Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

The cocrystal {4,4′-dimethoxy-2,2′-[propane-1,2-diylbis(nitrilomethylidyne)]diphenolato}methanol(pyridine)manganese(III) hexafluoridophosphate–{4,4′-dimethoxy-2,2′-[ethane-1,2-diylbis(nitrilomethylidyne)]diphenolato}methanol(pyridine)manganese(III) hexafluoridophosphate (1/1)

Mohammad Hossein Habibi,[a]‡ Elham Askari,[a] Suchada Chantrapromma[b]§ and Hoong-Kun Fun[c]*

[a]Catalysis Division, Chemistry Department, University of Isfahan, Isfahan 81746-73441, Iran, [b]Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat-Yai, Songkhla 90112, Thailand, and [c]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia
Correspondence e-mail: hkfun@usm.my

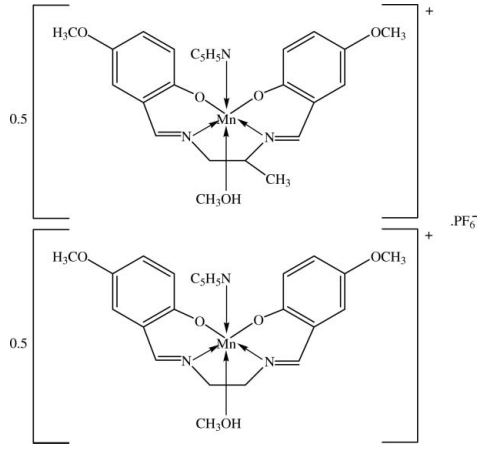
Received 26 October 2007; accepted 28 October 2007

Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; disorder in main residue; R factor = 0.049; wR factor = 0.138; data-to-parameter ratio = 21.0.

The title cocrystal, $[Mn(C_{19}H_{20}N_2O_2)(C_5H_5N)(CH_3OH)]PF_6\cdot[Mn(C_{18}H_{18}N_2O_2)(C_5H_5N)(CH_3OH)]PF_6$, is a 1:1 co-crystal of two Mn^{III} complexes with Schiff base ligands. In each structure, the Mn^{III} centre is in a six-coordinate distorted octahedral N_3O_3 environment, with the N_2O_2 donor atoms of the tetradentate Schiff base ligand as the equatorial plane and the pyridine and methanol molecules in the two axial positions. The difference in the two components of the co-crystal, which are disordered over the same site, is the addition of a methyl group to one of the two methylene C atoms linking the imine N atoms of the Schiff base ligand in one component. In the crystal structure, intermolecular O—H···O hydrogen bonds and weak intermolecular C—H···O interactions link the molecules into a network. A weak C—H···N intramolecular interaction is also observed in the structure of $[Mn(C_{19}H_{20}N_2O_2)(C_5H_5N)(CH_3OH)]PF_6$.

Related literature

For values of bond lengths, see Allen *et al.* (1987). For related structures, see, for example: Mitra *et al.* (2006); Naskar *et al.* (2004). For details of Schiff base complexes and their applications, see, for example: Clarke *et al.* (1998); Cozzi (2004); Darensbourg *et al.* (2006); Dimauro & Kozlowski (2002); Habibi *et al.* (2007); Marchetti *et al.* (1999); Kani *et al.* (2000); Paschke *et al.* (2002).



Experimental

Crystal data

$[Mn(C_{19}H_{20}N_2O_2)(C_5H_5N)(CH_4O)]PF_6\cdot[Mn(C_{18}H_{18}N_2O_2)(C_5H_5N)(CH_4O)]PF_6$
M_r = 1288.82
Monoclinic, $C2/c$
a = 23.4332 (6) Å
b = 16.3878 (4) Å
c = 14.2963 (4) Å
β = 93.988 (1)°
V = 5476.8 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.62 mm^{-1}
T = 100.0 (1) K
0.57 × 0.26 × 0.23 mm

Data collection

Bruker SMART APEX2 CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.716, T_{max} = 0.871
43484 measured reflections
7977 independent reflections
6665 reflections with $I > 2\sigma(I)$
R_{int} = 0.033

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.138
S = 1.04
7977 reflections
379 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 1.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.62 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O5—H1O5···O1^{i}	0.82 (3)	1.99 (3)	2.804 (2)	169 (3)
C17—H17A···O4^{ii}	0.93	2.57	3.465 (3)	161
C22—H22C···N3	0.96	2.62	3.318 (5)	130

Symmetry codes: (i) $-x, y, -z+\frac{3}{2}$; (ii) $x, -y, z-\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

‡ Additional correspondence author, email: habibi@chem.ui.ac.ir.
§ Additional correspondence author, email: suchada.c@psu.ac.th.

 doi:10.1107/S1600536807053883

MHH and EA thank the Isfahan University Centre of Excellence (Catalysts and Fuel Cells) for financial support. The authors also thank Universiti Sains Malaysia for Fundamental Research Grant Scheme (FRGS) grant No. 203/PFIZIK/671064.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2395).

