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A novel dinuclear Mo^{VI} complex with tris(3,5-dimethyl-1*H*-pyrazol-1-yl)methane

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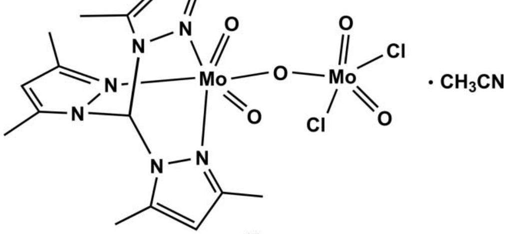
Recrystallization of $[MoO_2Cl\{HC(3,5\text{-}Me_2pz)_3\}]Cl$ [where $HC(3,5\text{-}Me_2pz)_3$ is tris(3,5-dimethyl-1*H*-pyrazol-1-yl)methane] led to the isolation of large quantities of the dinuclear complex dichlorido-2κ^2*Cl*-μ-oxido-κ^2*O*:*O*-tetraoxido-1κ^2*O*,2κ^2*O*-[tris(3,5-dimethyl-1*H*-pyrazol-1-yl-1κN^2)methane]dimolybdenum(IV) acetonitrile monosolvate, $[Mo_2Cl_2O_4(C_{16}H_{22}N_6)]\cdot CH_3CN$ or $[\{MoO_2Cl_2\}(\mu_2\text{-}O)\{MoO_2[HC(3,5\text{-}Me_2pz)_3]\}]\cdot CH_3CN$. At 150 K, this complex cocrystallizes in the orthorhombic space group *Pbcm* with an acetonitrile molecule. The complex has mirror symmetry: only half of the complex constitutes the asymmetric unit and all the heavy elements (namely Mo and Cl) are located on the mirror plane. The acetonitrile molecule also lies on a mirror plane. The two crystallographically independent Mo^{6+} centres have drastically different coordination environments: while one Mo atom is hexacoordinated and chelated to $HC(3,5\text{-}Me_2pz)_3$ (which occupies one face of the octahedron), the other Mo atom is instead pentacoordinated, having two chloride anions in the apical positions of the distorted trigonal bipyramid. This latter coordination mode of Mo^{VI} was found to be unprecedented. Individual complexes and solvent molecules are close-packed in the solid state, mediated by various supramolecular contacts.

Comment

It is just over 40 years since the first detailed report of the coordination chemistry of tripyrazolylmethane [Tpm or $HC(pz)_3$] ligands (Trofimenko, 1970). These tridentate ligands are members of the family of 'scorpionate' molecules and their complexes have found wide application in coordination, organometallic and bioinorganic chemistry (Bigmore *et al.*, 2005; Garcia *et al.*, 2009; Pettinari & Pettinari, 2005). Several 1:1 Tpm–Mo^{VI} complexes and related derivatives have been prepared as catalysts for the epoxidation of olefins (Gago *et al.*, 2010; Neves *et al.*, 2011; Santos *et al.*, 2001). The reaction of $[MoO_2X_2(THF)_2]$ (X = Cl, Br; THF is tetrahydrofuran) with $HC(pz)_3$ or tris(3,5-dimethyl-1*H*-pyrazol-1-yl)methane [$HC(3,5\text{-}Me_2pz)_3$] under dry conditions yields mononuclear complexes of the type $[MoO_2X(L)]X$ (Santos *et al.*, 2001). In the presence of residual amounts of water, these complexes have a tendency to form dinuclear derivatives *via* hydrolysis of the Mo—X bonds. Thus, starting from $[MoO_2Cl\{HC(3,5\text{-}Me_2pz)_3\}]BF_4$, the $[\{MoO_2[HC(3,5\text{-}Me_2pz)_3]\}_2(\mu_2\text{-}O)](BF_4)_2$ and $[\{MoO(O_2)_2(H_2O)\}(\mu_2\text{-}O)\{MoO_2[HC(3,5\text{-}Me_2pz)_3]\}]$ oxide-bridged species were isolated and their crystal structures established (Neves *et al.*, 2011). Pombeiro and co-workers described the crystal structures of three related symmetrical dimers containing the ligand tris(pyrazol-1-yl)methanesulfonate (Tpms), namely the Mo^{V} complexes $[\{MoO(\mu_2\text{-}O)(Tpms)\}_2]$ and $[\{MoOCl(Tpms)\}_2(\mu_2\text{-}O)]$, and the Mo^{VI} complex $[\{MoO_2(Tpms)\}_2(\mu_2\text{-}O)]$ (Dinoi *et al.*, 2010). In the present report, we describe the molecular and crystal structure of the dinuclear complex $[\{MoO_2Cl_2\}(\mu_2\text{-}O)\{MoO_2[HC(3,5\text{-}Me_2pz)_3]\}]\cdot CH_3CN$, (I), crystals of which were obtained during attempts to recrystallize the mononuclear complex $[MoO_2Cl\{HC(3,5\text{-}Me_2pz)_3\}]Cl$.



