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Molybdenum–Hydrazido(2–) Complexes with Tridentate Thiolate Ligands

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Recent EXAFS [1] studies of nitrogenase and other molybdo-proteins have stimulated interest in molybdenum complexes with sulfur ligands. However, none of the complexes so far reported bind or activate dinitrogen. In fact, there are very few examples of molybdenum–sulfur complexes which interact with small molecules that can function as inhibitors or alternative substrates for nitrogenase or indeed with any ligands relevant to nitrogen fixation. Hydrazido(2–) complexes are proven intermediates in both protonation [2] and the alkylation

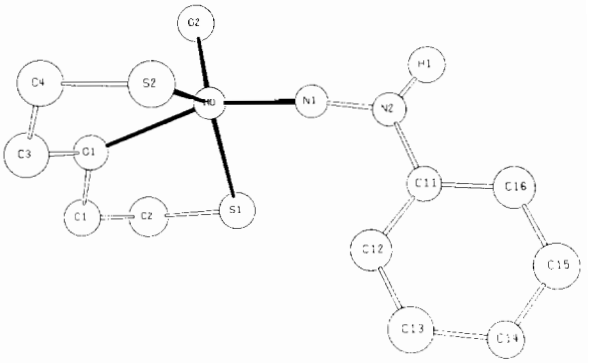

Fig. 1. Perspective view of the structure of [MoO(NNHPh)-$SCH_2CH_2OCH_2CH_2S$)], *I*. Mo-S1, 2.354(3); Mo–S2, 2.357(3); Mo–O1, 2.197(6); Mo–O3, 1.700(7); Mo–N1, 1.766(9); S1–Mo–S2, 133.6(1); S1–Mo–O1, 79.0(2); S2–Mo–O1, 79.8(2); O2–Mo–N1, 107.88(3); Mo–N1–N2, 173.2(6).

[3] or coordinated dinitrogen. This paper reports their use to probe the properties of a molybdenum site ligated to thiolate-containing ligands of the type L = $HSCH_2CH_2XCH_2CH_2SH$, where X = NR, PR, O, and S.

TABLE I. Comparison of Mo–N–N Geometries in Molybdenum–hydrazido and Molybdenum–diazenido Complexes.

Complex	Mo–N	N–N	Mo–N–N	Ref.
a. Six coordinate Mo				
$[MoO(N_2R_2)(dtc)_2]$[a]	1.799	1.29	168.0	7
$[Mo(N_2Ph_2)(dtc)_2]$	1.790	1.31	169.9	8
$[Mo(N_2PhMe)_2(dtc)_2]$	1.790	1.30	172.6	9
$[MoO(N_2Ph_2)(S_2N_2)]$[b]	1.778	1.309	172.9	10
$[Mo(N_2Ph)(S_2N_2)]$	1.82	1.28	170.4	10
$[MoO(N_2Me_2)(C_9H_6NO)_2]$	1.800	1.28	155.5	11
$[S_2MoS_2Mo(N_2Me_2)_2S_2MoS_2]^{2-}$	2.15	1.19	167.0	12
b. Seven coordinate Mo				
$[Mo(N_2Ph)(dtc)_3]$	1.781	1.233	171.5	13
$[Mo(N_2PhEt)(dtc)_3]^+$	1.715	1.37	170.0	14
$[Mo(N_2MePh)(NHHMePh)(dtc)_2^+$	1.75	1.29	169.6	15
$[Mo(N_2CO_2Me)(NHNHCO_2Me)(dtc)_2]$	1.74	1.30	177.1	16
$[Mo(NNMe_2)(SPS)]$[e]	1.775	1.265	178.3	
c. Five coordinate Mo				
$[MoO(N_2Me_2)(SPh)_3]^+$	1.806	1.30	176.7	17
$[MoO(N_2Me_2)(SSS)]$[c]	1.78	1.29	176.2	18
$[MoO(N_2Me_2)(SOS)]$[d]	1.79	1.29	174.3	This work
$[MoCl(N_2Me_2)_2(PPh_3)_2]^+$	1.761	1.25	173.9	19
$[S_2MoS_2Mo(N_2Me_2)_2(PPh_3)_2]$	1.78	1.30	165.0	20
	1.80	1.27	178.2	

[a]dtc = dithiocarbamate, $(S_2CNR_2)^-$. [b]S_2N_2 = $(SCH_2CH_2NRCH_2CH_2NRCH_2CH_2S)^-$. [c]SSS = $(SCH_2CH_2SCH_2CH_2S)^{2-}$. [e]SPS = $(SCH_2CH_2PPLCH_2CH_2S)^{2-}$.