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Bruker (2005). *APEX2* (Version 1.27), *SAINT* (Version 7.12A) and *SADABS* (Version 2004/1). Bruker AXS Inc., Madison, Wisconsin, USA.
Clarke, B., Clarke, N., Cunningham, D., Higgins, T., McArdle, P., Cholchuin, M. N. & Ogara, M. (1998). *J. Organomet. Chem.* **559**, 55–64.
Cozzi, P. G. (2004). *Chem. Soc. Rev.* **33**, 410–421.
Darensbourg, D. J., Ganguly, P. & Billodeaux, D. (2006). *Macromolecules*, **39**, 2722–2722.
Dimauro, E. F. & Kozlowski, M. C. (2002). *J. Am. Chem. Soc.* **124**, 12668–12669.
Habibi, M. H., Mokhtari, R., Harrington, R. W. & Clegg, W. (2007). *Acta Cryst.* E**63**, m2304.
Kani, Y., Ohba, S. & Nishida, Y. (2000). *Acta Cryst.* C**56**, e194.
Marchetti, F., Pettinari, C., Pettinari, R., Cingolani, A. & Leonesi, D. (1999). *Polyhedron*, **18**, 3041–3050.
Mitra, K., Biswas, S., Lucas, C. R. & Adhikary, B. (2006). *Inorg. Chim. Acta*, **359**, 1997–2003.
Naskar, S., Biswas, S., Mishra, D., Adhikary, B., Falvello, L. R., Soler, T., Schwalbe, C. H. & Chattopadhyay, S. K. (2004). *Inorg. Chim. Acta*, **357**, 4257–4264.
Paschke, R., Balkow, D. & Sinn, E. (2002). *Inorg. Chem.* **41**, 1949–1953.
Sheldrick, G. M. (1998). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

supplementary materials

Acta Cryst. (2007). E**63**, m2905-m2906 [**doi:10.1107/S1600536807053883**]

The cocrystal {4,4'-dimethoxy-2,2'-[propane-1,2-diylbis(nitrilomethylidyne)]diphenolato}methanol(pyridine)manganese(III) hexafluoridophosphate-{4,4'-dimethoxy-2,2'-[ethane-1,2-diylbis(nitrilomethylidyne)]diphenolato}methanol(pyridine)manganese(III) hexafluoridophosphate (1/1)

M. H. Habibi, E. Askari, S. Chantrapromma and H.-K. Fun

Comment

Transition metal compounds containing Schiff base ligands have been of interest for many years (Kani *et al.*, 2000; Habibi *et al.*, 2007; Paschke *et al.*, 2002), since they play an important role in the development of coordination chemistry, particularly in relation to catalysis and enzymatic reactions, as well as molecular magnetism (Cozzi *et al.*, 2004; Darensbourg *et al.*, 2006; Dimauro & Kozlowski, 2002). A considerable number of complexes with multidentate Schiff bases containing O,*N* donor atoms have been studied (Clarke *et al.*, 1998; Marchetti *et al.*, 1999). In this paper, we report the crystal structure of two co-crystallized Mn^{III}-Schiff base complexes.

The asymmetric unit of the cocrystal (Fig. 1) consists of a mixture of 0.5[$Mn(C_{19}H_{20}N_2O_2)(C_5H_5N)(CH_3OH)$], 0.5[$Mn(C_{18}H_{18}N_2O_2)(C_5H_5N)(CH_3OH)$] and PF_6. The difference between the two components of the co-crystal concerned the substituents on the C21 atom; in one case two H atoms were attached whereas in the other component one H atom is replaced by the methyl group (C22). The environment around Mn^{III} shows a distorted octahedral geometry with the N_2O_2 of tetradentate Schiff base ligand as the basal plane. The two phenolic O atoms and two imine N atoms are in *cis* positions. The pyridine and methanol molecules are in the two axial positions. The Mn1—O1 and Mn1—O2 distances of 1.8909 (13) Å and 1.8655 (14) Å, and Mn—N1 and Mn1—N2 distances of 1.9764 (17) Å and 1.9887 (16) Å, respectively lie in the same range as observed for closely related Mn^{III} complexes of Schiff base ligands (Mitra *et al.*, 2006; Naskar *et al.*, 2004). However there are elongations of the axial bonds Mn1—O5 = 2.2986 (16) Å and Mn1—N3 = 2.3532 (18) Å. The dihedral angle between the two benzene rings of the Schiff base ligand is 18.83 (9)°. One methoxy group is coplanar with the attached benzene ring while another one is slightly twisted out of the ring plane as indicated by the torsion angles C23—O3—C4—C5 = 0.6 (3)° and C24—O4—C11—C10 = −16.7 (4)°. Other bond lengths and angles in the ligands are in normal ranges (Allen *et al.*, 1987).

In the crystal packing (Fig. 2), the methanol molecule is involved in an intermolecular O—H···O hydrogen bond and weak C–H···O intermolecular interactions linking the molecules into a network (Table 1, Fig. 2). Morover in the structure of [$Mn(C_{19}H_{20}N_2O_2)(C_5H_5N)(CH_3OH)$] ion, a weak C–H···N interaction between the pyridine and the C22 methyl group was also present [C22—H22C···N3].

