METAL-ORGANIC COMPOUNDS

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trans-Diaquabis(hexafluoroacetylacetonato-*O*,*O′*)manganese(II) Monohydrate

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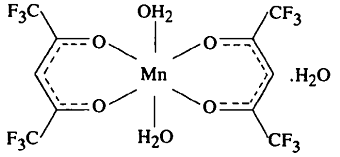
Abstract

In the crystals of *trans*-diaquabis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato-*O*,*O′*)manganese(II) monohydrate, $[Mn(C_5HF_6O_2)_2(H_2O)_2].H_2O$, the Mn atom and all three water molecules lie on a crystallographic mirror plane. Two of the water molecules are coordinated to the Mn atom in a *trans* geometry and the third links the structure into hydrogen-bonded sheets. The two planar hexafluoroacetylacetonato ligands related by the mirror plane form a dihedral angle of 41.6 (2)° with one another. One CF_3 group displayed significant disorder.

Comment

Metal complexes of the hexafluoroacetylacetonate ($hfac^-$) anion have been of interest for chemical vapor deposition due to the high vapor pressure they often exhibit. Neutral complexes of formula $M(hfac)_2$ are also excellent Lewis acids and can accept weakly basic ligands such as nitroxyl free radicals (Dickman, Porter & Doedens, 1986). The resulting nitroxyl adducts have been investigated for their unusual magnetic properties (Caneschi, Gatteschi & Rey, 1991).

During recrystallization of bis(2,2,6,6-tetramethylpiperidinyl-1-oxy)bis(hexafluoroacetylacetonato-*O*,*O′*)-manganese(II), a small number of crystals of the title compound, (I), were produced. The present structural analysis was performed in order to confirm the identity of the compound.



(I)

The structure of (I) (Fig. 1) reveals a *trans* geometry of the ligands, with the Mn atom and two *trans* water molecules (O3 and O4) residing on a crystallographic mirror plane. A third water molecule (O5*W*), also on the mirror plane, is an apparent hydrogen-bond acceptor from two coordinated waters of two different molecules, with O—H···O angles of 179 (6) and 177 (7)°. The O5*W* atom is also an apparent hydrogen-bond donor to two mirror-related $hfac^-$ O atoms on a third molecule, with an O—H···O angle of 147 (5)°. The other coordinated water molecule forms apparent hydrogen bonds with the remaining mirror-related $hfac^-$ O atoms on another adjacent complex, with an O—H···O angle of 145 (4)°. The O···O contact distances for these atoms ranged from 2.794 (5) to 2.914 (4) Å. Hydrogen-bond donation from water to coordinated $hfac^-$ O atoms was also seen in $[Cu(hfac)_2(H_2O)]$ (Pinkas, Huffman, Baxter, Chisholm & Caulton, 1995), which consists of hydrogen-bonded dimers. In the present structure, the apparent hydrogen-bonding interactions link the complexes into sheets which extend parallel to the *ac* plane. The two symmetry-related planar $hfac^-$ rings are not coplanar but form a dihedral angle of 41.5 (1)°; the Mn atom is 0.535 (4) Å out of the $hfac^-$ plane.

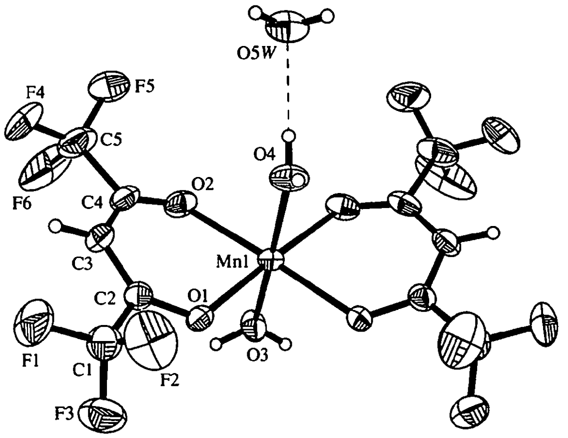


Fig. 1. View of $[Mn(C_5HF_6O_2)_2(H_2O)_2].H_2O$ showing the labeling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels and H atoms are drawn as small circles of arbitrary radii. Disordered F atoms have been omitted for clarity.

The *trans* geometry assumed by the $[Mn(hfac)_2(H_2O)_2]$ moiety of the title compound was also observed in the non-fluorinated derivative diaquabis(acetylacetonato)manganese(II) (Montgomery & Lingafelter, 1968; Onuma & Shibata, 1970). This is in contrast with the *cis* geometry found in the tetramethylpyrazine solvate of $[Mn(hfac)_2(H_2O)_2]$ (Adams, Bailey, Fenton & Khalil, 1993) and also in $[Ni(hfac)_2(H_2O)_2]$

(Romero, Cervantes-Lee & Porter, 1992). Evidently, the $[Mn(hfac)_2(H_2O)_2]$ molecule can adopt either a *cis* or *trans* geometry depending on its environment.

