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Monodentate Dialkyldithiocarbamate Complexes of Molybdenum(III). The Synthesis and X-ray Structural Characterization of $\{HB(3,5\text{-}Me_2C_3N_2H)_3\}Mo(S_2CNEt_2)(\eta^1\text{-}S_2CNEt_2)$

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Despite the rich chemistry shared by the early transition metals and dithiocarbamate ligands, $S_2CNR_2^-$, monodentate coordination of these ligands is almost exclusively restricted to transition metals of groups[†] 8 to 11 [1][**]. To date, $(\eta^5\text{-}C_5H_5)W(\eta^1\text{-}S_2CNMe_2)(CO)_3$ [2] is the only structurally characterized monodentate dithiocarbamate complex of the group 3 to group 7 transition metals. We report here the first preparation and X-ray structural characterization of monodentate dialkyldithiocarbamate complexes of molybdenum.

The anaerobic reaction of $Et_4N[\{HB(Me_2pz)_3\}Mo(CO)_3]$ [3] $\{HB(Me_2pz)_3^-$ = hydrotris(3,5-dimethylpyrazolyl)borate anion$\}$ with tetraalkylthiuram disulfides, $R_2NC(S)SSC(S)NR_2$, in refluxing acetonitrile results in the formation of yellow (R = Me, **1**) or orange (R = Et, **2**) crystals of the monomeric Mo(III) complexes $\{HB(Me_2pz)_3\}Mo(S_2CNR_2)_2$ (*ca.* 50% yield). The somewhat air sensitive complexes were formulated on the basis of elemental analyses and the following physical and spectroscopic data. The infrared spectra of the complexes exhibit bands due to $HB(Me_2pz)_3^-$ $\{\nu(BH)$, 2540 cm$^{-1}\}$, bidentate $S_2CNR_2^-$ $\{e.g.$, 2 $\nu(CN)$, 1504; $\nu(CS)$, 987 cm$^{-1}\}$, and monodentate $S_2CNR_2^-$ $\{e.g.$, 2 $\nu(CN)$, 1475; $\nu(CS)$, 987 and 1005 cm$^{-1}\}$ ligands. No bands due to terminal oxo- or sulfido-ligands are present. Magnetic properties (**1**, μ = 3.93 B.M.; **2**, μ = 3.84 B.M.) are consistent with a d^3 (S = 3/2) electron configuration. The formulation of the complexes as six-coordinate Mo(III) monomers, $\{HB(Me_2pz)_3\}Mo(S_2CNR_2)(\eta^1\text{-}S_2CNR_2)$, was confirmed by the X-ray crystal structure of **2**, using a crystal grown from a dichloromethane/methanol mixture, and sealed in a capillary.

Crystal Data

$C_{25}H_{42}BMoN_8S_4$, triclinic, space group $P\bar{1}$, a = 10.162(4), b = 11.089(4), c = 31.10(1) Å, α = 88.49(3), β = 86.34(3), γ = 68.37(3)°, V = 3251(3) Å^3, Z = 4. Data were collected on a Syntex $P2_1$ diffractometer using graphite monochromated Mo Kα radiation. The structure solution, performed by Patterson and difference Fourier methods, was based on 5547 reflections with $I_o > 3.0\sigma(I_o)$. The current R value is 0.043 (R_w = 0.049).

The unit cell of **2** contains two independent molecules of nearly identical structure (Fig. 1).

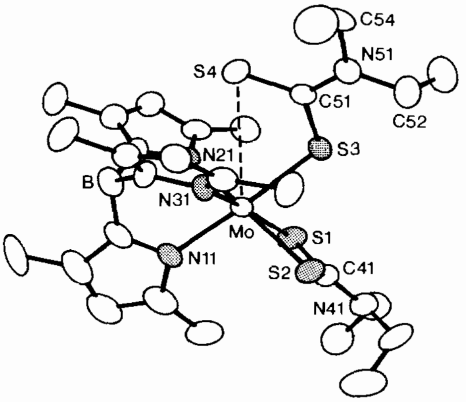

Fig. 1. Molecule **2** of $\{HB(Me_2pz)_3\}Mo(S_2CNEt_2)(\eta^1\text{-}S_2CNEt_2)$ (hydrogen atoms excluded) and a partial atom labelling scheme. Selected bond lengths (Å) and angles (deg) are: Molecule **1**, Mo–S1, 2.503(2); Mo–S2, 2.500(2); Mo–S3, 2.481(2); Mo–S4, 3.820(2); Mo–N11, 2.228(4); Mo–N21, 2.150(4); Mo–N31, 2.162(4); S3–C51, 1.753(5); S4–C51, 1.667(6) Å; S1–C41–S2, 115.1(3); S3–C51–S4, 123.1(3); Mo–S3–C51, 115.3(2); Mo–S1–C41, 86.6(2); Mo–S2–C41, 87.7(2)°. Molecule **2**, Mo–S1, 2.492(2); Mo–S2, 2.503(2); Mo–S3, 2.471(2); Mo–S4, 3.834(2); Mo–N11, 2.217(4); Mo–N21, 2.175(4); Mo–N31, 2.153(4); S3–C51, 1.753(5); S4–C51, 1.678(5) Å; S1–C41–S2, 114.9(3); S3–C51–S4, 122.1(3); Mo–S3–C51, 113.0(2); Mo–S1–C41, 87.3(2); Mo–S2–C41, 87.3(3)°.

