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Tetrakis(μ-phenoxyacetato-κ²O:O′)-bis[(1,10-phenanthroline-κ²N,N′)-manganese(II)] methanol hemisolvate

Dong-Hui Wu, Jian Shi, Yu-Jun Shi and Guo-Qing Jiang*

College of Chemistry and Chemical Engineering, Nantong University, Nantong 226019, People's Republic of China
Correspondence e-mail: jgq3518@163.com

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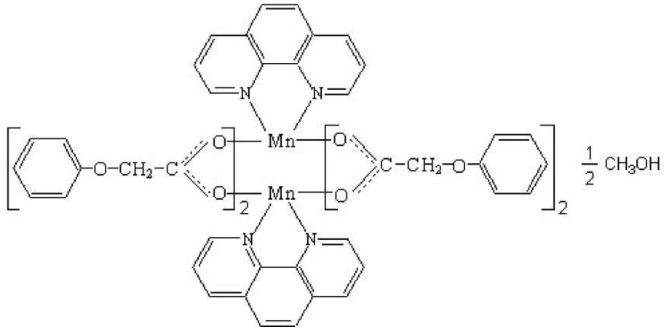
Key indicators: single-crystal X-ray study; T = 193 K; mean σ(C–C) = 0.005 Å; disorder in solvent or counterion; R factor = 0.066; wR factor = 0.149; data-to-parameter ratio = 15.2.

The title complex, $[Mn_2(C_8H_7O_3)_4(C_{12}H_8N_2)_2]\cdot 0.5CH_3OH$, is a carboxylate-bridged dinuclear Mn^{II} complex with four phenoxyacetate ions and two 1,10-phenanthroline molecules as ligands. Each of the four phenoxyacetate anions bridges the pair of Mn atoms. The asymmetric unit is completed by a half-occupancy methanol solvent molecule. Face-to-face π–π stacking interactions between the aromatic rings of 1,10-phenanthroline molecules belonging to adjacent Mn_2 complexes, with an interplanar separation of *circa* 3.4 Å, and weak C—H···O hydrogen bonds connect the dinuclear units into a three-dimensional supramolecular framework.

Related literature

For related literature, see: Jiang *et al.* (2005, 2006); Sessoli *et al.* (1993); Yaghi *et al.* (1997).



Experimental

Crystal data

$[Mn_2(C_8H_7O_3)_4(C_{12}H_8N_2)_2]\cdot 0.5CH_4O$
M_r = 1090.86
Triclinic, $P\overline{1}$
a = 12.4627 (10) Å
b = 12.8334 (10) Å
c = 17.1377 (13) Å
α = 77.421 (1)°
β = 87.635 (1)°
γ = 84.629 (1)°
V = 2662.8 (4) Å³
Z = 2
Mo $K\alpha$ radiation
μ = 0.54 mm⁻¹
T = 193 (2) K
0.30 × 0.24 × 0.22 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.848, T_{max} = 0.879
14596 measured reflections
10273 independent reflections
6679 reflections with $I > 2\sigma(I)$
R_{int} = 0.030

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.066
$wR(F^2)$ = 0.149
S = 1.08
10273 reflections
675 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.97 e Å⁻³
$\Delta\rho_{min}$ = −0.53 e Å⁻³

Table 1
Selected bond lengths (Å).

Mn1—O1	2.250 (3)	Mn2—O2	2.087 (2)
Mn1—O3	2.094 (2)	Mn2—O4	2.227 (3)
Mn1—O5	2.289 (2)	Mn2—O6	2.102 (2)
Mn1—O7	2.112 (3)	Mn2—O8	2.351 (3)
Mn1—N1	2.299 (3)	Mn2—N3	2.327 (3)
Mn1—N2	2.302 (3)	Mn2—N4	2.299 (3)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C20—H20···O10^{i}	0.93	2.70	3.627 (5)	175

Symmetry code: (i) $x, y+1, z$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BH2151).

