

and (2) are  $1.4 \times 10^{-4}$  and  $1.6 \times 10^{-4} \text{ s}^{-1}$ , respectively. It is clear that the larger the reaction cavity, the greater the rate constant. Such a relationship has been found for the polymorphic crystals of the 3-methylpyridine complex. This may indicate that the  $\beta$ - $\alpha$  photoisomerization is controlled by the crystal-line lattice in the early stages and that the size of the reaction cavity in the initial structure is a good guide when elucidating the reaction rate.

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## Structure of [Hydrotris(3,5-dimethyl-1-pyrazolyl)borato]dipropyldithiocarbamatoxomolybdenum(IV)

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**Abstract.** C<sub>22</sub>H<sub>36</sub>BMoN<sub>7</sub>OS<sub>2</sub>,  $M_r = 585.46$ , monoclinic,  $P2_1/n$ ,  $a = 9.753$  (2),  $b = 20.890$  (2),  $c = 14.065$  (2) Å,  $\beta = 106.07$  (1)°,  $V = 2753.6$  Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.41$ ,  $D_x = 1.41 \text{ g cm}^{-3}$ , Mo  $K\alpha$ ,  $\lambda = 0.71073$  Å,  $\mu = 6.4 \text{ cm}^{-1}$ ,  $F(000) = 1216$ ,  $T = 295 \text{ K}$ ,  $R = 0.046$ ,  $wR = 0.051$  for 3662 reflections. The central Mo atom adopts a distorted octahedral coordination geometry in which one face of the octahedron is occupied by the tridentate hydrotris(3,5-dimethyl-1-pyrazolyl)borate ligand and the opposite face by an oxo and dipropyldithiocarbamate ligand. The structure of the mononuclear complex is compared with that of the analogous diethyldithiocarbamate complex.

**Introduction.** Interest in metal oxo compounds has gained considerable momentum in recent years owing to the role of metal oxo species in certain catalytic processes of biological (Spiro, 1985) and industrial importance (Nugent & Mayer, 1988). These include the presence of mononuclear oxomolybdenum species in molybdenum hydroxylases (Bray, 1980; Spence, 1983; Cramer, 1983). The bulky hydrotris(3,5-dimethyl-1-pyrazolyl)borate ligand (L)

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has been utilized to prepare oxomolybdenum complexes with unusual structural features and to prevent the formation of polynuclear species. Compounds such as  $LMoOX_2$  ( $X =$  halide, pseudohalide, alkoxide, thiolate) (Cleland, Barnhart, Yamanouchi, Collison, Mabbs, Ortega & Enemark, 1987) and  $LMoO(S_2CNR_2)$  ( $R = \text{Me, Et, Pr, Bu}$ ) (Young, Roberts, Ortega & Enemark, 1987) have been prepared and characterized. We have recently prepared a series of vanadyl complexes of the form  $LVO(S_2CNR_2)$  ( $R = \text{Me, Et, Pr, Bu}$ ) (Sit, Collison, Mabbs & Cleland, 1989) and are investigating the detailed electron spin resonance spectra of these species in dilute single crystals. Crystals of the analogous  $LMoO(S_2CNR_2)$  complexes serve as diamagnetic host lattices for these studies. We herein report the structure of one of these complexes,  $LMoO(S_2CNPr_2)$ .

**Experimental.** The complex was prepared by the method of Young *et al.* (1987). Emerald green crystals obtained by liquid–liquid diffusion of methanol into a methylene chloride solution of  $LMoO[S_2CN(C_3H_7)_2]$  at 298 K, dimensions  $0.4 \times 0.25 \times 0.20$  mm, mounted on a glass fiber with cyanoacrylate glue,  $D_m$  by flotation ( $ZnBr_2$  and