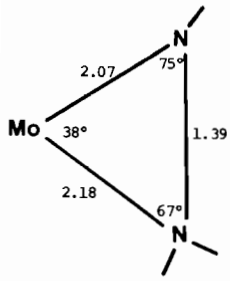

Fig. 2. Schematic representation of the 'side-on' bonding exhibited by hydrazido (1–) ligands.

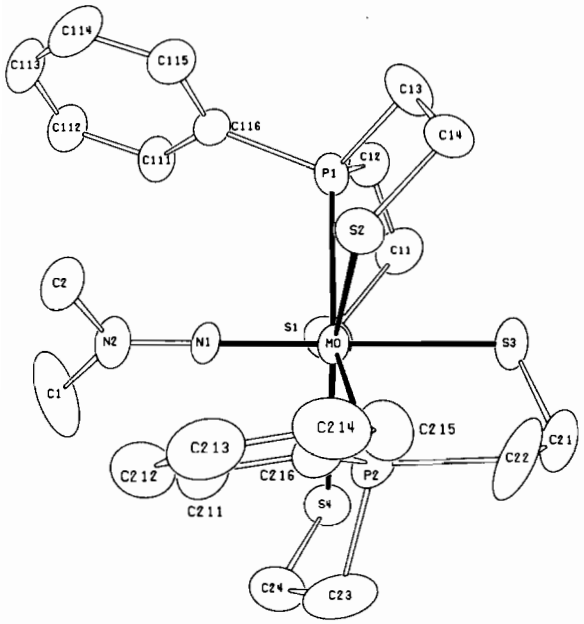

Fig. 3. ORTEP diagram of the structure of $[Mo(NNME_2)(SCH_2CH_2PPhCH_2CH_2S)_2]$. Mo–S1, 2.505(3); Mo–S2, 2.519(3); Mo–S3, 2.498(3); Mo–S4, 2.499(3); Mo–P1, 2.519(3); Mo–P2, 2.515(2); Mo–N1, 1.775(6); Mo–N1–N2, 178.3(5). Details of the structural study will appear elsewhere.

The synthesis and structural characterization of the precursor species $Mo_2O_3L_2$, where X = NR, O and S have been described elsewhere [4, 5]. Reactions of these complexes with phenylhydrazine result in the isolation of yellow, diamagnetic monomers $MoO(NNHC_6H_5)L$, *I*, whose structure is illustrated in Fig. 1. Reaction of *I* with Me_3SiCl in dry methanol results in protonation of the hydrazido-ligand to give the hydrazido(1–) species, $[MoO(N_2H_2Ph)L]^+$, *III*, isolated as the BPh_4^- salt. Protonation appears to occur at the metal-bound nitrogen to give the dihapto-coordination type previously described for $[Mo(dtc)_3(NNMePh)]BPh_4$ [6], shown schematically in Fig. 2.

Reactions of the precursor materials with disubstituted hydrazines, such as H_2NNMe_2, yield exclusively bis-hydrazido(2–) complexes, of the type $Mo(NNMe_2)_2L$, deep purple, diamagnetic monomeric materials, whose structural identification is in progress.

When L is $^-SCH_2CH_2PPhCH_2CH_2S^-$, the major product isolated upon reaction of the molybdenum precursor with disubstituted hydrazines is $[Mo(NNMe_2)L_2]$, *II*, a seven coordinate diamagnetic monomer, whose coordination geometry is illustrated in Fig. 3.

The geometry of the molybdenum-hydrazido(2–) grouping is similar for both *I* and *II*. Linear Mo–N–N moieties, with considerable double bond character in both the Mo–N and N–N bonds, are common to the structural chemistry of molybdenum-hydrazido-(2–) species, as illustrated in Table I. The exceptions to the common geometric type $[Mo_3S_8(NNMe_2)_2]^{2-}$ [7] and $[MoO(NNPh_2)(oxime)_2]$ [8] show unusual protonation chemistry and suggest that the course of protic degradation reactions of metal-bound hydrazides are sensitive to the M–N–N geometry.