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supplementary materials

Acta Cryst. (2008). E**64**, m161 [**doi:10.1107/S1600536807065269**]

Tetrakis(μ-phenoxyacetato-κ^2O:O')bis[(1,10-phenanthroline-κ^2N,N')manganese(II)] methanol hemisolvate

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Comment

The rational design, synthesis and characterization of novel supramolecular frameworks are currently of great interest. One of the greatest challenges in this area is the construction of porous materials from metal ions and organic ligands as building blocks (Yaghi *et al.*, 1997). As part of our search for new porous metal-organic frameworks, we are studying complexes of transition metals with phenoxyacetate ligands (Jiang *et al.*, 2005, 2006). Here, the title compound, (I), a novel dinuclear Mn^{II} complex with 1,10-phenanthroline as co-ligands, is reported.

Complex (I) exists as a dinuclear unit, with four bidentate phenoxyacetate anions bridging the pair of Mn^{II} atoms (Fig. 1). Two N atoms from 1,10-phenanthroline molecules bind to the Mn^{II} atoms, and both Mn^{II} atoms thus possess a distorted octahedral coordination geometry. The asymmetric unit is completed by 1/2 methanol solvate. The Mn—O distances are in the range 2.087 (2) to 2.351 (3) Å, and the average distance for Mn—N bonds is 2.31 Å. The planes of two coordinated phenanthroline molecules are set approximately perpendicular to each other.

Interestingly, The Mn_2 units further link to each other into a microporous framework (Fig. 2) by π-stacking from the plane of 1,10-phenanthroline of symmetry-related molecules and C—H···O hydrogen bond interactions between alternating molecules. These supramolecular interactions are illustrated in Fig. 3. The C—H···O hydrogen bonds that exist in the peripheral ligands of adjacent Mn_2 complexes are formed *via* the H donor atoms from phenyl group and acceptor O atoms of OCH_2 groups of phenoxyacetate ligands. It is noteworthy that the contacts are almost linear (C—H···O: 174.9°). The structural significance is that the dipole-monopole and dipole-dipole contributions to electrostatic energy are maximum at 180° and zero at 90°. Therefore, this interaction may be considered as an efficient C—H···O hydrogen bond.

The overall three-dimensional supramolecular structure is also stabilized by significant offset face-to-face π···π stacking interactions between the aromatic rings of 1,10-phenanthroline molecules belonging to adjacent Mn_2 complexes, with an interplanar separation of *ca* 3.4 Å and θ = 21.9° (Fig. 3).

Experimental

$[Mn_3O(O_2CCH_2OPh)_6(pyridine)_2(H_2O)]$ was synthesized according to the literature method of Sessoli *et al.*, (1993). To a solution of $[Mn_3O(O_2CCH_2OPh)_6(pyridine)_2(H_2O)]$ (0.15 mmol 0.18 g) in MeCN (8 ml) and CH_3OH (2 ml), powdered 1,10-phenanthroline (0.15 mmol 0.030 g) was added. The resulting solution was stirred for 0.5 h., filtered and layered with two volumes of Et_2O. After two weeks, light brown crystals of (I) were collected by filtration, washed with Et_2O, and dried *in vacuo*. The yield was approximately 20%.

Refinement

Carbon-bound H atoms were positioned geometrically, with C—H = 0.97 Å for methylene groups, 0.93 Å for aromatic groups, and 0.96 Å for the methyl groups of MeOH. They were refined using a riding model, with U_{iso}(H) = 1.2U_{eq}(carrier C) for the complex and U_{iso}(H) = 1.5U_{eq}(C57) for the MeOH molecule. The hydroxyl H atom H13*a* was positioned geometrically and freely refined. Occupancy for the methanol molecule was refined in preliminary cycles and fixed to 1/2 for final refinement. Finally, geometry for phenyl ring C1···C6 was constrained by fitting the six C atoms to a regular hexagon with C?C bond lengths of 1.39 Å.

Figures

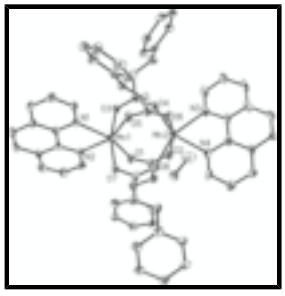

Fig. 1. The structure of (I), with displacement ellipsoids drawn at the 30% probability level. H atoms have been omitted.