(I)

The crystal structure of (I) is based on the novel dinuclear complex $[\{MoO_2Cl_2\}(\mu_2\text{-}O)\{MoO_2[HC(3,5\text{-}Me_2pz)_3]\}]$, which is formed by two crystallographically independent Mo^{VI} metallic centres bridged by an O atom (μ_2-bridging oxide group) which imposes an Mo1$\cdots$Mo2 distance of 3.7808 (5) Å and an Mo1—O1—Mo2 kink angle of 164.76 (16)° (Fig. 1). We note that the complex has mirror symmetry with only half of the molecule composing the asymmetric unit (all heavy atoms, in particular the Mo and Cl ones, are located on the mirror plane). A search of the literature and the Cambridge Structural Database (CSD; Version 5.32; Allen, 2002) reveals only a handful of crystallographic reports of dinuclear Mo^{n+} complexes with $HC(3,5\text{-}Me_2pz)_3$ as a ligand: $[\{MoOCl_2\}(\mu_2\text{-}O)_2\{MoO[HC(3,5\text{-}Me_2pz)_3]\}]$ and $[\{MoO(OC_6H_4O)\}(\mu_2\text{-}O)_2\{MoO[HC(3,5\text{-}Me_2pz)_3]\}]$, reported by Enemark and collaborators (Dhawan *et al.*, 1995), and the above-mentioned $[\{MoO_2[HC(3,5\text{-}Me_2pz)_3]\}_2(\mu_2\text{-}O)]^{2+}$ and $[\{MoO(O_2)_2(H_2O)\}(\mu_2\text{-}O)\{MoO_2[HC(3,5\text{-}Me_2pz)_3]\}]$ related complexes (Neves *et al.*, 2011).

As shown in Fig. 1, the two independent Mo^{VI} centres of (I) have very different coordination environments. Atom Mo1 is

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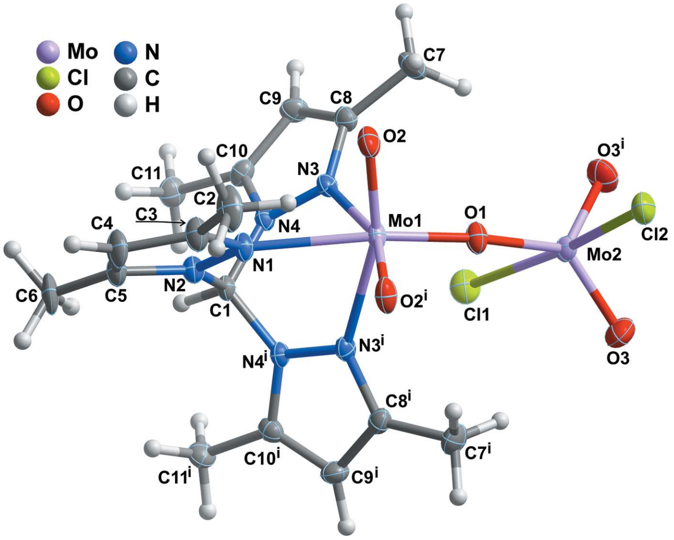

Figure 1

Schematic representation of the dinuclear title complex, (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. The acetonitrile solvent molecule has been omitted for clarity. [Symmetry code: (i) $x, y, -z + \frac{1}{2}$.]

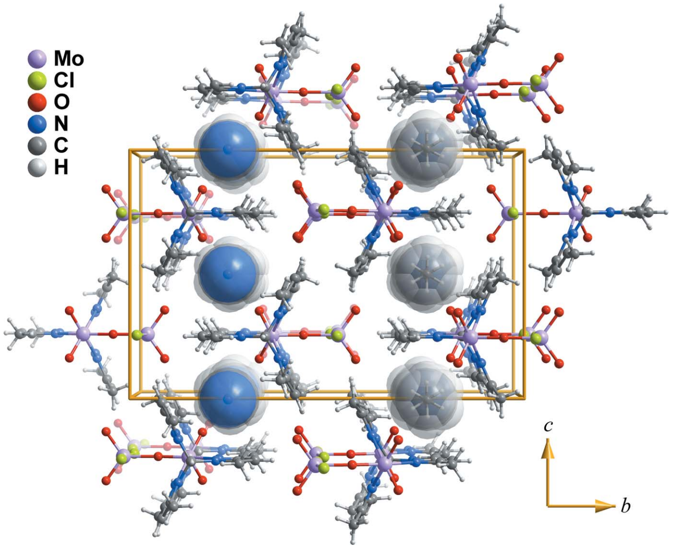

Figure 2

A perspective view, along the [100] direction of the unit cell, of the crystal packing of (I). The acetonitrile solvent molecules are represented in a mixed ball-and-stick and space-filling model.