Experimental

To a stirred solution of $Mn(CH_3COO)_2{\cdot}2H_2O$ (0.0662 g, 0.5 mmol) in methanol (25 ml) was added an equimolar quantity of (2-hydroxy 5-methoxy benzaldehyde and 1,2 diamino propane (0.171 g, 0.5 mmol). The pink solution turned dark brown immediately upon formation of the Mn^{II} complexes. To this solution was added 4 mmol of pyridine, and air was bubbled

through the reaction mixture for about 3 h. 0.5 mmol of NH_4PF_6 was then added to the resulting dark brown solution and stirred for 5 minutes. A dark brown microcrystalline solid was formed by slow evaporation of methanol at room temperature. Brown single crystals of the Mn^{III} complexes suitable for *x*-ray structure determination were obtained after recrystallization by slow evaporation from methanol/propanol (2:1 *v*/*v*) solution at room temperature after several days.

Refinement

The H atom attached to the O atom of the methanol ligand was located in a difference map and isotropically refined. The remaining H atoms were positioned geometrically and allowed to ride on their parent atoms, with the C—H distances in the range 0.93–0.98 Å. The U_{iso} values were constrained to be $1.5U_{eq}$ of the carrier atom for methyl H atoms and $1.2U_{eq}$ for the remaining H atoms. A rotating group model was used for the methyl groups.

Figures

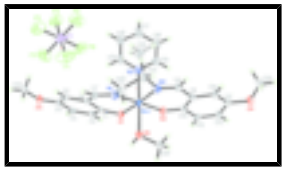


Fig. 1. The molecular structure of the title cocrystal, showing 50% probability displacement ellipsoids and the atomic numbering. Bonds to the C22 methyl group of the second component of the co-crystal are drawn as open lines. All other bonds are shown as filled lines.

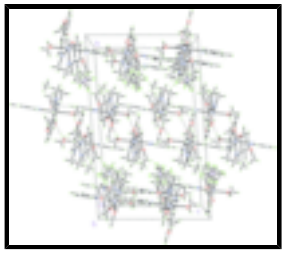


Fig. 2. The crystal packing of the title compound, viewed approximately along the *b* axis. C—H···O and O—H···O interactions were drawn as dashed lines.

{4,4'-dimethoxy-2,2'-[propane-1,2- diylbis(nitrilomethylidyne)]diphenolato}methanol(pyridine)manganese(III) hexafluorophosphate–{4,4'-dimethoxy-2,2'-[ethane-1,2-diylbis(nitrilomethylidyne)]diphenolato}methanol(pyridine)manganese(III) hexafluorophosphate (1/1)

Crystal data

$[Mn(C_{19}H_{20}N_2O_2)(C_5H_5N)(CH_4O)]PF_6 \cdot [Mn(C_{18}H_{18}N_2O_2)(C_5H_5N)(CH_4O)]PF_6$	F_{000} = 2640
M_r = 1288.82	D_x = 1.563 Mg m^{-3}
Monoclinic, *C*2/*c*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -C 2yc	Cell parameters from 7977 reflections
a = 23.4332 (6) Å	θ = 1.7–30.0º
b = 16.3878 (4) Å	μ = 0.62 mm^{-1}
c = 14.2963 (4) Å	*T* = 100.0 (1) K
β = 93.988 (1)º	Block, brown
V = 5476.8 (2) Å^3	0.57 × 0.26 × 0.23 mm
Z = 4	

Data collection

Bruker SMART APEX2 CCD area-detector diffractometer	7977 independent reflections
Radiation source: fine-focus sealed tube	6665 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.033$
Detector resolution: 8.33 pixels mm^{-1}	$\theta_{max} = 30.0°$
$T = 100.0(1)$ K	$\theta_{min} = 1.7°$
ω scans	$h = -32 \rightarrow 32$
Absorption correction: multi-scan (SADABS; Bruker, 2005)	$k = -23 \rightarrow 23$
$T_{min} = 0.716$, $T_{max} = 0.871$	$l = -19 \rightarrow 20$
43484 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.049$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.138$	$w = 1/[\sigma^2(F_o^2) + (0.0685P)^2 + 11.1129P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} = 0.001$
7977 reflections	$\Delta\rho_{max} = 1.40$ e Å^{-3}
379 parameters	$\Delta\rho_{min} = -0.62$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Experimental. The low-temparture data was collected with the Oxford Cyrosystem Cobra low-temperature attachment.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2$sigma(F^2) is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Mn1	0.086000 (11)	0.179324 (17)	0.64225 (2)	0.01968 (9)	
P1	0.22652 (3)	0.50955 (5)	0.58969 (6)	0.04204 (17)	