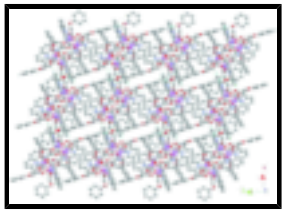

Fig. 2. View of the microporous network of (I) along [001]. The guest CH_3OH molecules and H atoms are omitted for clarity.

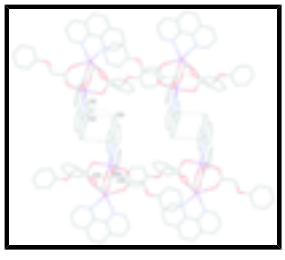

Fig. 3. The π···π interactions and C—H···O hydrogen interactions in (I) are shown (dashed lines). *Cg*1 is the centroid of the interacting aromatic ring of 1,10-phenanthroline molecule in the asymmetric unit.

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Crystal data

$[Mn_2(C_8H_7O_3)_4(C_{12}H_8N_2)_2]\cdot 0.5CH_4O$	$Z = 2$
$M_r = 1090.86$	$F_{000} = 1126.0$
Triclinic, $P\overline{1}$	$D_x = 1.363$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation λ = 0.71073 Å
$a = 12.4627$ (10) Å	Cell parameters from 14596 reflections
$b = 12.8334$ (10) Å	θ = 2.4–28.1°

c = 17.1377 (13) Å	μ = 0.54 mm^{-1}
α = 77.421 (1)º	T = 193 (2) K
β = 87.635 (1)º	Prism, light brown
γ = 84.629 (1)º	0.30 × 0.24 × 0.22 mm
V = 2662.8 (4) Å^3	

Data collection

Bruker SMART APEX CCD area detector diffractometer	10273 independent reflections
Radiation source: fine-focus sealed tube	6679 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.030
T = 193(2) K	θ_{max} = 26.0º
φ and ω scans	θ_{min} = 1.8º
Absorption correction: multi-scan (SADABS; Bruker, 2000)	h = −12→15
T_{min} = 0.848, T_{max} = 0.879	k = −15→15
14596 measured reflections	l = −21→20

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.066	H-atom parameters constrained
$wR(F^2)$ = 0.149	$w = 1/[\sigma^2(F_o^2) + (0.0726P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.08	$(\Delta/\sigma)_{max} < 0.001$
10273 reflections	$\Delta\rho_{max}$ = 0.97 e Å^{-3}
675 parameters	$\Delta\rho_{min}$ = −0.53 e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
C1	−0.14992 (18)	0.29242 (18)	0.19427 (14)	0.0413 (8)	
C2	−0.2086 (2)	0.29890 (17)	0.12587 (12)	0.0528 (10)	
H2	−0.1987	0.3532	0.0811	0.063*	
C3	−0.28204 (19)	0.2243 (2)	0.12443 (12)	0.0400 (8)	
H3	−0.3213	0.2286	0.0787	0.048*	
C4	−0.29687 (19)	0.14321 (18)	0.19139 (14)	0.0448 (9)	
H4	−0.3460	0.0933	0.1904	0.054*	
C5	−0.2382 (2)	0.13673 (19)	0.25979 (12)	0.0525 (11)	
H5	−0.2481	0.0825	0.3046	0.063*	
C6	−0.1647 (2)	0.2113 (2)	0.26123 (12)	0.0533 (11)	
H6	−0.1255	0.2070	0.3070	0.064*	
C7	−0.0082 (3)	0.3575 (3)	0.2531 (2)	0.0420 (9)	