Crystal Data. Complex *I*, $MoC_{10}H_{14}O_2N_2S_2$, crystallizes in the triclinic space group $P\bar{1}$ with a = 9.307(2) Å, b = 11.108(3) Å, c = 14.139(3) Å, α = 89.7(1)°, β = 91.88(1), γ = 107.91(2)°, V = 1390.0(9) Å^3 and Z = 4 to give D_{calc} = 1.69 g cm^{-3} and μ = 12.15 cm^{-1} (MoKα, λ = 0.71069 Å). A total of 1956 reflections with $I \geqslant 3.0\sigma(I)$ formed the basis for a full-matrix least squares refinement. Analysis converged at R = 0.045 and R_w = 0.042, with a 'goodness of fit' of 1.21.

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Monomeric Mo(V) and Mo(VI) Complexes with Sterically Constrained Metal Centers

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Bray has proposed a chemical mechanism for the reduction of xanthine oxidase by xanthine, which involves a monomeric molybdenum active center having *fac* stereochemistry [1]. This proposal has simulated our interest in preparation and characterization of monomeric Mo(V) and Mo(VI) complexes constrained to *fac* configuration by polydentate ligands such as hydrotris(3,5-dimethylpyrazolyl) borate, hereafter designated as $HB(Me_2pz)_3^-$.

The $HB(Me_2pz)_3^-$ ligand has been extensively used to stabilize a variety of low valent molybdenum compounds [2]. Moreover, the same ligand has been found to stabilize the Mo(V) center in $MoOCl_2\{HB(Me_2pz)_3\}$(*I*) [3]. The relative stability of these compounds is attributed partly to the steric bulk of 3-methyl group on the ligand.

Mo(V) complexes of the type $MoOXY\{HB(Me_2pz)_3\}$ (where X = Y = NCS; X = Cl, Y = OR or SPh; X = Y = SPh) have been prepared by the substitution reactions of *I* and spectroscopically characterized. Esr spectra of Mo(V) centers are sensitive to X and Y. Substitutions by thiolate ligands give smaller A_o(Mo) and larger g_o values. These substitutions also shift the Mo=O stretching vibration significantly to lower wave numbers. A preliminary kinetic study has revealed that the rates of ligand substitution are very slow in these complexes, compared to those of known $MoOCl_3L_2$ complexes (where L is a monodentate ligand) [4].

Mo(VI) complexes of the type $MoO_2X\{HB(Me_2pz)_3\}$ (X = Cl, Br, NCS) have been synthesized for the first time by the reaction of MoO_2X_2 (X = Cl, Br) or $MoO_2(NCS)_4^{2-}$ with the ligand, and characterized by spectroscopic methods including ^{95}Mo NMR.

Electrochemical studies and structural studies on these Mo(V) and Mo(VI) complexes will also be described.

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Active Site Fe^{3+} Ligation by Substrates and Transition State Analogs of Protocatechuate 3,4 Dioxygenase

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Current proposals for the mechanism [1] of Protocatechuate (PCA) 3,4 Dioxygenase (3,4 PCD) suggest monodentate (OH) binding of PCA to the active site Fe^{3+}. This would promote ketonization of PCA, thereby creating a carbanion at C-4 which could be directly attacked by O_2. We have tested this proposal using ketonized substrate analogs and various spectroscopic probes. Our results confirm that ketonization is an essential step in the mechanism, but suggest that it occurs later in the cycle than the initial substrate complex.

We have shown that water is a ligand for *Brevibacterium fuscum* 3,4 PCD by observing hyperfine broadening from $^{17}OH_2$ on all EPR resonances of the high spin Fe^{3+} [2]. The spectrum of the 3,4 PCD-PCA complex is too broad to detect direct displacement of H_2O by PCA. However, no broadening is observed in complexes with three slowly metabolized substrate analogs. In contrast, water remains bound in complexes with non-metabolized, monodentate analogs (*e.g.* 4-OH benzoate). Other small molecules also bind to Fe in 3,4 PCD. CN^- binds in two steps; first it forms a high spin and then a low spin complex. It is likely that 2 CN^- molccules bind sequen-