The major structural difference in the two molecules is in the tilting of the S_2CNC_2 plane of the monodentate ligand away from the plane passing through Mo, C41, N41, and the pyrazolyl ring containing N11. The dihedral angle between these planes is 8.8° in molecule **1** and 26.2° in molecule **2**. The monomeric molecules possess pseudo-octahedral coordination geometries constructed from *facially* coordinated $HB(Me_2pz)_3^-$, bidentate $S_2CNEt_2^-$ and monodentate $S_2CNEt_2^-$ ligands. Bond lengths and angles within the tridentate and bidentate ligands are

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[†] The periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 to 12, and the p-block elements comprise groups 13 to 18.

[**] Monodentate dithiocarbamate ligation has been structurally confirmed in the following cases: $Ru(S_2CNEt_2)_3(NO)$ [1a]; $Au(S_2CNEt_2)_3$, [1b]; $Pt(S_2CNBu^i_2)_2(PMe_2Ph)_2$ [1c]; $Pt(S_2CNEt_2)_2(PPh_3)$ [1d].

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comparable to values found elsewhere [4*, 5**]. For **2**, the Mo–S distances only range from 2.471(2) to 2.503(2) Å; the shortest Mo–S distances pertain to the monodentate ligands. The nonbonding Mo–S4 distances (*ca.* 3.83 Å) are larger than the sum of the covalent or van der Waals radii for these two elements [2]. The S3–C51–S4 angles of the monodentate ligands are *ca.* 8° larger than the S1–C41–S2 angles of the chelated ligands, however, the other structural features of the monodentate ligands are indicative of considerable thioureide character. The S3–C51 distances of 1.749(5) Å are only slightly longer than the S–C bonds of the bidentate ligands (1.732(6) Å), while the S4–C51 bonds (*ca.* 1.67 Å) are longer than a normal C=S bond (1.61 Å, [6]). The short C–N bond distances of 1.33(1) Å, and their equality with the analogous bonds of the bidentate ligands, also indicate extensive π-bonding in the S_2CN portion of the monodentate ligand [6†]. Moreover, the monodentate ligands are nearly planar with an average dihedral angle of *ca.* 8.5° between the planes defined by S3, C51, S4 and N51, C52, C54.

These η^1-dithiocarbamate complexes may also be considered models for an associative transition state in six-coordinate Mo(III) substitution reactions. The uncoordinated sulfur atom occupies a capping position above an SN_2 face of the pseudo-octahedron, the S–N interatomic distances being comparable to the sum of the van der Waals radii (3.34 Å) for these elements (S4–N21, 3.31 Å average; S4–N31, 3.38 Å average). Indeed, prolonged reaction times result in the formation of $Mo(S_2CNR_2)_4$, presumably by the further substitution of $S_2CNR_2^-$ for $HB(Me_2pz)_3^-$. It is unclear at present whether the substitution reactions precede, follow, or are concomitant with the further oxidation of the metal centre.

The preparation of these η^1-dialkyldithiocarbamatomolybdenum complexes by the oxidative decarbonylation of $[\{HB(Me_2pz)_3\}Mo(CO)_3]^-$ with tetraalkylthiuram disulfides probably involves a Mo(II) intermediate such as $[\{HB(Me_2pz)_3\}Mo(S_2CNR_2)_2]^-$. Further oxidation of the Mo(II) species by tetraalkylthiuram disulfide leads to the title complexes. It is likely that the sterically bulky *fac*-tridentate $HB(Me_2pz)_3^-$ ligand restricts the Mo atom to six-coordination, thereby forcing the monodentate coordination of the dithiocarbamate ligand. Oxidative addition of tetraalkylthiuram disulfides to other molybdenum complexes containing bulky *fac*-tridentate ligands, e.g., $(Me_3[9]aneN_3)Mo(CO)_3$ [7], may prove a general route to six-coordinate η^1-$S_2CNR_2^-$ complexes.

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*For $HB(Me_2pz)_3^-$.

**For $S_2CNEt_2^-$.

†Respective single and double bond distances are: C–N, 1.47 Å; C=N, 1.27 Å; C–S, 1.81 Å; C=S, 1.61 Å.