H7A	0.0371	0.2911	0.2558	0.050*
H7B	−0.0486	0.3521	0.3032	0.050*
C8	0.0627 (3)	0.4501 (3)	0.24232 (19)	0.0309 (7)
C9	0.5655 (3)	0.5993 (3)	0.1346 (2)	0.0354 (7)
C10	0.6748 (3)	0.5765 (3)	0.1533 (2)	0.0393 (8)
H10	0.7077	0.5077	0.1560	0.047*
C11	0.7337 (3)	0.6559 (3)	0.1676 (2)	0.0408 (8)
H11	0.8064	0.6402	0.1792	0.049*
C12	0.6876 (3)	0.7566 (3)	0.1652 (2)	0.0445 (9)
H12	0.7288	0.8095	0.1741	0.053*
C13	0.5785 (3)	0.7801 (3)	0.1493 (2)	0.0399 (8)
H13	0.5458	0.8483	0.1490	0.048*
C14	0.5185 (3)	0.7011 (3)	0.1337 (2)	0.0442 (9)
H14	0.4457	0.7172	0.1226	0.053*
C15	0.4190 (3)	0.5449 (3)	0.0745 (2)	0.0389 (8)
H15A	0.4078	0.4873	0.0480	0.047*
H15B	0.4283	0.6086	0.0333	0.047*
C16	0.3174 (3)	0.5660 (3)	0.1243 (2)	0.0310 (7)
C17	0.3770 (3)	1.0392 (3)	0.1738 (2)	0.0393 (8)
C18	0.3870 (3)	1.0841 (3)	0.2409 (2)	0.0452 (9)
H18	0.3741	1.0449	0.2923	0.054*
C19	0.4157 (3)	1.1856 (3)	0.2287 (2)	0.0438 (9)
H19	0.4190	1.2166	0.2727	0.053*
C20	0.4399 (3)	1.2444 (3)	0.1549 (2)	0.0480 (10)
H20	0.4620	1.3130	0.1485	0.058*
C21	0.4307 (3)	1.1994 (4)	0.0907 (3)	0.0535 (11)
H21	0.4451	1.2389	0.0397	0.064*
C22	0.4008 (3)	1.0974 (4)	0.0996 (2)	0.0508 (10)
H22	0.3967	1.0678	0.0549	0.061*
C23	0.3286 (4)	0.8737 (3)	0.2547 (2)	0.0484 (11)
H23A	0.2800	0.9126	0.2862	0.058*
H23B	0.3969	0.8562	0.2819	0.058*
C24	0.2811 (3)	0.7703 (3)	0.2477 (2)	0.0335 (7)
C25	−0.1736 (4)	0.7864 (3)	0.4493 (2)	0.0498 (10)
C26	−0.2615 (3)	0.8525 (3)	0.4155 (3)	0.0514 (10)
H26	−0.2677	0.8709	0.3602	0.062*
C27	−0.3402 (3)	0.8912 (3)	0.4640 (2)	0.0439 (9)
H27	−0.3979	0.9374	0.4412	0.053*
C28	−0.3331 (3)	0.8612 (3)	0.5466 (2)	0.0410 (8)
H28	−0.3857	0.8874	0.5793	0.049*
C29	−0.2472 (3)	0.7921 (3)	0.5800 (2)	0.0440 (9)
H29	−0.2430	0.7708	0.6353	0.053*
C30	−0.1684 (3)	0.7548 (4)	0.5324 (2)	0.0461 (9)
H30	−0.1111	0.7082	0.5556	0.055*
C31	−0.0959 (3)	0.7740 (3)	0.3230 (2)	0.0464 (9)
H31A	−0.0951	0.8511	0.3061	0.056*
H31B	−0.1633	0.7544	0.3063	0.056*
C32	−0.0029 (3)	0.7204 (3)	0.28230 (19)	0.0360 (8)
C33	0.1833 (3)	0.9173 (3)	0.0287 (2)	0.0370 (8)