six-coordinated, $\{MoN_3O_3\}$, by a whole HC(3,5-Me_2pz)$_3$ organic chelating linker, by two symmetry-related terminal oxide groups and by the aforementioned μ_2-bridging oxide group, exhibiting a highly distorted octahedral coordination environment, as reflected by the variation in the values of the Mo1—(N,O) bond lengths and the internal (N,O)—Mo1—(N,O) octahedral angles (see Table 1). As expected, the Mo1═O2 bond of the crystallographically independent terminal oxide group is shorter than the Mo1—O1 bond of the μ_2-bridging oxide group. In addition, the well known *trans* influence of the Mo═O bonds is clearly present in (I), with the Mo1—N3 connection being significantly longer than those *trans* (*i.e.* Mo1—N1) to the oxide bridge (see Fig. 1 and Table 1 for details). We note that the main structural features of the Mo1 coordination environment are very much comparable with those found in the octahedral centres of the related complexes mentioned in the previous paragraph (Neves *et al.*, 2011; Dhawan *et al.*, 1995).

In a similar fashion to that described for Mo1, the Mo2 centre is also coordinated by the O1 μ_2-bridging oxide group and two terminal oxide groups. The coordination is completed by two chloride anions, leading to a five-coordinated environment, $\{MoCl_2O_3\}$, the geometry of which strongly resembles a distorted trigonal bipyramid. Interestingly, as depicted in Fig. 1, the equatorial plane is composed solely of O atoms, while the axial positions are instead occupied by the two chloride anions (Fig. 1 and Table 1). To the best of our knowledge, this five-coordination mode observed for the Mo2 centre with trigonal–bipyramidal geometry is unprecedented. In fact, a cautious search of the literature and the CSD reveals only three other complexes with related $\{MoCl_2O_3\}$ environments, namely $[Mo_2O_4Cl_4]^{2-}$ (Mattes *et al.*, 1976), [{$MoOCl_2$}-(μ_2-O)$_2${MoO[HC(3,5-Me_2pz)$_3$]}] (Dhawan *et al.*, 1995) and [MoO(2,6-$Me_2C_6H_3O)_2Cl_2$] (Hanna *et al.*, 2004). However, in all these structures, the coordination polyhedron resembles a square pyramid, which is very different from that observed for Mo2.

Also worthy of note is the presence of intramolecular Mo2—Cl1$\cdots$*Cg*1 interactions (*Cg*1 is the centroid of the N3/N4/C8–C10 ring), with the Mo2$\cdots$*Cg*1 distance being 3.6140 (15) Å. These interactions occur between the Cl1 anion bound to atom Mo2 and the two adjacent mirror-related pyrazole rings of the HC(3,5-Me_2pz)$_3$ ligand chelated to atom Mo1 and strengthen (along with the μ_2-oxide bridge) the connection between the two crystallographically independent Mo^{VI} centres.

In the crystal structure of (I), each dinuclear [{MoO_2Cl_2}-(μ_2-O){MoO_2[HC(3,5-Me_2pz)$_3$]}] complex cocrystallizes with an acetonitrile solvent molecule which plays a decisive role in the stabilization of the compound, acting simultaneously as a space-filling entity and as a donor in weak supramolecular interactions (Fig. 2): the terminal –CH_3 group of the crystallographically independent acetonitrile molecule, atom C101, is engaged in a C—H$\cdots$O interaction with a neighbouring oxide group of a binuclear complex (see Table 2 for geometrical details).