F1	0.23555 (11)	0.46971 (17)	0.69076 (15)	0.0831 (7)
F2	0.28040 (8)	0.46209 (14)	0.55735 (16)	0.0696 (6)
F3	0.17260 (8)	0.55855 (15)	0.62030 (19)	0.0787 (7)
F4	0.21769 (8)	0.54870 (12)	0.48656 (14)	0.0568 (5)
F5	0.26607 (8)	0.58567 (14)	0.62166 (17)	0.0716 (6)
F6	0.18576 (9)	0.43551 (12)	0.55787 (15)	0.0648 (5)
O1	0.01672 (6)	0.23882 (8)	0.63767 (10)	0.0216 (3)
O2	0.04976 (6)	0.08047 (8)	0.61213 (11)	0.0225 (3)
O3	−0.01802 (6)	0.57202 (8)	0.61205 (11)	0.0262 (3)
O4	0.12736 (7)	−0.23205 (9)	0.55721 (13)	0.0325 (4)
O5	0.07737 (6)	0.15465 (9)	0.79891 (11)	0.0243 (3)
N1	0.13089 (7)	0.27512 (10)	0.68817 (14)	0.0257 (4)
N2	0.16274 (7)	0.12696 (10)	0.64994 (13)	0.0240 (3)
N3	0.10136 (7)	0.21039 (11)	0.48527 (13)	0.0258 (3)
C1	0.01127 (8)	0.32005 (11)	0.63213 (13)	0.0193 (3)
C2	−0.04206 (8)	0.35280 (12)	0.60048 (13)	0.0205 (3)
H2A	−0.0723	0.3178	0.5833	0.025*
C3	−0.05027 (8)	0.43644 (12)	0.59452 (14)	0.0218 (4)
H3A	−0.0859	0.4569	0.5735	0.026*
C4	−0.00546 (9)	0.49047 (11)	0.61986 (13)	0.0214 (4)
C5	0.04696 (8)	0.45992 (11)	0.65106 (13)	0.0206 (3)
H5A	0.0768	0.4955	0.6683	0.025*
C6	0.05608 (8)	0.37491 (11)	0.65722 (13)	0.0200 (3)
C7	0.11259 (8)	0.34918 (12)	0.69061 (15)	0.0237 (4)
H7A	0.1377	0.3888	0.7157	0.028*
C8	0.17357 (8)	0.05123 (12)	0.63493 (15)	0.0243 (4)
H8A	0.2117	0.0352	0.6386	0.029*
C9	0.13105 (8)	−0.01061 (11)	0.61284 (14)	0.0214 (4)
C10	0.15082 (8)	−0.09082 (12)	0.59678 (15)	0.0241 (4)
H10A	0.1899	−0.1016	0.6008	0.029*
C11	0.11268 (9)	−0.15269 (12)	0.57541 (15)	0.0241 (4)
C12	0.05378 (9)	−0.13682 (12)	0.57161 (15)	0.0243 (4)
H12A	0.0279	−0.1791	0.5589	0.029*
C13	0.03392 (8)	−0.05904 (12)	0.58664 (14)	0.0226 (4)
H13A	−0.0053	−0.0497	0.5845	0.027*
C14	0.07180 (8)	0.00630 (11)	0.60511 (14)	0.0205 (3)
C15	0.10906 (9)	0.14901 (14)	0.42499 (17)	0.0297 (4)
H15A	0.1081	0.0957	0.4472	0.036*
C16	0.11828 (13)	0.16116 (16)	0.33226 (19)	0.0413 (6)
H16A	0.1224	0.1169	0.2925	0.050*
C17	0.12144 (14)	0.24039 (17)	0.29851 (19)	0.0448 (6)
H17A	0.1274	0.2501	0.2358	0.054*
C18	0.11554 (13)	0.30451 (15)	0.36011 (18)	0.0403 (6)
H18A	0.1188	0.3583	0.3403	0.048*
C19	0.10472 (11)	0.28675 (14)	0.45162 (16)	0.0329 (5)
H19A	0.0995	0.3300	0.4923	0.039*
C20	0.18887 (10)	0.25330 (15)	0.7290 (2)	0.0430 (6)
H20A	0.1871	0.2342	0.7930	0.052*
H20B	0.2141	0.3003	0.7292	0.052*

