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A *cis*-Dioxomolybdenum(VI) Complex, [Mo{$N_2C_3H_3C(Me)_2O$}$_2$(O)$_2$]

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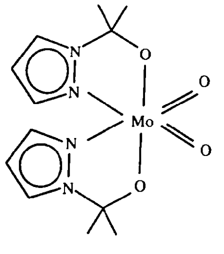
Abstract

In the *cis*-dioxomolybdenum(VI) complex bis[1-methyl-1-(1-pyrazolyl)ethanolato-N^2,O]dioxomolybdenum(VI), [Mo(O)$_2$($C_6H_9N_2O$)$_2$] or $C_{12}H_{18}MoN_4O_4$, the Mo atom has distorted octahedral coordination to two (*cis*) oxo ligands, and two N and two O atoms of the two substituted pyrazole ligands. Mo—O$_{oxo}$ bond distances [mean 1.698 (6) Å] correspond to double bonds, Mo—O$_{oxy}$ [mean 1.951 (2) Å] to single bonds, and Mo—N bonds [mean 2.326 (3) Å] are lengthened as a result of the effect of the oxo ligands, which are *trans* to the N atoms.

Comment

The interest in mononuclear high-valent oxomolybdenum complexes as structural and reactivity models of the molybdenum site in oxo-type molybdoenzymes is well documented (Garner & Bristow, 1985). In addition, O-atom-transfer reactions of dioxomolybdenum(VI) complexes have been discussed (Holm, 1987; Roberts *et al.*, 1988, 1990).

The present account details two synthetic routes to a novel *cis*-dioxomolybdenum(VI) complex, [Mo{$N_2C_3H_3C(Me)_2O$}$_2$(O)$_2$], (I), and describes its crystal and molecular structure. The first synthetic route, a serendipitous discovery, arose from an attempt to prepare acetone solutions of the all-Mo^{VI} octamolybdenum cluster species, $Mo_8(pz)_6O_{21}(pzH)_6.3pzH.0.5H_2O$, where pzH is pyrazole (Ehlert *et al.*, 1993). Instead of acting as a solvent, the acetone caused a breakdown of the cage structure, became part of a new chelating ligand, *i.e.* $N_2C_3H_3C(Me)_2O$, and was thereby incorporated into the new mononuclear *cis*-dioxomolybdenum complex (Fig. 1). The literature does contain a precedent for this type of reaction. Calhorda & Dias (1980) describe the reaction of Cp_2MoBr_2 with excess pyrazole and acetone in the presence of $TlPF_6$. One of the products from the reaction was formulated as [Cp_2Mo{$N_2C_3H_3$-$C(Me)_2O$}]$^+$.PF_6^- (where Cp is cyclopentadienyl) on the basis of elemental analyses and ^{1}H NMR data.



(I)

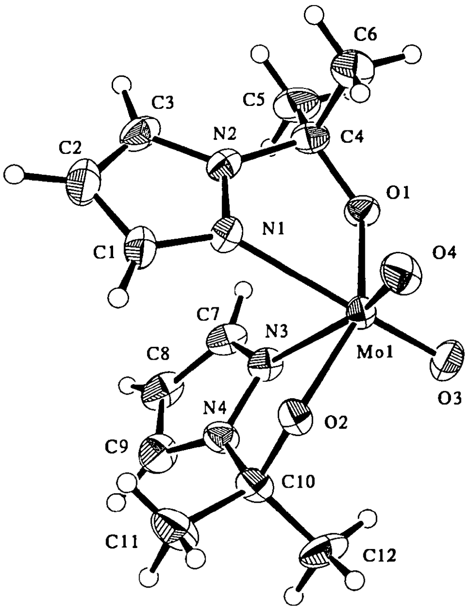


Fig. 1. View of the title molecule (30% probability displacement ellipsoids).

The proton NMR of the title compound in d_6-acetone displays, as expected, three signals for the three non-equivalent pyrazolyl protons [δ 6.35 $t(1)$, δ 7.43 $d(1)$, δ 7.92 $d(1)$, J_{HCCH} = 2 Hz]. In addition, a singlet at δ 3.45 (6) is assigned to the 'CMe_2' moieties in the molecule.

