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Bis(μ-1-acetimido-4-phenylpyrazolone-N^2:O)-μ-oxo-tetraoxodimolybdenum(VI) as its diacetonitrile adduct: a novel dinuclear molybdenum complex bridged by a 1-acetimido-4-phenylpyrazolone ligand

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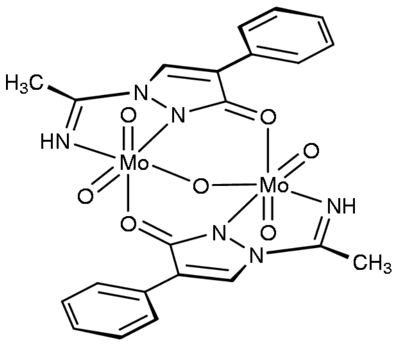
Key indicators
Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.003 Å
R factor = 0.032
wR factor = 0.088
Data-to-parameter ratio = 22.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $[Mo_2O_5(C_{11}H_{10}N_3O)_2]\cdot 2CH_3CN$, is a dinuclear molybdenum complex. It has crystallographic C_2 symmetry with the central O atom located on a twofold rotation axis. The Mo atoms, octahedrally coordinated by four O and two N atoms, are bridged by a μ-O and two μ-pyrazolonyl groups. An intermolecular N—H···O hydrogen bond stabilizes the crystal packing.

Comment

Ferrocene-based scorpionate ligands can serve as building blocks for the generation of redox-active, metal-containing polymers (Jäkle *et al.*, 1996; Fabrizi de Biani *et al.*, 1997; Herdtweck *et al.*, 1998). Molybdenum is a multivalent element and can be coordinated in various ways. When this element is employed as a central metal of the polymer, some novel and peculiar physical properties may be expected. We tried to synthesize the monomer $FcTp^{Ph}Mo(CO)_2(\eta^3\text{-}C_4H_7)$ [Fc = ferrocenyl, Tp^{Ph} = tris(4-phenylpyrazolyl)borate, C_4H_7 = 2-methylallyl; for the preparation of 4-phenyl pyrazole, see Tolf *et al.* (1979)], starting from $FcTp^{Ph}Li$ and $Mo(CO)_6$, followed by treatement with 3-bromo-2-methylpropene. Due to a leakage in the apparatus, the reaction mixture came into contact with air and moisture. As a result, the target compound was not obtained, but the title complex, (I), was isolated instead. Formation of (I) occurred *via* a complete breakdown of the scorpionate ligand, accompanied by molybdenum oxidation, as well as oxidative CH activation at the pyrazolyl moiety. Moreover, nucleophilic attack on acetonitrile by a pyrazolyl N atom led to the incorporation of solvent molecules into the complex.



(I)

Complex (I) (Fig. 1), characterized as its diacetonitrile adduct, has crystallographic C_2 symmetry with the central O atom located on a twofold rotation axis. The Mo atoms are

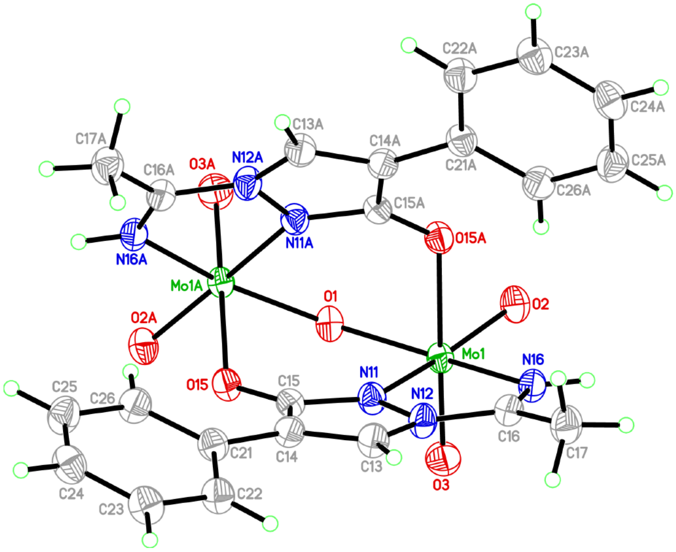


Figure 1

A perspective view of the title compound with the atom-numbering scheme. Displacement ellipsoids are at the 50% probability level.

octahedrally coordinated by four O atoms and two N atoms. The two Mo=O double bonds, Mo1=O2 and Mo1=O3, are almost of equal length (Table 1), but the fact that O2 acts as an acceptor for an intermolecular hydrogen bond (Table 2) is reflected by its elongated distance to Mo. The O atom bridging the Mo atoms displays an angle of 144.69 (9)°. The longest bond to Mo is that to O15, which also forms a double bond to the pyrazole ring. The length of this double bond is in agreement with 175 comparable structures retrieved from the Cambridge Structural Database (Version 5.21, April 2001; Allen & Kennard, 1993). For these structures, the following mean values were found: C=O 1.25 (4) Å, C—C 1.43 (3) Å and C=C 1.37 (3) Å. In contrast to the parent pyrazole, which exhibits two C—C bonds of equal length [1.37 (2) Å], the C13—C14 and C14—C15 bond distances in (I) are significantly different from each other, *i.e.* 1.364 (2) and 1.460 (2) Å, respectively. These alternating bonds indicate the aromatic system of the pyrazole ring to be severely perturbed, as is to be expected for a pyrazolone moiety. The pyrazolone and the phenyl ring are not coplanar, the dihedral angle between them is 21.41 (9)°. The gaps between the molecules of (I) are occupied by acetonitrile solvent molecules which form several weak hydrogen bonds (Table 2).