C21	0.21073 (9)	0.18537 (13)	0.6669 (2)	0.0375 (6)	
H21A	0.2419	0.1570	0.7028	0.045*	
H21B	0.2231	0.2068	0.6092	0.045*	0.50
C22	0.2334 (2)	0.2189 (3)	0.5850 (4)	0.0370 (10)	0.50
H22A	0.2450	0.1754	0.5456	0.055*	0.50
H22B	0.2658	0.2525	0.6031	0.055*	0.50
H22C	0.2046	0.2512	0.5514	0.055*	0.50
C23	0.02777 (10)	0.62700 (12)	0.63792 (16)	0.0291 (4)	
H23A	0.0143	0.6822	0.6315	0.044*	
H23B	0.0584	0.6185	0.5978	0.044*	
H23C	0.0413	0.6172	0.7018	0.044*	
C24	0.18388 (13)	−0.24614 (17)	0.5361 (3)	0.0666 (11)	
H24A	0.1873	−0.3007	0.5127	0.100*	
H24B	0.2088	−0.2395	0.5918	0.100*	
H24C	0.1943	−0.2079	0.4894	0.100*	
C25	0.08497 (9)	0.07339 (13)	0.83507 (16)	0.0272 (4)	
H25A	0.0795	0.0733	0.9010	0.041*	
H25B	0.1229	0.0549	0.8252	0.041*	
H25C	0.0576	0.0376	0.8032	0.041*	
H1O5	0.0485 (13)	0.1735 (18)	0.820 (2)	0.036 (8)*	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.01588 (14)	0.01570 (14)	0.02743 (16)	−0.00017 (9)	0.00126 (10)	−0.00030 (11)
P1	0.0271 (3)	0.0463 (4)	0.0540 (4)	−0.0051 (3)	0.0123 (3)	0.0030 (3)
F1	0.0822 (15)	0.115 (2)	0.0517 (12)	−0.0267 (15)	0.0045 (11)	0.0177 (13)
F2	0.0533 (11)	0.0738 (13)	0.0848 (15)	0.0268 (10)	0.0260 (10)	0.0223 (11)
F3	0.0429 (10)	0.0824 (15)	0.1151 (19)	−0.0016 (10)	0.0375 (11)	−0.0248 (14)
F4	0.0494 (10)	0.0566 (11)	0.0648 (12)	0.0035 (8)	0.0067 (8)	0.0195 (9)
F5	0.0468 (10)	0.0760 (14)	0.0926 (16)	−0.0250 (10)	0.0103 (10)	−0.0108 (12)
F6	0.0711 (13)	0.0595 (12)	0.0652 (12)	−0.0296 (10)	0.0135 (10)	−0.0030 (10)
O1	0.0177 (6)	0.0156 (6)	0.0316 (7)	0.0000 (5)	0.0021 (5)	0.0012 (5)
O2	0.0169 (6)	0.0165 (6)	0.0340 (8)	0.0001 (5)	0.0010 (5)	−0.0021 (5)
O3	0.0312 (7)	0.0160 (6)	0.0310 (8)	0.0016 (5)	0.0004 (6)	−0.0002 (6)
O4	0.0333 (8)	0.0180 (7)	0.0475 (10)	0.0032 (6)	0.0121 (7)	−0.0022 (6)
O5	0.0214 (6)	0.0211 (6)	0.0309 (8)	0.0022 (5)	0.0053 (5)	0.0007 (6)
N1	0.0184 (7)	0.0206 (8)	0.0374 (10)	0.0000 (6)	−0.0025 (6)	−0.0008 (7)
N2	0.0166 (7)	0.0208 (8)	0.0347 (9)	−0.0009 (6)	0.0019 (6)	0.0006 (7)
N3	0.0249 (8)	0.0247 (8)	0.0276 (9)	0.0025 (6)	0.0012 (6)	−0.0014 (7)
C1	0.0205 (8)	0.0176 (8)	0.0202 (8)	0.0004 (6)	0.0039 (6)	0.0004 (7)
C2	0.0201 (8)	0.0203 (8)	0.0213 (9)	−0.0004 (6)	0.0020 (6)	−0.0004 (7)
C3	0.0236 (8)	0.0200 (8)	0.0219 (9)	0.0032 (7)	0.0023 (7)	0.0009 (7)
C4	0.0298 (9)	0.0166 (8)	0.0182 (8)	0.0012 (7)	0.0049 (7)	0.0002 (7)
C5	0.0246 (8)	0.0179 (8)	0.0198 (8)	−0.0021 (7)	0.0045 (7)	−0.0011 (7)
C6	0.0216 (8)	0.0177 (8)	0.0209 (9)	0.0000 (6)	0.0028 (6)	0.0003 (7)
C7	0.0220 (8)	0.0194 (8)	0.0296 (10)	−0.0027 (7)	0.0012 (7)	−0.0020 (8)
C8	0.0182 (8)	0.0216 (9)	0.0335 (10)	0.0015 (7)	0.0040 (7)	0.0021 (8)

C9	0.0193 (8)	0.0189 (8)	0.0265 (9)	0.0012 (6)	0.0048 (7)	0.0013 (7)
C10	0.0227 (9)	0.0204 (9)	0.0298 (10)	0.0042 (7)	0.0065 (7)	0.0031 (8)
C11	0.0275 (9)	0.0178 (8)	0.0276 (10)	0.0030 (7)	0.0066 (7)	0.0027 (7)
C12	0.0262 (9)	0.0183 (8)	0.0286 (10)	−0.0013 (7)	0.0035 (7)	0.0015 (7)
C13	0.0213 (8)	0.0189 (8)	0.0276 (10)	−0.0003 (7)	0.0029 (7)	0.0000 (7)
C14	0.0211 (8)	0.0184 (8)	0.0223 (9)	0.0010 (6)	0.0034 (7)	0.0015 (7)
C15	0.0292 (10)	0.0261 (10)	0.0339 (11)	−0.0007 (8)	0.0034 (8)	−0.0040 (9)
C16	0.0591 (16)	0.0320 (12)	0.0333 (13)	0.0033 (11)	0.0065 (11)	−0.0090 (10)
C17	0.0682 (18)	0.0389 (13)	0.0279 (12)	0.0129 (13)	0.0071 (12)	−0.0003 (10)
C18	0.0598 (16)	0.0284 (11)	0.0328 (12)	0.0155 (11)	0.0038 (11)	0.0028 (10)
C19	0.0436 (12)	0.0265 (10)	0.0285 (11)	0.0109 (9)	0.0020 (9)	−0.0006 (9)
C20	0.0249 (10)	0.0292 (11)	0.0723 (19)	0.0044 (8)	−0.0146 (11)	−0.0136 (12)
C21	0.0186 (9)	0.0229 (10)	0.0709 (18)	−0.0023 (7)	0.0032 (10)	−0.0033 (11)
C22	0.027 (2)	0.030 (2)	0.054 (3)	−0.0042 (17)	0.0057 (19)	0.003 (2)
C23	0.0385 (11)	0.0178 (9)	0.0307 (11)	−0.0025 (8)	−0.0010 (8)	−0.0008 (8)
C24	0.0460 (16)	0.0268 (12)	0.132 (3)	0.0040 (11)	0.0426 (19)	−0.0128 (17)
C25	0.0290 (10)	0.0243 (9)	0.0287 (10)	0.0027 (8)	0.0049 (8)	0.0029 (8)