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Table 1. Refined positional parameters and their estimated standard deviations

	x	y	z	B*(Å <sup>2</sup> )
Mo	0.88961 (4)	0.17146 (2)	0.89557 (3)	2.618 (6)
S1	0.9368 (1)	0.16961 (7)	1.07549 (8)	3.31 (2)
S2	0.7814 (1)	0.26670 (7)	0.94681 (9)	3.78 (3)
O	1.0441 (3)	0.2017 (2)	0.8852 (2)	3.72 (8)
N11	0.6695 (4)	0.1098 (2)	0.8809 (3)	2.89 (8)
N12	0.6363 (4)	0.0649 (2)	0.8055 (3)	2.79 (8)
N21	0.9495 (4)	0.0740 (2)	0.8709 (3)	2.84 (8)
N22	0.8781 (4)	0.0400 (2)	0.7883 (3)	3.03 (8)
N31	0.7866 (4)	0.1777 (2)	0.7368 (3)	2.95 (8)
N32	0.7271 (4)	0.1249 (2)	0.6818 (3)	2.96 (8)
N41	0.8588 (4)	0.2803 (2)	1.1462 (3)	3.69 (9)
C11	0.5710 (5)	0.1024 (2)	0.9308 (3)	3.1 (1)
C12	0.4764 (5)	0.0536 (3)	0.8881 (4)	3.7 (1)
C13	0.5210 (5)	0.0312 (2)	0.8096 (3)	3.3 (1)
C14	0.5677 (5)	0.1408 (3)	1.0185 (3)	4.0 (1)
C15	0.4591 (7)	-0.0221 (3)	0.7389 (4)	5.6 (2)
C21	1.0723 (5)	0.0424 (2)	0.9118 (3)	3.0 (1)
C22	1.0788 (5)	-0.0113 (3)	0.8556 (4)	3.7 (1)
C23	0.9559 (5)	-0.0120 (2)	0.7790 (4)	3.5 (1)
C24	1.1769 (5)	0.0642 (3)	1.0054 (4)	4.0 (1)
C25	0.9064 (7)	-0.0603 (3)	0.6973 (4)	5.2 (1)
C31	0.7728 (5)	0.2265 (3)	0.6740 (3)	3.2 (1)
C32	0.7048 (5)	0.2063 (3)	0.5787 (4)	3.8 (1)
C33	0.6764 (5)	0.1426 (3)	0.5856 (3)	3.6 (1)
C34	0.8284 (6)	0.2921 (3)	0.7069 (4)	4.3 (1)
C35	0.6018 (7)	0.0961 (3)	0.5056 (4)	5.5 (2)
C41	0.8594 (5)	0.2443 (2)	1.0691 (3)	3.2 (1)
C42	0.7916 (6)	0.3439 (3)	1.1338 (4)	4.9 (1)
C43	0.6341 (7)	0.3415 (3)	1.1268 (5)	6.2 (2)
C44	0.5704 (8)	0.4081 (4)	1.1078 (6)	9.3 (2)
C45	0.9374 (6)	0.2598 (3)	1.2476 (4)	5.0 (1)
C46	0.8496 (7)	0.2451 (4)	1.3173 (5)	8.2 (2)
C47	0.7556 (9)	0.1922 (5)	1.2864 (6)	6.9 (2)
C47'	0.866 (4)	0.195 (2)	1.382 (2)	6.9 (8)
B	0.7249 (6)	0.0594 (3)	0.7315 (4)	3.1 (1)

\*Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:  $\frac{1}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$ .

