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Allomorphs of a Complex of $[Mo(O)_2(dmso)]$ with a Derivative of SADH

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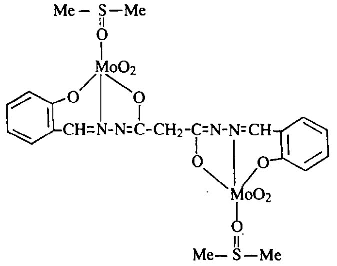
Abstract

In the title complex, [μ-2,2'-(4,6-dihydroxy-2,3,7,8-tetraaza-1,3,6,8-nonatetraene-1,9-diyl)diphenolato(4−)-N^2,O,O^4:N^8,O',O^6]bis[(dimethyl sulfoxide)dioxomolybdenum], $[\{Mo(O)_2(C_2H_6OS)\}_2(\mu\text{-}C_{17}H_{12}N_4O_4)]$, (I), a binuclear *cis*-dioxomolybdenum(VI) complex of salicylaldehyde malonyl dihydrazone, the interatomic distances Mo(1)···Mo(2) 7.370 (2) and S(1)···S(2) 5.097 (3) Å are different from those of 6.370 (6) and 9.636 (3) Å, respectively, found in the allomorphic complex (II) [Wang, Zhang & Liu (1993). Submitted to *Polyhedron*]. By comparing some of the bond lengths and torsion angles in (I) and (II) it is shown that the two complexes are allomorphs.

Comment

Molybdenum chemistry has aroused considerable interest in recent years in view of its importance in catalytic, materials and biochemical science (Bustos *et al.*, 1990). Here we report the synthesis and crystal structure of a binuclear molybdenum–Schiff base complex, (I).



(I)

The structure of (I), shown in Fig. 1, may be compared with that of the complex (II) (Wang, Zhang & Liu, 1993), which crystallizes in space group *P*2/*c* with $a = 9.856$ (2), $b = 7.646$ (1), $c = 18.373$ (2) Å, $\beta = 95.60$ (1)°, $V = 1377.95$ Å^3 and $Z = 2$. The difference between complexes (I) and (II) is only a difference of conformation. As shown in Fig. 1, complex (I) has a *trans* conformation in which the two Mo atoms lie on different sides of the bridging ligand. Complex (II) has a *cis* conformation, in which the two Mo atoms lie on the same side of the ligand. Some corresponding interatomic distances in (I) and (II) are listed in Table 3.

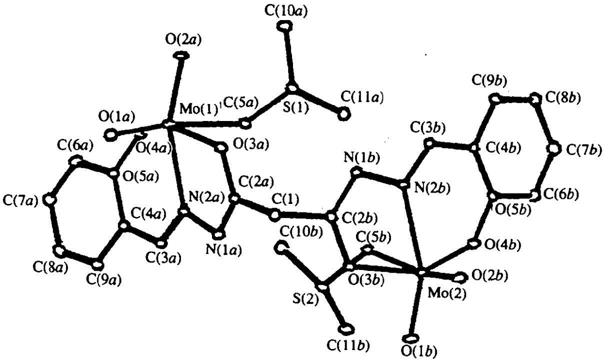


Fig. 1. The molecular structure of (I), showing the atomic labelling scheme.

The average length of the four Mo—O terminal bonds, 1.699 (4) Å, and the average of the O═Mo═O bond angles, 104.6 (8)°, in (I) are comparable to other values reported for the MoO_2^{2+} group (Bustos *et al.*, 1990; Zhai, Xu & Wang, 1992). The N(1*a*)—C(2*a*) [1.267 (8) Å], N(1*b*)—C(2*b*) [1.275 (8) Å], N(2*a*)—C(3*a*) [1.275 (7) Å] and N(2*b*—C(3*b*) [1.281 (7) Å] distances indicate that these correspond to double bonds (Bustos *et al.*, 1990). The Mo(1)—O(5*a*) [2.341 (4) Å] and Mo(2)—O(5*b*) [2.327 (4) Å] bonds are relatively long, as the coordinated solvent molecule (Me_2SO) is labile.