Geometric parameters (Å, °)

Mn1—O2	1.8655 (14)	C8—H8A	0.9300
Mn1—O1	1.8909 (13)	C9—C14	1.413 (3)
Mn1—N1	1.9764 (17)	C9—C10	1.418 (3)
Mn1—N2	1.9887 (16)	C10—C11	1.372 (3)
Mn1—O5	2.2986 (16)	C10—H10A	0.9300
Mn1—N3	2.3532 (18)	C11—C12	1.402 (3)
P1—F2	1.5792 (19)	C12—C13	1.379 (3)
P1—F3	1.584 (2)	C12—H12A	0.9300
P1—F1	1.586 (2)	C13—C14	1.404 (3)
P1—F6	1.5909 (19)	C13—H13A	0.9300
P1—F5	1.601 (2)	C15—C16	1.372 (4)
P1—F4	1.608 (2)	C15—H15A	0.9300
O1—C1	1.339 (2)	C16—C17	1.389 (4)
O2—C14	1.327 (2)	C16—H16A	0.9300
O3—C4	1.371 (2)	C17—C18	1.384 (4)
O3—C23	1.430 (3)	C17—H17A	0.9300
O4—C11	1.375 (2)	C18—C19	1.381 (3)
O4—C24	1.398 (3)	C18—H18A	0.9300
O5—C25	1.435 (2)	C19—H19A	0.9300
O5—H1O5	0.82 (3)	C20—C21	1.534 (4)
N1—C7	1.288 (3)	C20—H20A	0.9700
N1—C20	1.485 (3)	C20—H20B	0.9700
N2—C8	1.288 (3)	C21—C22	1.428 (6)
N2—C21	1.484 (3)	C21—H21A	0.9800
N3—C15	1.345 (3)	C21—H21B	0.9599
N3—C19	1.345 (3)	C22—H21B	0.4775
C1—C2	1.406 (3)	C22—H22A	0.9600
C1—C6	1.410 (3)	C22—H22B	0.9600
C2—C3	1.386 (3)	C22—H22C	0.9600

C2—H2A	0.9300	C23—H23A	0.9600
C3—C4	1.402 (3)	C23—H23B	0.9600
C3—H3A	0.9300	C23—H23C	0.9600
C4—C5	1.372 (3)	C24—H24A	0.9600
C5—C6	1.411 (3)	C24—H24B	0.9600
C5—H5A	0.9300	C24—H24C	0.9600
C6—C7	1.439 (3)	C25—H25A	0.9600
C7—H7A	0.9300	C25—H25B	0.9600
C8—C9	1.441 (3)	C25—H25C	0.9600
O2—Mn1—O1	93.66 (6)	C14—C9—C8	122.69 (17)
O2—Mn1—N1	171.76 (7)	C10—C9—C8	117.32 (17)
O1—Mn1—N1	92.16 (6)	C11—C10—C9	120.41 (18)
O2—Mn1—N2	91.92 (6)	C11—C10—H10A	119.8
O1—Mn1—N2	174.42 (6)	C9—C10—H10A	119.8
N1—Mn1—N2	82.30 (7)	C10—C11—O4	125.01 (18)
O2—Mn1—O5	90.15 (6)	C10—C11—C12	119.73 (18)
O1—Mn1—O5	89.48 (6)	O4—C11—C12	115.26 (18)
N1—Mn1—O5	84.08 (7)	C13—C12—C11	120.50 (18)
N2—Mn1—O5	90.61 (6)	C13—C12—H12A	119.7
O2—Mn1—N3	93.73 (6)	C11—C12—H12A	119.7
O1—Mn1—N3	92.48 (6)	C12—C13—C14	121.23 (18)
N1—Mn1—N3	91.83 (7)	C12—C13—H13A	119.4
N2—Mn1—N3	87.04 (7)	C14—C13—H13A	119.4
O5—Mn1—N3	175.53 (6)	O2—C14—C13	117.93 (16)
F2—P1—F3	178.74 (14)	O2—C14—C9	124.01 (17)
F2—P1—F1	90.30 (14)	C13—C14—C9	118.04 (17)
F3—P1—F1	90.88 (15)	N3—C15—C16	123.2 (2)
F2—P1—F6	90.97 (13)	N3—C15—H15A	118.4
F3—P1—F6	89.49 (12)	C16—C15—H15A	118.4
F1—P1—F6	89.19 (12)	C15—C16—C17	119.1 (2)
F2—P1—F5	90.50 (12)	C15—C16—H16A	120.4
F3—P1—F5	89.03 (12)	C17—C16—H16A	120.4
F1—P1—F5	91.31 (14)	C18—C17—C16	118.6 (2)
F6—P1—F5	178.45 (13)	C18—C17—H17A	120.7
F2—P1—F4	89.00 (11)	C16—C17—H17A	120.7
F3—P1—F4	89.82 (13)	C19—C18—C17	118.4 (2)
F1—P1—F4	179.15 (15)	C19—C18—H18A	120.8
F6—P1—F4	90.33 (11)	C17—C18—H18A	120.8
F5—P1—F4	89.19 (12)	N3—C19—C18	123.7 (2)
C1—O1—Mn1	126.35 (12)	N3—C19—H19A	118.2
C14—O2—Mn1	129.75 (12)	C18—C19—H19A	118.2
C4—O3—C23	116.11 (16)	N1—C20—C21	106.3 (2)
C11—O4—C24	116.77 (18)	N1—C20—H20A	110.5
C25—O5—Mn1	119.81 (12)	C21—C20—H20A	110.5
C25—O5—H1O5	108 (2)	N1—C20—H20B	110.5
Mn1—O5—H1O5	115 (2)	C21—C20—H20B	110.5
C7—N1—C20	120.88 (18)	H20A—C20—H20B	108.7
C7—N1—Mn1	125.93 (14)	C22—C21—N2	115.8 (3)
C20—N1—Mn1	113.00 (14)	C22—C21—C20	110.7 (3)