The Mo coordination in the title compound is very distorted octahedral (Fig. 1), with *trans* bond angles of 150.2 (1) (O1—Mo—O2), 159.9 (2) and 162.3 (1)°, and *cis* angles of 71.9 (1)–105.6 (2)°. The molecule has a C_2 symmetry axis, which (perhaps surprisingly) is not utilized in building up the crystal structure. Bond distances to the oxo ligands are normal (Barnhardt & Enemark, 1984; Roberts *et al.*, 1988, 1990); Mo═O3 = 1.689 (3) and Mo═O4 = 1.706 (3) Å. The remaining Mo—O (single) bonds, involving the O atoms of the chelating ligands, are much longer, at 1.950 (2) and 1.951 (2) Å. The Mo—N distances are affected by the strong *trans* influence of the oxo ligands and are considerably longer than normal single bonds at 2.330 (3) and 2.321 (4) Å, but quite comparable to similar *trans*-Mo—N bond lengths in other octahedral *cis*-dioxomolybdenum complexes (Roberts *et al.*, 1988, 1990). Interestingly, the O3—Mo—O4 angle of 105.6 (2)° is also comparable to the O—Mo—O angles of 103.4° in the tris(3,5-dimethylpyrazolyl)borate molybdenum dioxo species already reported (Roberts *et al.*, 1988, 1990), even though the steric crowding in the title compound is considerably less than that in the earlier examples.

Experimental

All materials used were of reagent grade. Pyrazole (Aldrich) and MoO_3 (MCB) were used as received. $Mo_8(pz)_6O_{21}(pzH)_6.3pzH.0.5H_2O$ was prepared as described previously (Ehlert *et al.*, 1993). Solvents were dried and distilled under an atmosphere of dinitrogen before use. The title compound, $[Mo\{N_2C_3H_3C(Me)_2O\}_2(O)_2]$, was synthesized by two methods. Method (i): to $Mo_8(pz)_6O_{21}(pzH)_6.3pzH.0.5H_2O$ (3.638 g) was added 100.0 ml of acetone. The mixture was stirred in the dark at room temperature for approximately 3 h and then filtered. The filtrate was concentrated to about 80 ml, during which time colorless crystals began to deposit. The mixture was cooled to 278 K and more colorless crystals deposited. The pale-yellow solution phase was decanted and the crystals collected, washed with diethyl ether and then dried under a stream of dinitrogen gas. More crystals were obtained on further concentration of the above filtrate, followed by cooling to 278 K. The total yield of crystals obtained was 2.122 g. Analysis calculated for $[Mo\{N_2C_3H_3C(Me)_2O\}_2(O)_2]$ C 38.10, H 4.76, N 14.81%; found C 38.22, H 4.76, N 14.88%. Method (ii): a mixture of MoO_3 (2.879 g, 20.0 mmol), pyrazole (2.723 g, 40.0 mmol) and acetone (250 ml) was refluxed with stirring for approximately 7 d. The mixture was then filtered and the resulting filtrate concentrated to a volume of 20 ml. The resulting pale-yellow solution was cooled to 278 K and yielded a crop of large X-ray quality colorless crystals of the desired product. Analysis calculated for $[Mo\{N_2C_3H_3C(Me)_2O\}_2(O)_2]$ C 38.10, H 4.76, N 14.81%; found C 38.02, H 4.92, N 14.90%.

Crystal data

$[Mo(O)_2(C_6H_9N_2O)_2]$
M_r = 378.24
Monoclinic
Cc
a = 14.381 (3) Å
b = 7.697 (3) Å
c = 14.2869 (12) Å
β = 100.801 (10)°
V = 1553.4 (5) Å^3
Z = 4
D_x = 1.617 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 17.7–20.8°
μ = 0.863 mm^{-1}
T = 294 K
Prism
0.20 × 0.20 × 0.15 mm
Colorless

Data collection

Rigaku AFC-6S diffractometer
ω–2θ scans
Absorption correction: ψ scans (North *et al.*, 1968)
T_{min} = 0.820, T_{max} = 0.879
3105 measured reflections
2811 independent reflections

1766 reflections with $I > 3\sigma(I)$
R_{int} = 0.070
θ_{max} = 32.53°
$h = 0 \rightarrow 21$
$k = 0 \rightarrow 11$
$l = -21 \rightarrow 21$
3 standard reflections every 200 reflections intensity decay: 6.2%