H33	0.2324	0.9084	0.0695	0.044*	
C34	0.1832 (3)	1.0099 (3)	−0.0315 (2)	0.0450 (9)	
H34	0.2307	1.0612	−0.0304	0.054*	
C35	0.1116 (3)	1.0241 (3)	−0.0925 (2)	0.0446 (9)	
H35	0.1099	1.0854	−0.1331	0.054*	
C36	0.0412 (3)	0.9455 (3)	−0.0928 (2)	0.0389 (8)	
C37	0.0465 (3)	0.8542 (3)	−0.02921 (19)	0.0313 (7)	
C38	−0.0349 (3)	0.9524 (3)	−0.1547 (2)	0.0484 (10)	
H38	−0.0397	1.0125	−0.1964	0.058*	
C39	−0.0986 (3)	0.8749 (3)	−0.1535 (2)	0.0400 (9)	
H39	−0.1480	0.8822	−0.1940	0.048*	
C40	−0.0930 (3)	0.7803 (3)	−0.0912 (2)	0.0404 (9)	
C41	−0.0215 (3)	0.7696 (3)	−0.0285 (2)	0.0341 (7)	
C42	−0.1555 (3)	0.6923 (3)	−0.0897 (2)	0.0398 (8)	
H42	−0.2046	0.6951	−0.1296	0.048*	
C43	−0.1425 (3)	0.6043 (4)	−0.0292 (2)	0.0494 (10)	
H43	−0.1804	0.5451	−0.0287	0.059*	
C44	−0.0725 (3)	0.6034 (3)	0.0315 (2)	0.0420 (8)	
H44	−0.0673	0.5439	0.0737	0.050*	
C45	0.4660 (3)	0.4104 (3)	0.3261 (2)	0.0489 (10)	
H45	0.4630	0.4243	0.2706	0.059*	
C46	0.5584 (3)	0.3533 (4)	0.3622 (2)	0.0520 (11)	
H46	0.6151	0.3290	0.3319	0.062*	
C47	0.5625 (4)	0.3341 (3)	0.4441 (3)	0.0555 (12)	
H47	0.6232	0.2966	0.4697	0.067*	
C48	0.4771 (3)	0.3700 (3)	0.4897 (3)	0.0520 (11)	
C49	0.4763 (3)	0.3541 (3)	0.5763 (3)	0.0514 (11)	
H49	0.5364	0.3193	0.6042	0.062*	
C50	0.3923 (3)	0.3878 (3)	0.6161 (2)	0.0427 (9)	
H50	0.3940	0.3756	0.6715	0.051*	
C51	0.2991 (3)	0.4425 (3)	0.5758 (2)	0.0429 (9)	
C52	0.2071 (3)	0.4781 (3)	0.6160 (2)	0.0407 (9)	
H52	0.2050	0.4660	0.6715	0.049*	
C53	0.1195 (3)	0.5313 (3)	0.5726 (2)	0.0430 (9)	
H53	0.0574	0.5537	0.5986	0.052*	
C54	0.1259 (4)	0.5508 (4)	0.4887 (2)	0.0514 (10)	
H54	0.0674	0.5879	0.4599	0.062*	
C55	0.2979 (3)	0.4632 (3)	0.4909 (2)	0.0407 (9)	
C56	0.3875 (3)	0.4251 (3)	0.4477 (2)	0.0396 (9)	
C57	0.0849 (6)	0.9332 (6)	0.4635 (5)	0.0479 (19)	0.50
H57A	0.0356	0.9278	0.4233	0.072*	0.50
H57B	0.1132	1.0022	0.4502	0.072*	0.50
H57C	0.0478	0.9250	0.5144	0.072*	0.50
Mn1	0.10626 (4)	0.68940 (4)	0.13078 (3)	0.03282 (14)	
Mn2	0.23017 (4)	0.55146 (4)	0.31185 (3)	0.03575 (15)	
N1	0.1173 (2)	0.8407 (2)	0.03126 (18)	0.0357 (6)	
N2	−0.0120 (2)	0.6833 (2)	0.03250 (16)	0.0330 (6)	
N3	0.3823 (3)	0.4459 (2)	0.36634 (18)	0.0380 (7)	
N4	0.2115 (3)	0.5187 (2)	0.44880 (17)	0.0392 (7)	

O1	0.0482 (2)	0.5285 (2)	0.18646 (15)	0.0429 (6)	
O2	0.1310 (2)	0.4354 (2)	0.29637 (15)	0.0419 (6)	
O3	0.23937 (19)	0.6113 (2)	0.08234 (13)	0.0364 (5)	
O4	0.3193 (2)	0.5381 (2)	0.19865 (14)	0.0407 (6)	
O5	0.2302 (2)	0.7683 (2)	0.18841 (14)	0.0422 (6)	
O6	0.2997 (2)	0.6956 (2)	0.30779 (14)	0.0421 (6)	
O7	−0.0072 (2)	0.7512 (2)	0.20771 (14)	0.0419 (6)	
O8	0.0669 (2)	0.6563 (2)	0.32082 (14)	0.0429 (6)	
O9	−0.0808 (2)	0.3710 (2)	0.18956 (16)	0.0488 (7)	
O10	0.5155 (2)	0.5172 (2)	0.11822 (17)	0.0502 (7)	
O11	0.34476 (19)	0.93894 (19)	0.17765 (14)	0.0364 (5)	
O12	−0.0909 (2)	0.7446 (2)	0.40745 (14)	0.0436 (6)	
O13	0.1737 (5)	0.8490 (6)	0.4676 (4)	0.0653 (17)	0.50
H13A	0.1493	0.7918	0.4678	0.098*	0.50