C8—N2—C21	119.55 (17)	N2—C21—C20	106.44 (18)
C8—N2—Mn1	126.47 (14)	C22—C21—H21A	107.7
C21—N2—Mn1	113.76 (13)	N2—C21—H21A	108.0
C15—N3—C19	116.9 (2)	C20—C21—H21A	107.9
C15—N3—Mn1	119.05 (15)	N2—C21—H21B	111.5
C19—N3—Mn1	123.99 (15)	C20—C21—H21B	111.4
O1—C1—C2	118.52 (17)	H21A—C21—H21B	111.3
O1—C1—C6	123.55 (17)	C21—C22—H22A	109.5
C2—C1—C6	117.92 (17)	C21—C22—H22B	109.5
C3—C2—C1	120.92 (18)	H22A—C22—H22B	109.5
C3—C2—H2A	119.5	C21—C22—H22C	109.5
C1—C2—H2A	119.5	H22A—C22—H22C	109.5
C2—C3—C4	120.70 (18)	H22B—C22—H22C	109.5
C2—C3—H3A	119.6	O3—C23—H23A	109.5
C4—C3—H3A	119.6	O3—C23—H23B	109.5
O3—C4—C5	124.35 (18)	H23A—C23—H23B	109.5
O3—C4—C3	116.23 (17)	O3—C23—H23C	109.5
C5—C4—C3	119.41 (17)	H23A—C23—H23C	109.5
C4—C5—C6	120.58 (18)	H23B—C23—H23C	109.5
C4—C5—H5A	119.7	O4—C24—H24A	109.5
C6—C5—H5A	119.7	O4—C24—H24B	109.5
C1—C6—C5	120.45 (17)	H24A—C24—H24B	109.5
C1—C6—C7	123.34 (17)	O4—C24—H24C	109.5
C5—C6—C7	116.21 (17)	H24A—C24—H24C	109.5
N1—C7—C6	124.55 (18)	H24B—C24—H24C	109.5
N1—C7—H7A	117.7	O5—C25—H25A	109.5
C6—C7—H7A	117.7	O5—C25—H25B	109.5
N2—C8—C9	124.98 (18)	H25A—C25—H25B	109.5
N2—C8—H8A	117.5	O5—C25—H25C	109.5
C9—C8—H8A	117.5	H25A—C25—H25C	109.5
C14—C9—C10	119.98 (18)	H25B—C25—H25C	109.5
O2—Mn1—O1—C1	−163.78 (16)	O1—C1—C6—C5	−178.93 (18)
N1—Mn1—O1—C1	22.05 (16)	C2—C1—C6—C5	0.4 (3)
O5—Mn1—O1—C1	106.10 (16)	O1—C1—C6—C7	0.6 (3)
N3—Mn1—O1—C1	−69.88 (16)	C2—C1—C6—C7	179.99 (19)
O1—Mn1—O2—C14	−177.40 (17)	C4—C5—C6—C1	−0.5 (3)
N2—Mn1—O2—C14	2.71 (18)	C4—C5—C6—C7	179.89 (18)
O5—Mn1—O2—C14	−87.91 (17)	C20—N1—C7—C6	−176.6 (2)
N3—Mn1—O2—C14	89.87 (17)	Mn1—N1—C7—C6	−1.9 (3)
O2—Mn1—O5—C25	38.30 (14)	C1—C6—C7—N1	10.8 (3)
O1—Mn1—O5—C25	131.96 (14)	C5—C6—C7—N1	−169.7 (2)
N1—Mn1—O5—C25	−135.81 (14)	C21—N2—C8—C9	−176.6 (2)
N2—Mn1—O5—C25	−53.61 (14)	Mn1—N2—C8—C9	−2.4 (3)
O1—Mn1—N1—C7	−11.3 (2)	N2—C8—C9—C14	0.1 (3)
N2—Mn1—N1—C7	168.0 (2)	N2—C8—C9—C10	178.9 (2)
O5—Mn1—N1—C7	−100.59 (19)	C14—C9—C10—C11	−1.2 (3)
N3—Mn1—N1—C7	81.22 (19)	C8—C9—C10—C11	−179.99 (19)
O1—Mn1—N1—C20	163.71 (18)	C9—C10—C11—O4	178.9 (2)
N2—Mn1—N1—C20	−16.97 (18)	C9—C10—C11—C12	−1.5 (3)