Refinement

Refinement on F^2
$R(F)$ = 0.027
$wR(F^2)$ = 0.053
S = 1.14
2811 reflections
188 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o)^2]$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 2.6 e Å^{-3} (0.56 Å from Mo)
$\Delta\rho_{min}$ = −5.3 e Å^{-3} (at Mo site)

Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: refinement of the other polarity gave slightly higher R factors (R = 0.0278 and wR = 0.0556)

Table 1. *Selected geometric parameters (Å, °)*

Mo1—O1	1.950 (2)	Mo1—O4	1.706 (3)
Mo1—O2	1.951 (2)	Mo1—N1	2.330 (3)
Mo1—O3	1.689 (3)	Mo1—N3	2.321 (4)
O1—Mo1—O2	150.22 (10)	O3—Mo1—N1	162.32 (14)
O3—Mo1—O4	105.6 (2)	O4—Mo1—N3	159.89 (15)

H atoms were placed in calculated positions, with C—H = 0.98 Å and U(H) = 1.2U(bonded C).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1989). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: direct methods *via SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1386). Services for accessing these data are described at the back of the journal.

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Tetrakis[1-(1-phenylcyclohexyl)piperidinium] Tetrachloromanganate(II) Dichloride

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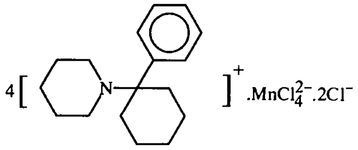
Abstract

The crystal structure of the title compound, $(C_{17}H_{26}N)_4[MnCl_4]Cl_2$, has been determined. The cation is 1-(1-phenylcyclohexyl)piperidinium. The metal atom is located on a $\bar{4}$ rotation axis with four Cl atoms coordinated to form a flattened tetrahedron.

Comment

The present structural investigation was carried out because of our interest in the geometry and environment of the tetrachlorometallate(II) anion (Harlow *et al.*, 1974, 1975; Nelson & Simonsen, 1981). The structure of the title compound, (I), is isostructural with the Cu and Ni salts. The four Cl atoms around each metal atom form a flattened tetrahedron with two equal large angles and four equal smaller angles: 121.10 (3) and 103.99 (1)° for Mn, 132.6 (1) and 99.3 (1)° for Cu, and 122.4 (1) and 103.4 (1)° for Ni (Nelson & Simonsen, 1981). Each Cl^- ion is hydrogen bonded to the N atoms of two symmetry-related 1-(1-phenylcyclohexyl)piperidinium (PCP) cations [N···Cl 3.183 (2) Å].



(I)

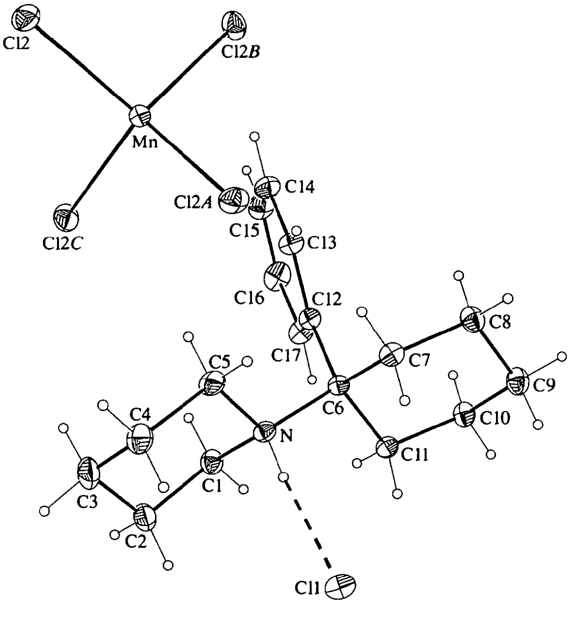


Fig. 1. A view of the title compound showing the atom-labeling scheme. Displacement ellipsoids are scaled to the 30% probability level. H atoms are drawn to an arbitrary scale.

Experimental

Crystals of the title compound were provided by Dr William J. Wells III.

Crystal data

$(C_{17}H_{26}N)_4[MnCl_4]Cl_2$	Mo $K\alpha$ radiation
$M_r = 1245.20$	$\lambda = 0.71073$ Å

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† Deceased.