The angle C(2*a*)—C(1)—C(2*b*) in (I) [108.0 (6)°] is greater than the angle C(2)—C(1)—C(2) [106 (2)°] in (II). The other corresponding angles in (I) and (II) are similar. From Table 3, it can be seen that the Mo(1)···Mo(2) distance [7.370 (2) Å] and O(3*a*)···O(3*b*) distance [4.306 (7) Å] in (I) are 1.000 and 0.607 Å longer, respectively, than those in complex (II), while both the S(1)···S(2) and C(3*a*)···C(3*b*) distances are significantly shorter (by 4.540 and 0.921 Å, respectively). The torsion angles in (I) and (II) are very different. The angles N(2)—N(1)—C(2)—C(1) [180 (1)°], N(1)—N(2)—C(3)—C(4) [180 (1)°] and N(2)—C(3)—C(4)—C(9) [−179 (1)°] in (II) indicate that each of these groups is planar, while the corresponding angles in complex (I), N(2*a*)—N(1*a*)—C(2*a*)—C(1) [179.7 (6)°] N(2*b*)—N(1*b*)—C(2*b*)—C(1) [−173.4 (6)°], N(1*a*—N(2*a*)—C(3*a*)—C(4*a*) [178.0 (7)°], N(1*b*)—N(2*b*)—C(3*b*)—C(4*b*) [−173.1 (7)°], N(2*a*)—C(3*a*)—C(4*a*)—C(9*a*) [−170.7 (8)°] and N(2*b*)—C(3*b*)—C(4*b*)—C(9*b*) [177.8 (8)°], indicate that, with the exception of the N(2*a*)—N(1*a*)—C(2*a*)—C(1) group, none of these groups are planar. The difference in the density of (I) (1.856 Mg m^{-3}) and (II) (1.804 Mg m^{-3}) means that the molecular arrangement in the unit cells of (I) and (II) is different. These differences between (I) and (II) indicate that the two complexes are allomorphs.

Experimental

A solution of $MoO_2(acac)_2$ (0.5 mmol) was added to a suspension of the SADH derivative (0.5 mmol) at a speed of 1 drop s^{-1}. The reaction mixture was heated under reflux to give a yellow solid. The crude product was recrystallized from DMSO–CH_3OH to give crystals suitable for X-ray analysis. The density D_m was measured by flotation.

Crystal data

$[Mo_2(O)_4(C_{17}H_{12}N_4O_4)(C_2H_6OS)_2]$
M_r = 748.45
Triclinic
$P\overline{1}$
a = 8.405 (2) Å
b = 12.846 (3) Å
c = 13.739 (4) Å
α = 114.45 (2)°
β = 90.53 (2)°
γ = 83.14 (3)°
V = 1339 (1) Å^3
Z = 2
D_x = 1.856 Mg m^{-3}
D_m = 1.853 Mg m^{-3}

Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 19 reflections
θ = 10–22°
μ = 9.80 mm^{-1}
T = 294 (1) K
Prism
0.35 × 0.20 × 0.20 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans [width (0.6 + 0.140tanθ)°]
Absorption correction: empirical
T_{min} = 0.859, T_{max} = 0.998
4171 measured reflections
3783 independent reflections
3337 observed reflections [$F > 3.0\sigma(F)$]

R_{int} = 0.044
θ_{max} = 60°
$h = -9 \rightarrow 9$
$k = -14 \rightarrow 14$
$l = 0 \rightarrow 15$
3 standard reflections
frequency: 90 min
intensity variation: 4.1%

Refinement

Refinement on F
R = 0.043
wR = 0.050
S = 2.16
3337 reflections
352 parameters
Unit weights applied
$(\Delta/\sigma)_{max}$ = 0.15