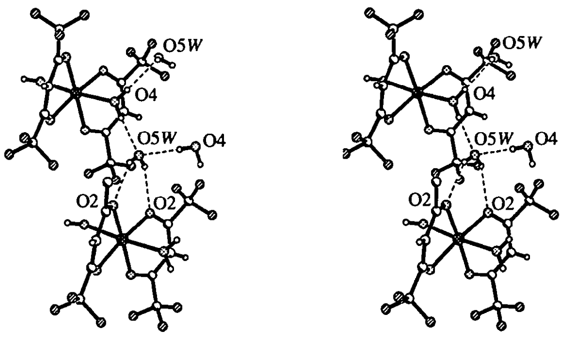


Fig. 2. Stereoview showing the environment of the non-coordinated water molecule. Apparent hydrogen-bonding contacts are shown as dotted lines. Some atoms have been omitted for clarity.

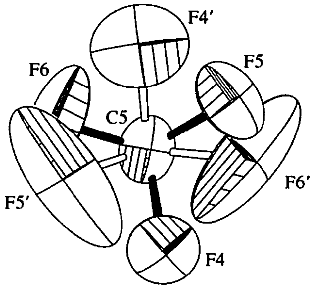


Fig. 3. View down the C5—C4 bond showing the disordered F atoms. Displacement ellipsoids are shown at 50% probability levels.

Experimental

Bis(2,2,6,6-tetramethylpiperidinyl-1-oxy)bis(hexafluoroacetylacetonato)manganese(II) was prepared as described previously (Dickman, Porter & Doedens, 1986). A sample of this material was recrystallized by heating about 0.5 g in 20 ml of undried *n*-heptane in an open beaker. The resulting solution was allowed to cool overnight, whereupon crystals of the red nitroxyl adduct formed and were collected by filtration. On standing, the filtrate deposited yellow crystals of the title compound.

Crystal data

$[Mn(C_5HF_6O_2)_2(H_2O)_2].H_2O$
$M_r = 523.10$
Orthorhombic
Pnma
$a = 7.2380\,(10)$ Å
$b = 22.149\,(3)$ Å
$c = 11.2440\,(10)$ Å
$V = 1802.6\,(4)$ Å^3
$Z = 4$
$D_x = 1.928$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 38 reflections
$\theta = 4.93–12.36°$
$\mu = 0.884$ mm^{-1}
$T = 173\,(2)$ K
Plate
0.30 × 0.30 × 0.04 mm
Yellow

Data collection

Siemens *P4/RA* diffractometer
ω scans
Absorption correction: none
2835 measured reflections
2135 independent reflections
1558 reflections with $I > 2\sigma(I)$
$R_{int} = 0.0346$

$\theta_{max} = 27.51°$
$h = -1 \rightarrow 9$
$k = -28 \rightarrow 1$
$l = -1 \rightarrow 14$
3 standard reflections every 97 reflections intensity decay: 7.36% (linear decay correction applied)

Refinement

Refinement on F^2
$R(F) = 0.0455$
$wR(F^2) = 0.1165$
$S = 1.075$
2135 reflections
187 parameters
H atoms refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.0523P)^2 + 0.8707P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.016$
$\Delta\rho_{max} = 0.492$ e Å^{-3}
$\Delta\rho_{min} = -0.295$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Mn1	0.17605 (9)	1/4	0.54015 (5)	0.0236 (2)
O1	0.3388 (3)	0.31940 (8)	0.6211 (2)	0.0286 (4)
O2	0.0307 (3)	0.32483 (10)	0.4600 (2)	0.0343 (5)
O3	−0.0200 (5)	1/4	0.6853 (3)	0.0395 (8)
O4	0.3561 (5)	1/4	0.3843 (3)	0.0355 (8)
O5*W*	0.2399 (5)	1/4	0.1420 (3)	0.0439 (9)
C1	0.5256 (6)	0.4045 (2)	0.6354 (3)	0.0435 (9)
C2	0.3582 (4)	0.37213 (13)	0.5816 (3)	0.0285 (6)
C3	0.2528 (5)	0.40215 (14)	0.4982 (3)	0.0361 (7)
C4	0.0967 (5)	0.37685 (14)	0.4459 (3)	0.0348 (7)
C5	−0.0141 (6)	0.4166 (2)	0.3603 (3)	0.0556 (11)
F1	0.5469 (4)	0.46047 (10)	0.6007 (3)	0.0739 (9)
F2	0.6809 (3)	0.37438 (12)	0.6078 (3)	0.0769 (8)
F3	0.5184 (4)	0.40362 (11)	0.7527 (2)	0.0635 (7)
F4†	0.0899 (6)	0.4651 (2)	0.3201 (4)	0.0639 (11)
F5†	−0.0538 (11)	0.3889 (2)	0.2638 (4)	0.073 (2)
F6†	−0.1507 (10)	0.4407 (4)	0.4146 (6)	0.103 (3)
F4′‡	−0.1880 (13)	0.3899 (5)	0.3438 (14)	0.097 (3)
F5′‡	−0.088 (4)	0.4657 (7)	0.3946 (14)	0.183 (13)
F6′‡	0.036 (2)	0.4066 (11)	0.2502 (9)	0.183 (12)

† Site occupancy = 0.67. ‡ Site occupancy = 0.33.