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0321 (18)	0.047 (2)	0.048 (2)	−0.0083 (16)	0.0017 (16)	−0.0154 (17)
C2	0.039 (2)	0.064 (3)	0.059 (3)	−0.0034 (19)	−0.0030 (19)	−0.020 (2)
C3	0.041 (2)	0.047 (2)	0.0373 (19)	−0.0152 (16)	−0.0023 (16)	−0.0153 (16)
C4	0.052 (2)	0.048 (2)	0.040 (2)	−0.0109 (18)	0.0000 (17)	−0.0187 (17)
C5	0.047 (2)	0.069 (3)	0.041 (2)	−0.036 (2)	0.0106 (18)	−0.0006 (19)
C6	0.054 (2)	0.063 (3)	0.042 (2)	−0.028 (2)	−0.0052 (19)	−0.0007 (19)
C7	0.046 (2)	0.040 (2)	0.038 (2)	−0.0128 (17)	−0.0056 (16)	−0.0006 (16)
C8	0.0352 (18)	0.0359 (18)	0.0220 (16)	−0.0106 (14)	0.0027 (13)	−0.0045 (13)
C9	0.0341 (18)	0.0407 (19)	0.0306 (18)	−0.0041 (14)	0.0080 (14)	−0.0066 (14)
C10	0.0315 (18)	0.041 (2)	0.043 (2)	0.0055 (15)	0.0025 (15)	−0.0088 (16)
C11	0.0355 (19)	0.055 (2)	0.0354 (19)	−0.0203 (17)	0.0029 (15)	−0.0103 (16)
C12	0.043 (2)	0.039 (2)	0.051 (2)	−0.0162 (17)	0.0105 (18)	−0.0062 (17)
C13	0.040 (2)	0.0389 (19)	0.0410 (19)	−0.0214 (15)	0.0001 (15)	−0.0022 (15)
C14	0.041 (2)	0.052 (2)	0.036 (2)	−0.0127 (17)	0.0000 (16)	0.0011 (17)
C15	0.046 (2)	0.0366 (19)	0.0373 (19)	−0.0051 (15)	0.0008 (16)	−0.0141 (15)
C16	0.0316 (17)	0.0262 (16)	0.0341 (19)	−0.0034 (13)	−0.0061 (14)	−0.0027 (13)
C17	0.0369 (19)	0.0340 (19)	0.046 (2)	−0.0066 (14)	−0.0044 (16)	−0.0050 (15)
C18	0.044 (2)	0.048 (2)	0.051 (2)	−0.0303 (18)	0.0025 (18)	−0.0148 (18)
C19	0.0401 (19)	0.055 (2)	0.050 (2)	−0.0270 (17)	0.0058 (16)	−0.0336 (19)
C20	0.063 (3)	0.035 (2)	0.045 (2)	−0.0208 (18)	0.0022 (19)	−0.0008 (16)
C21	0.040 (2)	0.060 (3)	0.052 (2)	−0.0241 (19)	−0.0029 (18)	0.014 (2)
C22	0.054 (2)	0.058 (3)	0.042 (2)	−0.022 (2)	0.0002 (18)	−0.0060 (18)
C23	0.078 (3)	0.035 (2)	0.0332 (19)	−0.0255 (19)	−0.0205 (19)	0.0022 (15)
C24	0.0406 (19)	0.0219 (16)	0.0368 (19)	−0.0077 (13)	−0.0052 (15)	−0.0008 (14)
C25	0.057 (2)	0.049 (2)	0.042 (2)	−0.0091 (19)	0.0114 (18)	−0.0055 (17)
C26	0.050 (2)	0.041 (2)	0.058 (3)	0.0090 (18)	0.0098 (19)	−0.0052 (18)
C27	0.041 (2)	0.042 (2)	0.046 (2)	0.0180 (16)	0.0153 (17)	−0.0147 (17)
C28	0.043 (2)	0.042 (2)	0.039 (2)	−0.0013 (16)	0.0110 (16)	−0.0127 (16)
C29	0.047 (2)	0.045 (2)	0.043 (2)	−0.0116 (17)	0.0154 (17)	−0.0158 (17)
C30	0.038 (2)	0.064 (3)	0.038 (2)	−0.0127 (18)	0.0077 (16)	−0.0131 (18)