$\Delta\rho_{max}$ = 0.55 e Å^{-3}
$\Delta\rho_{min}$ = −0.76 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Mo(1)	0.70762 (8)	0.05534 (5)	0.77997 (5)	3.09 (1)
Mo(2)	0.70210 (8)	−0.55503 (5)	0.67574 (5)	3.10 (1)
S(1)	0.7246 (3)	−0.0691 (2)	0.9542 (2)	3.52 (5)
S(2)	0.9986 (2)	−0.4232 (2)	0.6412 (2)	3.25 (5)
O(1*a*)	0.6397 (7)	0.1160 (5)	0.6970 (4)	4.3 (1)
O(1*b*)	0.8294 (7)	−0.6392 (5)	0.5676 (4)	4.5 (2)
O(2*a*)	0.6077 (8)	0.1389 (5)	0.9003 (5)	5.1 (2)
O(2*b*)	0.5352 (7)	−0.6201 (5)	0.6518 (5)	4.2 (1)
O(3*a*)	0.5626 (6)	−0.0701 (4)	0.7368 (4)	3.2 (1)
O(3*b*)	0.6244 (6)	−0.4406 (4)	0.6135 (4)	3.3 (1)
O(4*a*)	0.9227 (7)	0.0989 (4)	0.7939 (4)	3.8 (1)
O(4*b*)	0.7818 (7)	−0.5870 (4)	0.7941 (4)	3.9 (1)
O(5*a*)	0.8246 (6)	−0.0497 (4)	0.8724 (4)	3.6 (1)
O(5*b*)	0.9029 (6)	−0.4353 (4)	0.7283 (4)	3.4 (1)
N(1*a*)	0.7434 (8)	−0.1958 (5)	0.6052 (5)	3.3 (2)
N(1*b*)	0.5099 (8)	−0.3089 (5)	0.7761 (5)	3.0 (1)
N(2*a*)	0.8316 (7)	−0.1018 (5)	0.6459 (5)	2.9 (1)
N(2*b*)	0.5850 (7)	−0.3941 (5)	0.8073 (4)	2.8 (1)
C(1)	0.493 (1)	−0.2587 (6)	0.6258 (6)	3.3 (2)
C(2*a*)	0.6093 (9)	−0.1704 (6)	0.6562 (6)	3.0 (2)
C(2*b*)	0.5437 (9)	−0.3404 (6)	0.6769 (6)	2.9 (2)
C(3*a*)	0.9634 (9)	−0.1119 (6)	0.5958 (6)	3.1 (2)
C(3*b*)	0.5740 (9)	−0.3674 (6)	0.9079 (6)	2.9 (2)
C(4*a*)	1.0658 (9)	−0.0218 (7)	0.6253 (6)	3.3 (2)
C(4*b*)	0.6570 (9)	−0.4369 (6)	0.9580 (6)	2.9 (2)
C(5*a*)	1.0374 (9)	0.0815 (6)	0.7189 (6)	3.3 (2)
C(5*b*)	0.754 (1)	−0.5423 (6)	0.8998 (6)	3.3 (2)
C(6*a*)	1.139 (1)	0.1666 (7)	0.7375 (7)	4.6 (2)
C(6*b*)	0.832 (1)	−0.6030 (7)	0.9555 (7)	4.3 (2)
C(7*a*)	1.260 (1)	0.1518 (8)	0.6659 (8)	4.8 (2)
C(7*b*)	0.814 (1)	−0.5578 (8)	1.0646 (7)	5.3 (2)
C(8*a*)	1.290 (1)	0.0502 (8)	0.5746 (7)	4.6 (2)
C(8*b*)	0.718 (1)	−0.4531 (8)	1.1234 (6)	4.8 (2)
C(9*a*)	1.195 (1)	−0.0362 (7)	0.5552 (6)	4.1 (2)
C(9*b*)	0.638 (1)	−0.3951 (7)	1.0692 (6)	3.8 (2)
C(10*a*)	0.750 (1)	0.0448 (8)	1.0819 (7)	4.9 (2)
C(10*b*)	1.086 (1)	−0.2948 (7)	0.7099 (7)	4.4 (2)
C(11*a*)	0.844 (1)	−0.1810 (7)	0.9750 (7)	4.9 (2)
C(11*b*)	1.177 (1)	−0.5235 (8)	0.6158 (7)	4.4 (2)