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

Mn1—O1	2.140 (2)	O2—C4	1.257 (4)
Mn1—O2	2.160 (2)	C1—C2	1.533 (5)
Mn1—O3	2.162 (3)	C2—C3	1.379 (5)
Mn1—O4	2.183 (3)	C3—C4	1.392 (5)
O1—C2	1.258 (3)	C4—C5	1.531 (4)
O1—Mn1—O1^{i}	91.85 (10)	C4—O2—Mn1	124.8 (2)
O1—Mn1—O2^{i}	175.39 (8)	Mn1—O4—O5*W*	126.2 (2)
O1—Mn1—O2	83.94 (8)	O1—C2—C3	128.7 (3)
O2^{i}—Mn1—O2	100.21 (12)	O1—C2—C1	112.5 (3)
O1—Mn1—O3	92.31 (9)	C3—C2—C1	118.7 (3)
O2—Mn1—O3	89.72 (9)	C2—C3—C4	122.9 (3)
O1—Mn1—O4	90.73 (9)	O2—C4—C3	128.6 (3)
O2—Mn1—O4	87.47 (9)	O2—C4—C5	114.1 (3)
O3—Mn1—O4	175.62 (15)	C3—C4—C5	117.3 (3)
C2—O1—Mn1	125.3 (2)		

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

H atoms were refined isotropically in observed positions. After anisotropic refinement of the non-H atoms, one of the CF_3 groups (C5) showed evidence of disorder, manifested in larger fluorine displacement parameters and significant residual electron density between the fluorine atomic positions. A disorder model including 28 additional parameters lowered wR_2(all data) from 22.16 to 11.20%. Several different disorder models were tried, including combinations of restrictions on C—F bond distances and restraints on anisotropic displacement parameters. None of the models tried were completely satisfactory in that a wide range of C—F bond lengths were observed for the disordered atoms. In the final model, restraints on displacement parameters were not included since these tended to raise the *R* factors without influencing the observed CF_3 group geometry. Restraints were applied, however, to C—F bond distances on the C5 atom using a C—F bond distance of 1.34 Å, with a standard deviation of 0.01. The final C—F distances for C1 ranged from 1.309 (4) to 1.343 (5) Å, with a mean of 1.32 [2] Å; on the C5 atom, the range was 1.271 (9) to 1.403 (8) Å, with a mean C—F distance of 1.32 [6] Å. The angles around C1 ranged from 104.9 (3) to 114.7 (3)°, with a mean of 109 [3]°, while the angles around C5 ranged from 91.3 (12) to 123.3 (11)°, with a mean of 109 [10]°.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXTL-Plus*.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BS1010). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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μ-Hydrido-μ-dicyclohexylphosphido-bis[dicyclohexylphosphine(tricarbonyl)rhenium]

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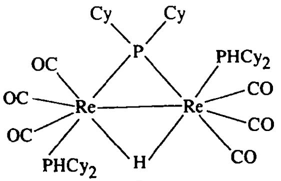
Abstract

The title compound, hexacarbonyl-1κ^3C,2κ^3C-μ-dicyclohexylphosphido-1:2κ^2P-bis(dicyclohexylphosphine)-1κP,2κP-μ-hydrido-dirhenium(*Re*—*Re*), $[Re_2H(C_{12}H_{22}P)(C_{12}H_{23}P)_2(CO)_6]$, has an Re—Re bond length of 3.2185 (8) Å which is symmetrically bridged by a H and a P atom. Two terminal $PH(C_6H_{11})_2$ ligands adopt *cis* positions with respect to the phosphido bridge and have a mutually *trans* configuration.

Comment

The study of phosphido-bridged homo- and heteronuclear transition metal cluster compounds is of great interest due to their metal–metal bond stabilities under various reaction conditions (Haupt, Balsaa & Flörke, 1988). The title compound, $[Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_6(PHCy_2)_2]$, (I) (Cy is cyclohexyl), is a new dinuclear example which was obtained from the reaction of $[Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_6(NCCH_3)_2]$ with $HPCy_2$ in $CHCl_3$ solution at 343 K.



(I)

The Re atom in (I) is surrounded by six non-metal ligands forming a distorted-octahedral coordination geometry (Fig. 1). These ligands are three carbonyl groups in *trans* positions with respect to the bridging μ-H and μ-P atoms, and a $PHCy_2$ ligand attached in an axial position. The second half of the molecule is symmetry related by a crystallographic twofold axis which runs through both bridging ligands. The two coordination octahedra around the metal atoms thus share one common edge along this axis.

The Re—Re bond length of 3.2185 (8) Å fulfills the requirement of 18 valence electrons for each metal atom.