Table 2. Selected interatomic distances (Å) and bond angles (°)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Mo—O	1.676 (4)	Mo—N31	2.184 (3)
Mo—S1	2.444 (1)	S1—C41	1.725 (5)
Mo—S2	2.451 (1)	S2—C41	1.741 (5)
Mo—N11	2.462 (4)	C41—N41	1.320 (6)
Mo—N21	2.171 (4)		
O—Mo—S1	100.4 (1)	Mo—S1—C41	88.7 (2)
O—Mo—S2	100.9 (1)	Mo—S2—C41	88.1 (2)
O—Mo—N11	166.7 (2)	S2—Mo—N31	98.0 (1)
O—Mo—N21	93.0 (2)	S2—Mo—N21	164.6 (1)
O—Mo—N31	93.4 (1)	N11—Mo—N21	76.3 (1)
S1—Mo—S2	71.42 (4)	N11—Mo—N31	78.6 (1)
S1—Mo—N11	89.34 (9)	N31—Mo—N21	87.7 (1)
S1—Mo—N31	164.0 (1)	S1—C41—N41	125.0 (3)
S1—Mo—N21	99.7 (1)	S2—C41—N41	124.0 (4)
S2—Mo—N11	90.7 (1)	S1—C41—S2	111.1 (3)

H<sub>2</sub>O). Monoclinic crystal class, limiting conditions identified space group  $P2_1/n$  ( $h0l$ :  $h + l = 2n$ ;  $0k0$ :  $k = 2n$ ), 20 reflections for measuring lattice parameters,  $16 \leq 2\theta \leq 28^\circ$ . Enraf-Nonius CAD-4 diffractometer, graphite-monochromated Mo  $K\alpha$  (0.71073 Å),  $\mu = 6.4 \text{ cm}^{-1}$ .  $\theta$ - $2\theta$  scans,  $2\theta_{\text{max}} = 60^\circ$ ,

$0 \leq h \leq 13$ ,  $0 \leq k \leq 29$ ,  $-19 \leq l \leq 18$ , standard reflection  $\bar{1}20$ , no decay, no correction made. 8650 data measured, 7792 unique data, 3662 with  $F_o > 3\sigma(F_o)$  used in refinement.  $R_{\text{int}} = 0.032$ . Coordinates of Mo from Patterson, 34 non-H atoms from difference electron density maps. Full-matrix least squares on  $F$ , all non-H atoms anisotropic. H atoms included at calculated positions but not refined. Final refinement of  $F$  (3662 reflections, 316 parameters) resulted in  $R = 0.046$ ,  $wR = 0.051$ , where  $w = 4F_o^2/[\sigma^2(I) + (pF_o^2)^2]$  with  $p$  set to 0.04,  $(\Delta\rho)_{\text{max}} = 0.87 \text{ e } \text{Å}^{-3}$  near Mo,  $(\Delta\rho)_{\text{min}} = -1.49 \text{ e } \text{Å}^{-3}$  near Mo,  $(\Delta/\sigma)_{\text{max}} = 0.0$ . Disorder was found in the last C atom of one of the propyl groups, atom C47' was added at 0.20 occupancy and refined.  $(\Delta/\sigma)$  for this atom was zero after three cycles. Atomic scattering factors from Cromer & Waber (1974) and anomalous-dispersion factors from Cromer (1974). Programs *SDP* (Frenz, 1978) run on a MicroVAX II.

**Discussion.** Atomic coordinates with standard deviations are listed in Table 1 and selected interatomic distances and bond angles in Table 2. The molecular structure is shown in Fig. 1.\* The structure consists of discrete mononuclear molecules of  $[\text{HB}(\text{C}_5\text{H}_7\text{N}_2)_3]\text{MoO}[\text{S}_2\text{CN}(\text{C}_3\text{H}_7)_2]$ . Each Mo atom adopts a distorted octahedral coordination geometry. The structural constraints of the ligand,  $L$ ,

\* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53292 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

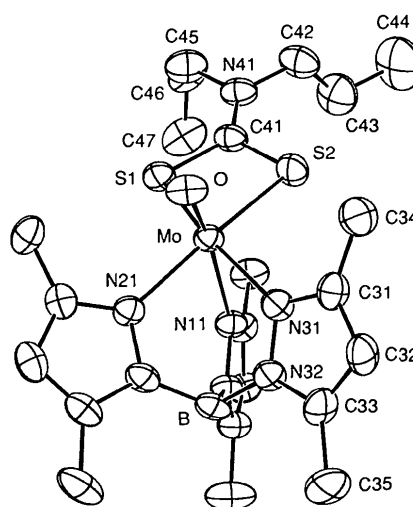


Fig. 1. The structure of  $[\text{HB}(\text{C}_5\text{H}_7\text{N}_2)_3]\text{MoO}[\text{S}_2\text{CN}(\text{C}_3\text{H}_7)_2]$ . The atom numbering for the unlabeled pyrazole rings follows the same pattern as the labeled ring.

