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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1075). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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mer-[2'-(2-Benzoyl-1-methylethylidene)-1-naphthohydrazido(2-)](methanol)-*cis*-dioxo-molybdenum(VI)

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Abstract

In the molecule of the title compound, [MoO₂(L)(CH₃OH)] [L is the dianion of 2'-(2-benzoyl-1-methylethylidene)-1-naphthohydrazide, C₂₁H₁₆N₂O₂], the Mo atom displays distorted octahedral coordination geometry,

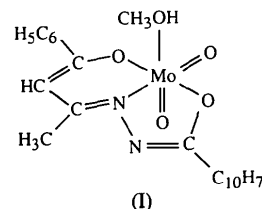
being coordinated by two mutually *cis* oxo ligands, the methanol O atom and the tridentate ligand L bonded through the azomethine N atom, the enolic O atom and the oxazine O atom (equatorially disposed). The packing in the crystal structure involves a hydrogen bond from the methanol OH as donor to an oxo ligand as acceptor.

Comment

Owing to the diverse properties of carboxylic acid hydrazides and hydrazones and their wide application in many fields (*e.g.* medicine and analytical chemistry), particularly for the preparation of new heterogeneous catalysts for oxido-reduction processes (Troepol'skaya & Munin, 1977; Kogan, Zelentsov, Larin & Lukov, 1990), increased attention has been devoted to the study of their complexing affinities towards different transition metals. The complexation of such a ligand with molybdenum as a bioelement is of great interest, since molybdenum is a component of several redox enzymes and is essential for the biological binding of molecular nitrogen (Cotton & Wilkinson, 1988; Kamenar, 1981).

Special significance is attached to Mo^{VI}O₂ complexes because the active site of the molybdenum coordination sphere is considered to be that *trans* to the oxo O atom. The *trans* ligand is replaced by the substrate molecule, thus making possible the basic principal function of the enzyme.

The title compound, [MoO₂(L)(CH₃OH)] [L is the dianion of 2'-(2-benzoyl-1-methylethylidene)-1-naphthohydrazide], (I), is one of several complexes that we have synthesized (Leovac, Ivanović, Andjelković & Mitrovski, 1995). In order to confirm our proposal of the structure, and to determine the molecular dimensions in detail, we have undertaken the crystal structure analysis of (I). The structure consists of monomeric molecules; a perspective view showing the atomic numbering scheme is given in Fig. 1.



The Mo atom is coordinated by a pair of mutually *cis* oxo ligands and the tridentate equatorially disposed L ligand bonded *via* the azomethine N atom, the enolic O atom (O2) and the α -oxazine atom (O1). Distorted octahedral coordination is completed by the O atom of the methanol. The enolic O atom is *trans* to the α -oxazine O atom, and the O4 oxo ligand is *trans* to the azomethine N atom. The interatomic distances Mo—O4 and Mo—O5 of 1.714 (2) and 1.689 (3) Å,

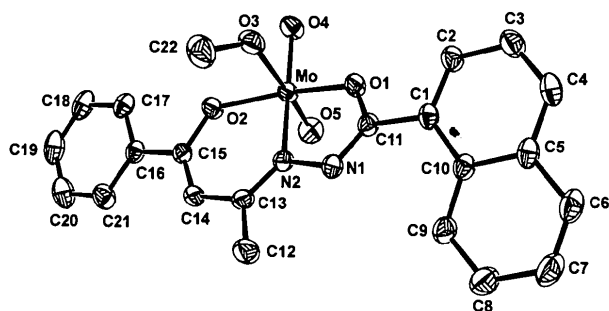


Fig. 1. Numbering of atoms and geometry of the complex.

respectively, are typical of Mo—O double bonds, *cf.* other monomeric octahedral dioxo complexes of Mo^{VI} (Sergienko, Abramenko & Minacheva, 1993).

The *trans* influence of the terminal O atoms O4 and O5 is demonstrated by the bond lengths from Mo to the azomethyne N atom and to the methanol O atom. This effect is especially prominent for Mo—O3 [2.415 (3) Å]. Corresponding effects have been observed in other molybdenum complexes containing similar tridentate ligands (Ivegeš, Leovac, Pavlović & Penavić, 1992; Ilyukhin, Sergienko & Abramenko, 1994). A relatively weak Mo—solvent bond allows ready substitution of the monodentate ligand.

Bond lengths and angles in the ligand are in accordance with the fact that, upon complexation with the metal, the system of conjugated bonds extends over the five-membered MoOCNN and six-membered MoOC—CCN heterocycles.

The conformation of the five-membered chelate ring is a very flat O1 envelope, whereas the six-membered chelate ring is found to be more puckered. The angle between least-square planes through the two heterocycles is 9.15 (3)°. The naphthalene group and the benzene ring are rotated around the C1—C11 and C15—C16 bonds, respectively, in the same sense and are mutually coplanar within 5°.