Experimental

$FcTp^{Ph}Li$ (0.31 g, 0.50 mmol) and $Mo(CO)_6$ (0.20 g, 0.75 mmol) were dissolved in acetonitrile (25 ml) and the mixture was refluxed for 6 h. After filtration, the filtrate was driven off under reduced pressure. The residue was dissolved in toluene (30 ml) and then 3-bromo-2-methylpropene (0.10 ml, 0.99 mmol) was added. The mixture was kept under reflux for 7 h, then cooled to 293 K. The solvent was removed *in vacuo* and the solid residue washed with hexane (15 ml). The crude product was recrystallized from CH_3CN/toluene (1:2). Upon standing in air for several days, the title complex was obtained as yellow crystals as the diacetonitrile adduct. ^{1}H NMR (250.1 MHz, DMSO-d^6): δ = 2.07 (*s*, 3H, CH_3CN), 2.19 (*s*, 6H, $CH_3C{=}NH$), 7.34 (mult, 6H, Ph–H3,4,5), 7.74 [*d*, 4H, *J*(HH) = 6.9 Hz, Ph-H2,6], 8.54 (*s*, 2H, pz–H).

Crystal data

$[Mo_2O_5(C_{11}H_{10}N_3O)_2]\cdot 2CH_3CN$
$M_r = 754.43$
Orthorhombic, *Pbcn*
$a = 14.2861$ (4) Å
$b = 11.8522$ (4) Å
$c = 17.2215$ (6) Å
$V = 2915.97$ (16) Å^3
$Z = 4$
$D_x = 1.718$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 85437 reflections
$\theta = 4.3$–61.3°
$\mu = 0.92$ mm^{-1}
$T = 173$ (2) K
Needle, yellow
0.50 × 0.14 × 0.08 mm

Data collection

Stoe IPDS-II two-circle diffractometer
ω scans
Absorption correction: empirical (*MULABS*; Spek, 1990; Blessing, 1995)
$T_{min} = 0.657$, $T_{max} = 0.930$
83 661 measured reflections
4464 independent reflections
3841 reflections with $I > 2\sigma(I)$
$R_{int} = 0.056$
$\theta_{max} = 30.6°$
$h = -20 \rightarrow 20$
$k = -16 \rightarrow 16$
$l = -24 \rightarrow 24$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.088$
$S = 1.05$
4464 reflections
198 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0652P)^2 + 0.018P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.74$ e Å^{-3}
$\Delta\rho_{min} = -0.72$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0082 (5)

Table 1

Selected geometric parameters (Å, °).

Mo1—O3	1.7098 (14)	N11—C15	1.3476 (19)
Mo1—O2	1.7206 (12)	N12—C13	1.373 (2)
Mo1—O1	1.9074 (5)	C13—C14	1.364 (2)
Mo1—N16	2.1676 (14)	C14—C15	1.460 (2)
Mo1—N11	2.2216 (13)	C15—O15	1.2790 (19)
Mo1—O15^i	2.2347 (14)	C16—N16	1.297 (2)
O3—Mo1—O2	103.31 (6)	O1—Mo1—N11	84.25 (5)
O3—Mo1—O1	99.69 (5)	N16—Mo1—N11	70.40 (5)
O2—Mo1—O1	108.40 (5)	O3—Mo1—O15^i	169.42 (6)
O3—Mo1—N16	93.80 (6)	O2—Mo1—O15^i	83.52 (5)
O2—Mo1—N16	92.05 (5)	O1—Mo1—O15^i	85.52 (4)
O1—Mo1—N16	151.94 (6)	N16—Mo1—O15^i	77.73 (5)
O3—Mo1—N11	93.39 (6)	N11—Mo1—O15^i	77.88 (5)
O2—Mo1—N11	156.66 (5)	Mo1^i—O1—Mo1	144.69 (9)

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

Table 2

Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N16—H16···O2^i	0.88	2.19	2.9209 (18)	141
C13—H13···N1L	0.95	2.57	3.358 (3)	140
C24—H24···N1L^{ii}	0.95	2.67	3.379 (3)	132
C25—H25···N1L^{ii}	0.95	2.98	3.531 (3)	118

Symmetry codes: (i) $1 - x, -y, -z$; (ii) $x, 1 - y, \frac{1}{2} + z$.

All H atoms were located by difference Fourier synthesis and refined with fixed individual displacement parameters [$U_{iso}(H) = 1.2U_{eq}(N)$, 1.2 $U_{eq}(C)$ or $1.5U_{eq}(C_{methyl})$] using a riding model with N—H = 0.88 Å, aromatic C—H = 0.95 Å or methyl C—H = 0.98 Å.

The methyl groups were allowed to rotate about their local threefold axes.

Data collection: *X-Area* (Stoe & Cie, 2001); cell refinement: *X-Area*; data reduction: *X-Area*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991).

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.

Fabrizi de Biani, F., Jäkle, F., Spiegler, M., Wagner, M. & Zanello, P. (1997). *Inorg. Chem.* **36**, 2103–2111.

Herdtweck, E., Peters, F., Scherer, W. & Wagner, M. (1998). *Polyhedron*, **17**, 1149–1157.

Jäkle, F., Polborn, K. & Wagner, M. (1996). *Chem. Ber.* **129**, 603–606.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1991). *SHELXTL-Plus.* Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.

Stoe & Cie (2001). *X-Area*. Stoe & Cie, Darmstadt, Germany.

Tolf, B.-R., Piechaczek, J., Dahlbom, R., Theorell, H., Åkeson, Å. & Lundquist, G. (1979). *Acta Chem. Scand. Ser. B*, **33**, 483–487.