require that it occupy a facial stereochemical position of an octahedron. This in turn requires the oxo group and each S atom of the dithiocarbamate ligand to be mutually *cis* to each other. The molecule has approximate C<sub>s</sub> symmetry with the plane of symmetry containing the pyrazole ring possessing N11 of L, Mo, O, and C41, N41 of the dithiocarbamate. Overall C<sub>s</sub> symmetry is broken by the two different conformations of the propyl groups of the dithiocarbamate.

The Mo—O distance [1.676 (4) Å] is equal to the average reported for a large number of oxomolybdenum(IV) complexes (1.678 Å) and is also essentially the same as the Mo—O distance for the analogous diethyldithiocarbamate complex [1.669 (3) Å] (Young *et al.*, 1987). In a statistical treatment of the structural data on 122 molybdenum monooxo complexes (Mayer, 1988), it was found that mean Mo—O distances for Mo<sup>VI</sup>, Mo<sup>V</sup>, and Mo<sup>IV</sup> complexes are 1.674, 1.677 and 1.678 Å, respectively. Further, the narrow range of Mo—O values was found to be insensitive to coordination number as well as to oxidation state. This phenomenon has been explained in terms of the high Mo—O bond strength (Mayer, 1988). Comparison of the Mo—O bond distance of the title complex with that of the closely related Mo<sup>V</sup> complex, LMoO(SPh)<sub>2</sub> (Cleland *et al.*, 1987), shows that they are identical [1.676 (4) Å], in agreement with the findings mentioned above.

The Mo—N11 bond distance is elongated by 0.28 Å relative to Mo—N21 and Mo—N31, owing to the *trans*-labilizing effect of the oxo group. A lengthening of the Mo—N11 bond in LMoO(S<sub>2</sub>CNEt<sub>2</sub>) is also observed and is of identical magnitude. The Mo atom is displaced 0.267 Å

toward the O atom above the plane defined by S1,S2,N21,N31 and is 0.32 Å above the plane containing S1,S2,C41,N41. Analogous displacements for the Mo atom in LMoO(S<sub>2</sub>CNEt<sub>2</sub>) are 0.276 Å and 0.33 Å, respectively (Young *et al.*, 1987). Bond distances and angles within the S<sub>2</sub>CNC<sub>2</sub> portions of —S<sub>2</sub>CNPr<sub>2</sub> are very similar to those of the analogous —S<sub>2</sub>CNEt<sub>2</sub> complex (Young *et al.*, 1987). The bond distances and angles in the hydrotrispyrazolyborate ligand, L, are normal (Cleland *et al.*, 1987).

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## Structures of Trichlorobis(*N,N,N',N'*-tetramethylurea)indium(III) and Trichlorobis(*N,N,N',N'*-tetramethylthiourea)indium(III)

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**Abstract.** (1) Trichlorobis(*N,N,N',N'*-tetramethylurea)indium(III), [InCl<sub>3</sub>(C<sub>10</sub>H<sub>24</sub>N<sub>4</sub>O<sub>2</sub>)], *M<sub>r</sub>* = 453.3,

monoclinic, C2/c, *a* = 18.687 (3), *b* = 8.112 (2), *c* = 17.929 (2) Å, β = 134.91 (2)°, *V* = 1924.8 Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.56 g cm<sup>-3</sup>, λ(Mo Kα) = 0.71069 Å, μ = 17.5 cm<sup>-1</sup>, *F*(000) = 912, *R* = 4.1% for 1595 reflec-

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