There is one intermolecular hydrogen bond between the methanol O3 atom and the oxo ligand O4 (1 - *x*, 2 - *y*, 2 - *z*), with O3...O4 2.785 (3) Å [O3—HO3 0.92, O4...HO3 1.927 Å, O3—HO3...O4 154°]. The crystal cohesion is, therefore, mainly the result of van der Waals interactions.

Experimental

For the preparation of the title compound, a solution of H₂L in hot absolute methanol in molar ratio 1:1 was mixed with a solution of MoO₂(*acac*)₂ and heated for 10 min. The dark red crystalline product was filtered off and washed with methanol.

Crystal data

[MoO₂(C₂₁H₁₆N₂O₂)—
(CH₄O)]

Mo Kα radiation
λ = 0.71069 Å

M_r = 488.36

Triclinic

*P*1̄

a = 7.418 (1) Å

b = 10.814 (2) Å

c = 14.039 (2) Å

α = 105.40 (1)°

β = 90.26 (1)°

γ = 109.97 (1)°

V = 1014.9 (3) Å³

Z = 2

D_x = 1.60 Mg m⁻³

D_m = 1.59 Mg m⁻³

D_m measured by flotation in
CHBr₃/CCl₄ mixture

Cell parameters from 25
reflections

θ = 11.5–15.8°

μ = 0.663 mm⁻¹

T = 293 (2) K

Prismatic

0.40 × 0.35 × 0.25 mm

Dark red

Data collection

Enraf–Nonius CAD-4

diffractometer

ω/2θ scans

Absorption correction:

none

4662 measured reflections

4215 independent reflections

3768 observed reflections

[*F* > 3σ(*F*)]

R_{int} = 0.016

θ_{max} = 27°

h = -9 → 9

k = -13 → 13

l = 0 → 17

3 standard reflections

frequency: 120 min

intensity decay: 0.1%

Refinement

Refinement on *F*

R = 0.030

wR = 0.035

S = 0.88

3768 reflections

272 parameters

H atoms riding

w = 1/σ²(*F_o*)

(Δ/σ)_{max} = 0.01

Δρ_{max} = 0.833 e Å⁻³

Δρ_{min} = -0.540 e Å⁻³

Extinction correction: *SDP*
(Frenz, 1982)

Extinction coefficient:
0.03654 (3)

Atomic scattering factors
from *International Tables*
for *X-ray Crystallography*
(1974, Vol. IV, Table
2.3.1)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Mo	0.27174 (4)	0.81685 (3)	0.83250 (2)	0.0313 (1)
O1	0.4042 (3)	1.0076 (2)	0.8302 (2)	0.036 (1)
O2	0.2841 (3)	0.6385 (2)	0.8222 (2)	0.041 (1)
O3	0.5786 (3)	0.8796 (2)	0.9265 (2)	0.049 (1)
O4	0.2017 (3)	0.8630 (2)	0.9488 (2)	0.045 (1)
O5	0.0746 (4)	0.7726 (3)	0.7524 (2)	0.052 (1)
N1	0.5795 (4)	0.9422 (2)	0.7051 (2)	0.035 (1)
N2	0.4762 (4)	0.8135 (2)	0.7195 (2)	0.032 (1)
C1	0.6090 (4)	1.1819 (3)	0.7666 (2)	0.033 (1)
C2	0.6052 (5)	1.2753 (3)	0.8537 (3)	0.040 (1)
C3	0.6797 (5)	1.4172 (3)	0.8650 (3)	0.046 (1)
C4	0.7558 (5)	1.4638 (3)	0.7877 (3)	0.045 (1)
C5	0.7597 (4)	1.3724 (3)	0.6964 (2)	0.037 (1)
C6	0.8347 (5)	1.4220 (3)	0.6154 (3)	0.049 (1)
C7	0.8368 (6)	1.3353 (4)	0.5263 (3)	0.055 (1)
C8	0.7622 (6)	1.1926 (4)	0.5121 (3)	0.053 (1)
C9	0.6892 (5)	1.1405 (3)	0.5889 (2)	0.043 (1)
C10	0.6866 (4)	1.2278 (3)	0.6833 (2)	0.033 (1)
C11	0.5288 (4)	1.0349 (3)	0.7638 (2)	0.032 (1)
C12	0.6596 (5)	0.7286 (3)	0.5909 (3)	0.050 (1)
C13	0.5167 (5)	0.7109 (3)	0.6658 (2)	0.034 (1)

