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Structure of Oxobis(phenolato)[tris(3,5-dimethyl-1-pyrazolyl)hydroborato]molybdenum(V)

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Abstract. $C_{27}H_{32}BMoN_6O_3$, $M_r = 595{\cdot}34$, monoclinic, $P2_1/n$, $a = 16{\cdot}376\ (6)$, $b = 10{\cdot}438\ (5)$, $c = 17{\cdot}016\ (8)$ Å, $\beta = 107{\cdot}25\ (3)°$, $V = 2777{\cdot}8$ Å^3, $Z = 4$, $D_m = 1{\cdot}37$, $D_x = 1{\cdot}43$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 5{\cdot}02$ cm^{-1}, $F(000) = 1228$, $T = 296$ K, $R = 0{\cdot}038$, $wR = 0{\cdot}045$ for 2457 reflections. This molecule is the first structurally characterized mononuclear molybdenum complex containing a terminal aryl oxide ligand. The central molybdenum atom adopts a distorted octahedral coordination geometry with one face of the octahedron occupied by the tridentate pyrazolylborate ligand and the opposite face by the oxo and the two phenolato ligands. The structure is compared with that of the analogous benzenethiolate complex.

Introduction. We have been interested in the synthesis and characterization of molybdenum compounds as models for oxomolybdenum enzyme active sites, especially that of sulfite oxidase (Spence, 1983; Garner & Bristow, 1985). Sulfite oxidase has been shown to contain a mononuclear Mo center (Cramer, 1983), which cycles between the Mo^{VI}, Mo^{V}, and Mo^{IV} oxidation states (Rajagopalan, 1980; Kipke, Cusanovich, Tollin, Sunde & Enemark, 1988). Because the one-electron-reduced molybdenum site is readily characterized by EPR, the preparation of model complexes in the Mo^{V} oxidation state is of particular interest (Bray, 1980). Dimerization of oxo-Mo^{V} complexes in the presence of water has been circumvented in our studies by using the bulky tridentate ligand tris(3,5-dimethyl-1-pyrazolyl)hydroborate (L). The 3-methyl groups of the pyrazole rings project beyond the molybdenum, create a steric pocket, prevent dimerization and allow preparation of a series of mononuclear Mo^{V} complexes (Cleland, Barnhart, Yamanouchi, Collison, Mabbs, Ortega & Enemark, 1987). Here we present the structure of one of these complexes, LMoO(OPh)$_2$.

Experimental. The complex was prepared by the method of Cleland *et al.* (1987). Ruby red blocks obtained by the slow evaporation of a benzene solution of LMoO(OPh)$_2$ at 298 K, dimensions 0·30 × 0·25 ×

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Table 1. *Refined positional and thermal parameters with estimated standard deviations in parentheses*

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:

$$8\pi^2(U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	B(Å^2)
Mo	0·01957 (3)	0·20206 (4)	0·19277 (3)	3·353 (9)
O1	0·0085 (2)	0·2877 (4)	−0·1213 (2)	4·46 (9)
O2	0·0617 (2)	0·3330 (3)	0·2516 (2)	4·01 (9)
O3	0·0842 (2)	0·1943 (4)	−0·2835 (2)	4·31 (9)
N11	0·0782 (3)	0·0604 (4)	−0·2665 (3)	3·6 (1)
N12	0·1301 (3)	0·0385 (4)	0·2273 (3)	3·7 (1)
N21	0·1479 (3)	0·1807 (4)	−0·1096 (3)	3·6 (1)
N22	0·1856 (3)	0·0623 (4)	0·0890 (3)	3·6 (1)
N31	0·0060 (3)	0·0221 (4)	−0·1391 (3)	3·4 (1)
N32	0·0538 (3)	−0·0747 (4)	−0·1213 (3)	3·5 (1)
C11	0·1620 (3)	0·1006 (6)	−0·2808 (3)	4·1 (1)
C12	0·1308 (4)	0·0432 (6)	−0·3558 (3)	4·5 (1)
C13	0·0789 (3)	0·0563 (6)	0·3451 (3)	3·9 (1)
C14	0·2204 (4)	0·2148 (7)	−0·2551 (4)	5·5 (2)
C15	0·0295 (4)	0·1489 (7)	−0·4085 (4)	5·6 (2)
C21	0·2607 (3)	0·0770 (6)	−0·0298 (3)	4·1 (1)
C22	0·2709 (3)	0·2063 (7)	−0·0114 (3)	4·7 (1)
C23	0·2001 (3)	0·2673 (5)	−0·0613 (3)	4·0 (1)
C24	0·3178 (4)	−0·0316 (7)	0·0067 (4)	5·9 (2)
C25	0·1788 (4)	0·4064 (6)	0·0658 (4)	5·6 (2)
C31	0·0234 (4)	0·1722 (5)	0·0856 (3)	4·1 (1)
C32	0·0544 (4)	0·1366 (6)	−0·0780 (3)	4·4 (1)
C33	0·0712 (3)	−0·0158 (5)	−0·1117 (3)	3·6 (1)
C34	0·0711 (4)	−0·2948 (6)	0·0610 (4)	5·6 (2)
C35	0·1474 (4)	0·0656 (6)	0·1177 (4)	4·7 (1)
C41	0·0317 (3)	0·4479 (5)	0·2855 (3)	3·9 (1)
C42	0·0278 (4)	0·5174 (6)	0·2611 (4)	5·3 (2)
C43	0·0510 (5)	0·6388 (7)	0·2935 (4)	6·2 (2)
C44	0·0163 (5)	0·6902 (6)	−0·3505 (4)	5·7 (2)
C45	0·0417 (4)	0·6205 (7)	0·3755 (4)	6·2 (2)
C46	0·0665 (4)	0·5014 (6)	0·3429 (4)	5·6 (2)
C51	0·1529 (3)	0·1151 (6)	−0·3083 (3)	3·9 (1)
C52	0·2345 (4)	0·1674 (6)	−0·3199 (4)	4·5 (1)
C53	0·3049 (4)	0·0874 (7)	−0·3438 (4)	5·5 (2)
C54	0·2958 (4)	−0·0409 (7)	−0·3564 (4)	5·7 (2)
C55	0·2167 (4)	−0·0903 (7)	−0·3459 (4)	5·8 (2)
C56	0·1442 (4)	0·0133 (6)	−0·3223 (4)	4·8 (2)
B	0·1422 (4)	0·0578 (6)	0·1357 (4)	3·7 (1)