O5—Mn1—N1—C20	74.46 (18)	C24—O4—C11—C10	−16.7 (4)
N3—Mn1—N1—C20	−103.73 (18)	C24—O4—C11—C12	163.7 (3)
O2—Mn1—N2—C8	1.1 (2)	C10—C11—C12—C13	1.8 (3)
N1—Mn1—N2—C8	175.2 (2)	O4—C11—C12—C13	−178.60 (19)
O5—Mn1—N2—C8	91.29 (19)	C11—C12—C13—C14	0.7 (3)
N3—Mn1—N2—C8	−92.52 (19)	Mn1—O2—C14—C13	176.23 (14)
O2—Mn1—N2—C21	175.65 (17)	Mn1—O2—C14—C9	−5.4 (3)
N1—Mn1—N2—C21	−10.24 (17)	C12—C13—C14—O2	175.21 (19)
O5—Mn1—N2—C21	−94.18 (17)	C12—C13—C14—C9	−3.3 (3)
N3—Mn1—N2—C21	82.00 (17)	C10—C9—C14—O2	−174.86 (19)
O2—Mn1—N3—C15	−30.74 (16)	C8—C9—C14—O2	3.9 (3)
O1—Mn1—N3—C15	−124.58 (16)	C10—C9—C14—C13	3.5 (3)
N1—Mn1—N3—C15	143.18 (16)	C8—C9—C14—C13	−177.73 (19)
N2—Mn1—N3—C15	60.99 (16)	C19—N3—C15—C16	−2.0 (3)
O2—Mn1—N3—C19	151.36 (18)	Mn1—N3—C15—C16	179.99 (19)
O1—Mn1—N3—C19	57.52 (18)	N3—C15—C16—C17	1.8 (4)
N1—Mn1—N3—C19	−34.72 (18)	C15—C16—C17—C18	0.4 (4)
N2—Mn1—N3—C19	−116.91 (18)	C16—C17—C18—C19	−2.3 (4)
Mn1—O1—C1—C2	160.46 (14)	C15—N3—C19—C18	−0.1 (4)
Mn1—O1—C1—C6	−20.2 (3)	Mn1—N3—C19—C18	177.9 (2)
O1—C1—C2—C3	179.18 (18)	C17—C18—C19—N3	2.2 (4)
C6—C1—C2—C3	−0.2 (3)	C7—N1—C20—C21	−145.7 (2)
C1—C2—C3—C4	0.1 (3)	Mn1—N1—C20—C21	39.0 (3)
C23—O3—C4—C5	0.6 (3)	C8—N2—C21—C22	84.9 (3)
C23—O3—C4—C3	−179.98 (17)	Mn1—N2—C21—C22	−90.0 (3)
C2—C3—C4—O3	−179.58 (17)	C8—N2—C21—C20	−151.6 (2)
C2—C3—C4—C5	−0.2 (3)	Mn1—N2—C21—C20	33.5 (3)
O3—C4—C5—C6	179.76 (18)	N1—C20—C21—C22	81.6 (3)
C3—C4—C5—C6	0.4 (3)	N1—C20—C21—N2	−45.0 (3)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H1O5···O1^{i}	0.82 (3)	1.99 (3)	2.804 (2)	169 (3)
C17—H17A···O4^{ii}	0.93	2.57	3.465 (3)	161
C22—H22C···N3	0.96	2.62	3.318 (5)	130

Symmetry codes: (i) −*x*, *y*, −*z*+3/2; (ii) *x*, −*y*, *z*−1/2.

Fig. 1

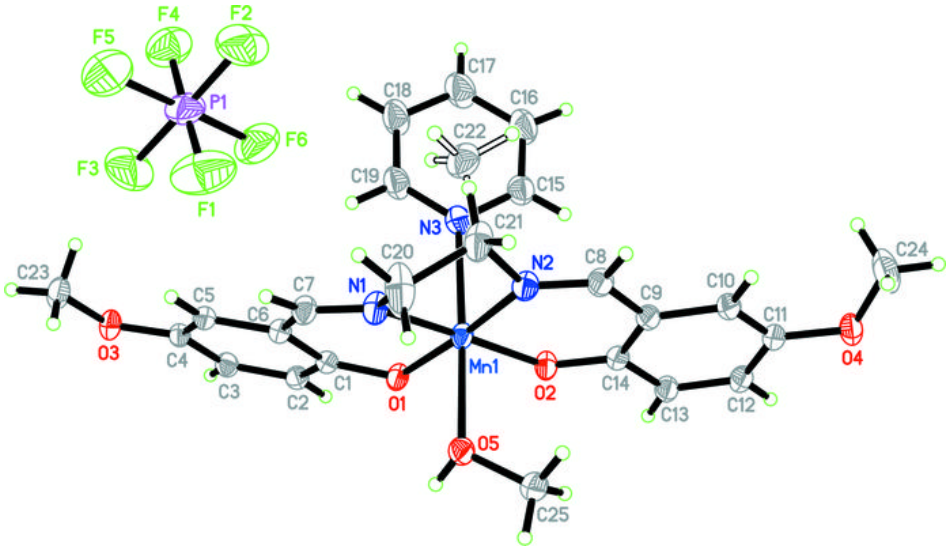

F4
F2
F5
P1
F6
F3
F1
C17
C18
C16
C22
C19
C15
N3
C21
C20
N2
C8
C23
C5
C7
N1
C9
C10
C6
C11
O3
C4
Mn1
O4
C3
C1
O2
C14
C2
O1
C13
C12
O5
C25
C24

Fig. 2