Table 2. *Selected geometric parameters* (Å, °)

Mo(1)—O(1*a*)	1.688 (5)	O(3*a*)—C(2*a*)	1.321 (7)
Mo(1)—O(2*a*)	1.712 (4)	O(3*b*)—C(2*b*)	1.323 (8)
Mo(1)—O(3*a*)	2.024 (4)	O(4*a*)—C(5*a*)	1.347 (7)
Mo(1)—O(4*a*)	1.941 (4)	O(4*b*)—C(5*b*)	1.333 (7)

Mo(1)—O(5*a*)	2.341 (4)	N(1*a*)—N(2*a*)	1.403 (6)
Mo(1)—N(2*a*)	2.239 (4)	N(1*a*)—C(2*a*)	1.267 (8)
Mo(2)—O(1*b*)	1.716 (4)	N(1*b*)—N(2*b*)	1.413 (6)
Mo(2)—O(2*b*)	1.680 (4)	N(1*b*)—C(2*b*)	1.275 (8)
Mo(2)—O(3*b*)	2.030 (4)	N(2*a*)—C(3*a*)	1.275 (7)
Mo(2)—O(4*b*)	1.932 (4)	N(2*b*)—C(3*b*)	1.281 (7)
Mo(2)—O(5*b*)	2.327 (4)	C(1)—C(2*a*)	1.510 (9)
Mo(2)—N(2*b*)	2.228 (5)	C(1)—C(2*b*)	1.507 (9)
O(1*a*)—Mo(1)—O(2*a*)	105.0 (3)	O(2*b*)—Mo(2)—O(4*b*)	100.7 (2)
O(1*a*)—Mo(1)—O(3*a*)	97.9 (2)	O(2*b*)—Mo(2)—O(5*b*)	169.7 (2)
O(1*a*)—Mo(1)—O(4*a*)	98.1 (2)	O(2*b*)—Mo(2)—N(2*b*)	94.0 (2)
O(1*a*)—Mo(1)—O(5*a*)	171.3 (2)	O(3*b*)—Mo(2)—O(4*b*)	150.2 (2)
O(1*a*)—Mo(1)—N(2*a*)	93.0 (2)	O(3*b*)—Mo(2)—O(5*b*)	79.8 (1)
O(2*a*)—Mo(1)—O(3*a*)	95.0 (2)	O(3*b*)—Mo(2)—N(2*b*)	71.4 (1)
O(2*a*)—Mo(1)—O(4*a*)	106.1 (2)	O(4*b*)—Mo(2)—O(5*b*)	80.1 (2)
O(2*a*)—Mo(1)—O(5*a*)	83.7 (2)	O(4*b*)—Mo(2)—N(2*b*)	82.5 (2)
O(2*a*)—Mo(1)—N(2*a*)	159.2 (2)	O(5*b*)—Mo(2)—N(2*b*)	75.8 (1)
O(3*a*)—Mo(1)—O(4*a*)	149.1 (2)	N(2*a*)—N(1*a*)—C(2*a*)	110.0 (4)
O(3*a*)—Mo(1)—O(5*a*)	80.8 (2)	N(2*b*)—N(1*b*)—C(2*b*)	108.4 (5)
O(3*a*)—Mo(1)—N(2*a*)	71.7 (2)	N(1*a*)—N(2*a*)—C(3*a*)	116.6 (5)
O(4*a*)—Mo(1)—O(5*a*)	79.5 (2)	N(1*b*)—N(2*b*)—C(3*b*)	114.7 (4)
O(4*a*)—Mo(1)—N(2*a*)	81.4 (2)	C(2*a*)—C(1)—C(2*b*)	108.0 (6)
O(5*a*)—Mo(1)—N(2*a*)	78.5 (2)	O(3*a*)—C(2*a*)—N(1*a*)	124.3 (5)
O(1*b*)—Mo(2)—O(2*b*)	104.3 (2)	O(3*a*)—C(2*a*)—C(1)	116.4 (5)
O(1*b*)—Mo(2)—O(3*b*)	93.7 (2)	N(1*a*)—C(2*a*)—C(1)	119.4 (5)
O(1*b*)—Mo(2)—O(4*b*)	106.2 (2)	O(3*b*)—C(2*b*)—N(1*b*)	124.7 (6)
O(1*b*)—Mo(2)—O(5*b*)	85.2 (2)	O(3*b*)—C(2*b*)—C(1)	116.0 (6)
O(1*b*)—Mo(2)—N(2*b*)	157.6 (2)	N(1*b*)—C(2*b*)—C(1)	119.3 (6)
O(2*b*)—Mo(2)—O(3*b*)	95.4 (2)		