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

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

Mo O1	1·680 (3)	Mo O2	1·938 (3)
Mo O3	1·929 (3)	Mo–N11	2·323 (4)
Mo N21	2·169 (4)	Mo–N31	2·183 (4)
O1 Mo O2	102·4 (2)	O1–Mo O3	103·7 (2)
O2 Mo O3	88·9 (2)	O1–Mo–N11	167·3 (2)
O1 Mo N21	90·2 (2)	O1 Mo–N31	91·5 (2)
O2 Mo N11	84·4 (1)	O2–Mo N21	89·1 (1)
O2 Mo N31	164·8 (1)	O3–Mo–N11	87·0 (1)
O3 Mo N21	166·1 (1)	O3 Mo–N31	93·8 (1)
N11 Mo N21	79·1 (1)	N11 Mo N31	80·8 (1)
N21 Mo N31	84·7 (1)	Mo O2 C41	134·7 (3)
Mo O3 C51	136·6 (3)		

0·10 mm, mounted on a quartz fiber with epoxy, D_m by flotation ($ZnBr_2$ and H_2O). Symmetry of axial photographs confirmed monoclinic crystal class, limiting conditions identified space group $P2_1/n$ ($h0l$: $h+l = 2n$; $0k0$: $k = 2n$). 25 reflections for measuring lattice parameters, $30° \leq 2\theta \leq 40°$. Syntex $P2_1$ diffractometer, graphite-monochromated Mo $K\alpha$, no absorption correction applied. θ–2θ scans, $2\theta_{\max} = 45°$, $-17 \leq h \leq 16$, $0 \leq k \leq 11$, $-1 \leq l \leq 18$, standard reflections $10\bar{1}$, 412, $\bar{2}02$, average decay of 1%, no correction made. 3639 unique reflections, 2457 with $F_o^2 > 3\sigma(F_o^2)$ used in refinement. $R_{\rm int} = 0{\cdot}021$. Coordinates of Mo from Patterson map, 38 non-hydrogen atoms from difference electron density map. Full-matrix least squares on F, all non-hydrogen atoms anisotropic. H atoms included at calculated positions but not refined. Final refinement of F (2457 reflections, 343 parameters) resulted in $R = 0{\cdot}038$, $wR = 0{\cdot}045$, where $w = 4F_o^2/[\sigma^2(I) + (pF_o^2)^2]$ with p set to 0·04, $(\Delta\rho)_{\max} = 0{\cdot}4$, $(\Delta\rho)_{\min} = -0{\cdot}24$ e Å^{-3}, $(\Delta/\sigma)_{\max} = 0{\cdot}03$. Atomic scattering factors from Cromer & Waber (1974) and anomalous-dispersion factors from Cromer (1974). Programs *SDP* (Frenz, 1978) run on a PDP 11/34a.