C14	0.4256 (5)	0.5757 (3)	0.6769 (2)	0.037 (1)
C15	0.3156 (4)	0.5434 (3)	0.7494 (2)	0.033 (1)
C16	0.2308 (4)	0.4032 (3)	0.7605 (2)	0.035 (1)
C17	0.1519 (5)	0.3848 (3)	0.8480 (3)	0.043 (1)
C18	0.0723 (5)	0.2536 (3)	0.8594 (3)	0.055 (1)
C19	0.0697 (5)	0.1422 (3)	0.7847 (3)	0.061 (1)
C20	0.1435 (6)	0.1585 (4)	0.6979 (4)	0.061 (1)
C21	0.2246 (5)	0.2882 (3)	0.6852 (3)	0.049 (1)
C22	0.7167 (6)	0.8171 (4)	0.9210 (4)	0.066 (1)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Mo—O1	1.968 (2)	N1—N2	1.410 (3)
Mo—O2	1.930 (2)	N1—C11	1.284 (5)
Mo—O3	2.415 (3)	N2—C13	1.297 (5)
Mo—O4	1.714 (2)	C1—C11	1.484 (5)
Mo—O5	1.689 (3)	C12—C13	1.498 (5)
Mo—N2	2.201 (3)	C13—C14	1.437 (4)
O1—C11	1.333 (4)	C14—C15	1.352 (5)
O2—C15	1.329 (4)	C15—C16	1.481 (4)
O3—C22	1.399 (6)		
O1—Mo—O2	148.5 (2)	N2—N1—C11	109.4 (2)
O1—Mo—O3	77.41 (9)	Mo—N2—N1	115.0 (2)
O1—Mo—O4	94.0 (1)	Mo—N2—C13	129.3 (3)
O1—Mo—O5	100.0 (1)	N1—N2—C13	115.7 (3)
O1—Mo—N2	72.74 (9)	C2—C1—C11	116.8 (3)
O2—Mo—O3	78.9 (1)	C10—C1—C11	123.0 (2)
O2—Mo—O4	103.1 (1)	O1—C11—C1	114.3 (3)
O2—Mo—O5	100.5 (1)	N1—C11—C1	123.2 (3)
O2—Mo—N2	81.6 (1)	O1—C11—N1	122.5 (3)
O3—Mo—O4	82.2 (2)	N2—C13—C12	121.6 (3)
O3—Mo—O5	171.9 (1)	N2—C13—C14	120.6 (3)
O3—Mo—N2	75.65 (9)	C12—C13—C14	117.9 (3)
O4—Mo—O5	105.7 (1)	C13—C14—C15	126.2 (3)
O4—Mo—N2	156.12 (9)	O2—C15—C14	122.0 (3)
O5—Mo—N2	96.2 (1)	O2—C15—C16	113.4 (3)
Mo—O1—C11	120.1 (2)	C14—C15—C16	124.4 (3)
Mo—O2—C15	134.0 (2)	C15—C16—C17	119.7 (3)
Mo—O3—C22	133.0 (2)	C15—C16—C21	121.7 (4)

The structure was solved by Patterson and difference Fourier methods and refined by full-matrix least-squares methods. All H atoms were found in the difference Fourier map, but they were placed at calculated positions (C—H and N—H 0.95 Å, O—H 0.92 Å). H atoms were allowed to ride on their attached atom with $U(\text{H}) = 1.2U(\text{carrier atom})$.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *CAD-4 Software*. Program(s) used to solve structure: *SDP* (Frenz, 1982). Program(s) used to refine structure: *SDP*. Molecular graphics: *ORTEX3* (McArdle, 1994). Software used to prepare material for publication: *CSU* (Vicković, 1988).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1096). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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trans-Tetrachlorobis(triphenylphosphine)-*P*-rhenium(IV)–*mer-trans*-Trichlorooxobis(triphenylphosphine)-*P*-rhenium(V) (0.86/0.14)

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Abstract

trans-Tetrachlorobis(triphenylphosphine)rhenium(IV), (1), is isomorphous with the triclinic polymorph of *mer-trans*-trichlorooxobis(triphenylphosphine)rhenium(V), (2) [Lebuis & Beauchamp (1993). *Can. J. Chem.* **71**, 441–449]. The sample of (1) has been partially oxidized (14–25%) to (2) by aerial oxidation, resulting in the title compound, $[\text{ReCl}_4(\text{C}_{18}\text{H}_{15}\text{P})_2]_{0.86}\cdot[\text{ReCl}_3\text{O}(\text{C}_{18}\text{H}_{15}\text{P})_2]_{0.14}$. In the crystal lattice, the oxo ligand is located primarily at one of six possible sites. The molecules have *trans*-octahedral coordination geometry, with Re—P distances in the range 2.564(1)–2.580(1) Å, having a mean value of 2.571(7) Å, and Re—Cl distances in the range 2.291(3)–2.339(1) Å.

Comment

There are 1.5 molecules in the asymmetric unit of the title compound [(1):(2) 0.86:0.14], with one molecule situated at a centre of symmetry [molecule (1); Fig. 1] and one in a general position [molecule (2); Fig. 2]. The red crystals are isomorphous with the yellow triclinic crystal form of the oxidation product *mer-trans*-trichlorooxobis(triphenylphosphine)rhenium(V), (2) (Lebuis & Beauchamp, 1993). The structure of the monoclinic polymorph of (2) was also reported by Lebuis &