Experimental

Tris(3,5-dimethyl-1*H*-pyrazol-1-yl)methane {HC(3,5-Me_2pz)$_3$} (Julia *et al.*, 1984; Neves *et al.*, 2011) and [MoO_2Cl{HC(3,5-Me_2pz)$_3$}]Cl (Santos *et al.*, 2001) were prepared according to published procedures. Single crystals of (I) were obtained from the recrystallization of the mononuclear complex by slow diffusion of diethyl ether into a concentrated acetonitrile solution. FT–IR (KBr, ν, cm^{-1}): 956 [*s*, ν_{sym}(Mo═O)], 939 [*s*, ν_{sym}(Mo═O)], 916 [*vs*, ν_{asym}(Mo═O)], 904 [*vs*, ν_{asym}(Mo═O)], 778 [*vs*, *br*, ν(Mo—O—Mo)]; ^{1}H NMR (500 MHz, 298 K, $CDCl_3$): δ 8.13 (*s*, 1H, CH), 6.31 (*s*, 1H, H4), 6.25 (*s*, 2H, H4), 2.86 (*s*, 3H, methyl group in position 3), 2.83 (*s*, 6H, methyl groups in position 3), 2.75 (*s*, 9H, methyl groups in position 5).

Table 1
Selected geometric parameters (Å, °).

Mo1—O1	1.854 (3)	Mo2—O1	1.960 (3)
Mo1—O2	1.706 (2)	Mo2—O3	1.693 (2)
Mo1—N1	2.258 (3)	Mo2—Cl1	2.3935 (11)
Mo1—N3	2.299 (2)	Mo2—Cl2	2.3997 (11)
O1—Mo1—N1	159.35 (12)	O1—Mo2—Cl1	84.38 (8)
O1—Mo1—N3	88.17 (9)	O1—Mo2—Cl2	83.52 (8)
O2—Mo1—O1	104.48 (9)	O3—Mo2—O1	125.62 (9)
O2^{i}—Mo1—O2	103.83 (16)	O3—Mo2—O3^{i}	108.75 (18)
O2—Mo1—N1	87.99 (9)	O3—Mo2—Cl1	93.76 (8)
O2—Mo1—N3	87.71 (10)	O3—Mo2—Cl2	93.28 (9)
O2—Mo1—N3^{i}	159.81 (9)	Cl1—Mo2—Cl2	167.90 (4)
N1—Mo1—N3	75.75 (9)	Mo1—O1—Mo2	164.97 (16)
N3^{i}—Mo1—N3	76.86 (11)		

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

Crystal data

$[Mo_2Cl_2O_4(C_{16}H_{22}N_6)]\cdot C_2H_3N$
M_r = 682.23
Orthorhombic, *Pbcm*
a = 8.6346 (5) Å
b = 21.6152 (12) Å
c = 13.6021 (8) Å
V = 2538.7 (3) Å^3
Z = 4
Mo *Kα* radiation
μ = 1.24 mm^{-1}
T = 150 K
0.11 × 0.08 × 0.06 mm

Data collection

Bruker APEXII X8 KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1998)
T_{min} = 0.876, T_{max} = 0.929
59602 measured reflections
3526 independent reflections
3061 reflections with $I > 2\sigma(I)$
R_{int} = 0.062

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.115
S = 1.11
3526 reflections
176 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.89 e Å^{-3}
$\Delta\rho_{min}$ = −1.53 e Å^{-3}

H atoms bound to C atoms were placed at idealized positions and included in the final structural model in the riding-motion approximation, with C—H = 1.00 (tertiary C—H), 0.95 (aromatic) or 0.98 Å (methyl), and with U_{iso}(H) = 1.2U_{eq}(C) (for tertiary and aromatic C—H) or 1.5U_{eq}(C) (for methyl H).

Data collection: *APEX2* (Bruker, 2006); cell refinement: *APEX2*; data reduction: *SAINT-Plus* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2009); software used to prepare material for publication: *SHELXTL*.

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Table 2
Selected short supramolecular interactions (Å, °) in (I).

*Cg*1 is the centroid of the N3/N4/C8–C10 ring.

A—*B*···*C*	*A*—*B*	*B*···*C*	*A*···*C*	*A*—*B*···*C*
Y—*X*···*Cg* contacts				
Mo2—Cl1···*Cg*1†	2.3935 (11)	3.6140 (15)	4.8687 (12)	106.50 (3)
Possible weak hydrogen bonds				
C4—H4···Cl1^{i}	0.95	2.80	3.704 (4)	158
C11—H11*A*···Cl2^{ii}	0.98	2.72	3.556 (3)	143
C11—H11*B*···O3^{iii}	0.98	2.46	3.427 (4)	170
C101—H10*C*···O2	0.98	2.47	3.310 (5)	144

† Two contacts with symmetry-related centroids, one with that belonging to the asymmetric unit and another generated by the symmetry code ($x, y, -z + \frac{1}{2}$). Symmetry codes: (i) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $x - 1, y, z$; (iii) $-x, -y + 2, z + \frac{1}{2}$.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3427). Services for accessing these data are described at the back of the journal.

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