Discussion. Atomic coordinates with estimated standard deviations are listed in Table 1 and selected interatomic distances and bond angles in Table 2.* Fig. 1 shows the molecular structure. To our knowledge LMoO(OPh)$_2$ is the first structurally characterized mononuclear oxomolybdenum complex containing a unidentate aryl oxide ligand.† The terminal oxo group and the phenolate ligands are constrained to be mutually *cis* to each other by the *fac* stereochemistry of L. The bond angles around Mo differ significantly from

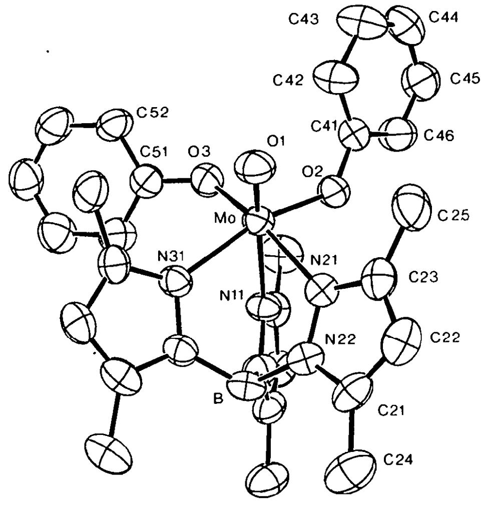

Fig. 1. The structure of $[HB(C_5H_7N_2)_3]MoO(C_6H_5O)_2$. The atom numbering for the unlabeled pyrazole rings and the phenol ring follows the same pattern as the labeled rings.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, and bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51645 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† No examples of a mononuclear oxomolybdenum(V) complex containing an aryl oxide ligand were obtained from a connectivity search of mononuclear O=Mo–O–C fragments using the Cambridge Structural Database, Cambridge Crystallographic Data Centre, Cambridge CB2 1EW, England.

octahedral geometry, and the approximate coordination symmetry is C_s. The two Mo—O(phenolate) distances, Mo—O2 = 1·938 (3) and Mo—O3 = 1·929 (3) Å, are similar to those of the only other reported mononuclear molybdenum complex containing a unidentate alkoxide ligand (Chisholm, Folting, Huffman & Kirkpatrick, 1984) and suggest some *R*O-to-Mo π bonding (Chisholm, Heppert & Huffman, 1984). The Mo—O_t distance for *L*MoO(OPh)$_2$ is the same as the Mo—O_t distance observed for the analogous bis(thiophenolate) structure (Cleland *et al.*, 1987). The elongation of the Mo—N11 bond *trans* to the terminal oxygen atom is of the expected magnitude. Distances and angles in the polypyrazolylborate ligand are normal (Cleland *et al.*, 1987).

The phenyl group containing O2 projects into the pocket formed by the 3-methyl groups of *L*, while the phenyl ring containing O3 lies between two pyrazole rings of *L*. Despite the differing environments of the phenolate ligands, the O1—Mo—O2 and O1—Mo—O3 bond angles are not different, whereas in the analogous SPh complex these angles differ by 4·9° (97·8 *vs* 102·7°). The disparity in orientations of the two phenyl rings in the complex is characterized by differences in the O—Mo—O—C torsional angles. In *L*MoO(OPh)$_2$, the O—Mo—O—C torsional angles are −49° (O1—Mo—O2—C41) and −90° (O1—Mo—O3—C51), similar to those in the analogous SPh complex (−34 and −110°) (Cleland *et al.*, 1987). While the phenyl-ring orientations in these two structures are similar, they are quite different from those in the analogous nitrosyl complex *L*Mo(NO)(SPh)$_2$ (Roberts & Enemark, 1989) where the filled d_{xz} and d_{yz} orbitals on the molybdenum restrict the ON—Mo—S—C torsional angles to values near 0 and 180°.

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Structures of [(*R*)- and (*S*)-Prolinato](Optically Active Cyclen)cobalt(III) Complexes*

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Abstract. *cis*-(*SSSR*)-β_1-(*R*)-{[(*R*)-Prolinato](2*R*,5*R*,8*R*,11*R*-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane)}cobalt(III) bromide perchlorate monohydrate (2), $[Co(C_5H_8NO_2)(C_{16}H_{36}N_4)]Br(ClO_4).H_2O$, $M_r = 654{\cdot}91$, tetragonal, $P4_3$, $a = 14{\cdot}427$ (6), $c = 13{\cdot}678$ (2) Å, $U = 2846{\cdot}9$ (2) Å^3, $Z = 4$, $D_m = 1{\cdot}530$, $D_x = 1{\cdot}528$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu =$

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* Structural Studies on Metal Complexes of Chiral Cyclen. 10. Part 9: Tsuboyama, Tsuboyama & Sakurai (1989).