Table 3. *Selected interatomic distances* (Å) *in* (I) *and* (II)

	(I)	(II)
Mo(1)···Mo(2)	7.370 (2)	6.370 (3)
S(1*a*)···S(1*b*)	5.097 (3)	9.636 (3)
C(3*a*)···C(3*b*)	7.37 (1)	8.294 (5)
O(3*a*)···O(3*b*)	4.306 (7)	3.699 (1)

H atoms were located in difference Fourier syntheses and were included in the structure-factor calculations but their positions were not refined. Data collection was performed using CAD-4 diffractometer software (Enraf–Nonius, 1977). The structure was solved by direct methods using *MULTAN*11/82 (Main *et al.*, 1982) and refined by a full-matrix least squares using *SDP* (Frenz, 1978).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, bond distances and angles involving H atoms and torsion angles have been deposited with the IUCr (Reference: BR1062). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Distorted Planar Palladium Complex with Maleonitriledithiolato and Triphenylphosphine Ligands, $[Pd(PPh_3)_2(mnt)]$

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Abstract

cis-[2,3-Disulfido-2-butenedinitrile(2−)-*S*,*S*′]bis(triphenylphosphine)palladium(II), $[Pd(C_4N_2S_2)(C_{18}H_{15}P)_2]$, is a distorted planar palladium complex. The *trans* P—Pd—S angles in the complex are 170.3 (1) and 165.4 (1)°. The distortion may be caused by intermolecular contacts between a cyano N atom and phenyl C atoms in the crystal.

Comment

Maleonitriledithiolate (mnt^{2-}) forms square-planar $[M(mnt)_2]^{2-}$ complexes with Group 10 atoms. These complexes oxidize to the corresponding monoanions in which the presence of unpaired electrons has been investigated and determined using ESR, XPS, IR spectroscopy and MO calculations (McCleverty, 1968; Eisenberg, 1970; Burns & McAuliffe, 1979). The bis(maleonitriledithiolato)palladium complexes which have been reported are mainly in the monoanion form, some examples being $K[Pd(mnt)_2].H_2O$, $(NH_4)[Pd(mnt)_2].H_2O$ (Hursthouse, Short, Clemenson & Underhil, 1989) and $(perylene)_2[Pd(mnt)_2]$ (Domingos *et al.*, 1988). A complex containing a dianion, $MV[Pd(mnt)_2]$ (MV = *N*,*N*′-dimethyl-4,4′-bipyridinium), has been reported recently (Lemke, Knoch & Kisch, 1993). However, only a few complexes of Group 10 elements which contain one maleonitriledithiolato ligand and two monodentate ligands have been reported. The structure of $[Pt(PPhMe_2)_2(mnt)]$ is an example (Fitzmaurice, Slawin, Williams, Woollins & Lindsay, 1990).

The title complex, (I), was obtained as a by-product during our studies of mixed-metal complexes of the general formula $[M(mnt)_2\{Ag(PR_3)_2\}_2]$ (M = Ni, Pd, Pt; R = Ph, ^{n}Bu). The related complex $[Pt(PPhMe_2)_2(mnt)]$ is square planar with *trans* P—Pt—S angles of nearly 180°. However, $[Pd(PPh_3)_2(mnt)]$ is considerably distorted from the ideal planar structure with *trans* P—Pd—S angles of 170.3 (1) and 165.4 (1)°. Since the

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