C31	0.049 (2)	0.050 (2)	0.038 (2)	−0.0007 (18)	0.0033 (17)	−0.0077 (17)
C32	0.047 (2)	0.0372 (19)	0.0220 (16)	−0.0050 (15)	−0.0011 (14)	−0.0018 (14)
C33	0.0399 (19)	0.0396 (19)	0.0289 (17)	−0.0075 (15)	−0.0081 (14)	0.0014 (14)
C34	0.047 (2)	0.041 (2)	0.042 (2)	−0.0131 (17)	−0.0026 (17)	0.0049 (16)
C35	0.047 (2)	0.044 (2)	0.035 (2)	−0.0064 (17)	−0.0016 (17)	0.0102 (16)
C36	0.046 (2)	0.040 (2)	0.0242 (17)	0.0077 (16)	−0.0019 (15)	0.0005 (14)
C37	0.0304 (17)	0.0383 (18)	0.0235 (16)	0.0053 (14)	0.0006 (13)	−0.0070 (13)
C38	0.054 (2)	0.050 (2)	0.034 (2)	0.0077 (19)	−0.0127 (17)	0.0049 (17)
C39	0.042 (2)	0.044 (2)	0.0320 (18)	0.0144 (17)	−0.0149 (15)	−0.0081 (15)
C40	0.0336 (18)	0.060 (2)	0.0252 (17)	0.0065 (17)	−0.0031 (14)	−0.0077 (16)
C41	0.0268 (16)	0.0376 (19)	0.0351 (18)	−0.0027 (13)	−0.0019 (13)	−0.0017 (14)
C42	0.0388 (19)	0.048 (2)	0.041 (2)	−0.0062 (16)	−0.0086 (16)	−0.0249 (17)
C43	0.044 (2)	0.062 (3)	0.044 (2)	−0.0156 (19)	−0.0107 (18)	−0.0097 (19)
C44	0.043 (2)	0.052 (2)	0.0322 (19)	−0.0139 (17)	−0.0020 (16)	−0.0065 (16)
C45	0.058 (3)	0.045 (2)	0.045 (2)	−0.0003 (19)	−0.022 (2)	−0.0084 (18)
C46	0.052 (2)	0.061 (3)	0.044 (2)	0.008 (2)	−0.0162 (19)	−0.015 (2)
C47	0.061 (3)	0.045 (2)	0.059 (3)	−0.0033 (19)	−0.044 (2)	0.0002 (19)
C48	0.049 (2)	0.041 (2)	0.063 (3)	−0.0059 (18)	−0.028 (2)	0.0015 (19)
C49	0.033 (2)	0.053 (2)	0.060 (3)	−0.0105 (17)	−0.0170 (19)	0.011 (2)
C50	0.036 (2)	0.044 (2)	0.041 (2)	−0.0145 (16)	−0.0165 (16)	0.0147 (16)
C51	0.045 (2)	0.047 (2)	0.0339 (19)	−0.0225 (17)	−0.0198 (16)	0.0090 (16)
C52	0.040 (2)	0.043 (2)	0.039 (2)	−0.0278 (16)	−0.0008 (16)	0.0012 (16)
C53	0.051 (2)	0.042 (2)	0.037 (2)	−0.0132 (17)	−0.0002 (17)	−0.0077 (16)
C54	0.058 (3)	0.062 (3)	0.0269 (19)	−0.006 (2)	−0.0062 (17)	0.0067 (17)
C55	0.048 (2)	0.0348 (18)	0.0367 (19)	−0.0167 (16)	−0.0159 (16)	0.0060 (15)
C56	0.053 (2)	0.0313 (18)	0.0329 (18)	−0.0128 (16)	−0.0225 (17)	0.0052 (14)
