* thiolato coordination, which the oxo-group apparently precludes [11].

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