C57	0.035 (4)	0.043 (4)	0.055 (5)	−0.009 (3)	−0.008 (3)	0.016 (3)
Mn1	0.0289 (3)	0.0314 (3)	0.0355 (3)	−0.0038 (2)	−0.0041 (2)	0.0000 (2)
Mn2	0.0364 (3)	0.0314 (3)	0.0366 (3)	−0.0078 (2)	−0.0083 (2)	0.0024 (2)
N1	0.0320 (15)	0.0337 (15)	0.0381 (16)	0.0000 (12)	−0.0022 (12)	−0.0015 (12)
N2	0.0281 (14)	0.0394 (16)	0.0318 (15)	−0.0061 (12)	−0.0016 (12)	−0.0064 (12)
N3	0.0462 (17)	0.0304 (15)	0.0382 (16)	−0.0065 (13)	−0.0141 (14)	−0.0050 (12)
N4	0.0487 (18)	0.0388 (17)	0.0282 (15)	−0.0106 (14)	−0.0076 (13)	0.0009 (12)
O1	0.0521 (15)	0.0384 (14)	0.0366 (14)	−0.0138 (12)	−0.0076 (12)	0.0012 (11)
O2	0.0519 (15)	0.0366 (14)	0.0357 (13)	−0.0156 (11)	−0.0117 (12)	0.0026 (10)
O3	0.0327 (12)	0.0483 (15)	0.0283 (12)	0.0008 (11)	−0.0049 (10)	−0.0093 (10)
O4	0.0439 (14)	0.0495 (15)	0.0262 (13)	0.0004 (11)	−0.0043 (10)	−0.0038 (11)
O5	0.0565 (16)	0.0384 (14)	0.0318 (13)	−0.0130 (12)	−0.0175 (12)	−0.0012 (10)
O6	0.0509 (15)	0.0380 (14)	0.0333 (13)	−0.0109 (11)	−0.0137 (11)	0.0066 (11)
O7	0.0435 (14)	0.0519 (16)	0.0258 (13)	0.0047 (12)	−0.0031 (10)	−0.0016 (11)
O8	0.0459 (15)	0.0510 (16)	0.0263 (12)	0.0064 (12)	−0.0057 (11)	0.0000 (11)
O9	0.0467 (15)	0.0524 (16)	0.0472 (16)	−0.0239 (13)	−0.0109 (12)	−0.0003 (12)
O10	0.0340 (14)	0.0604 (18)	0.0550 (17)	0.0028 (12)	−0.0024 (12)	−0.0129 (14)
O11	0.0392 (13)	0.0359 (13)	0.0351 (13)	−0.0214 (10)	−0.0053 (10)	−0.0017 (10)
O12	0.0621 (17)	0.0379 (14)	0.0248 (12)	0.0096 (12)	0.0077 (11)	−0.0011 (10)
O13	0.055 (4)	0.069 (4)	0.077 (5)	−0.015 (3)	0.019 (3)	−0.026 (4)

Geometric parameters (Å, °)

C1—O9	1.374 (3)	C31—H31B	0.9700
C1—C2	1.3900	C32—O8	1.243 (4)
C1—C6	1.3900	C32—O7	1.255 (4)
C2—C3	1.3900	C33—N1	1.332 (5)
C2—H2	0.9300	C33—C34	1.394 (5)
C3—C4	1.3900	C33—H33	0.9300
C3—H3	0.9300	C34—C35	1.372 (5)
C4—C5	1.3900	C34—H34	0.9300
C4—H4	0.9300	C35—C36	1.399 (6)
C5—C6	1.3900	C35—H35	0.9300
C5—H5	0.9300	C36—C37	1.415 (5)
C6—H6	0.9300	C36—C38	1.434 (5)
C7—O9	1.415 (4)	C37—N1	1.361 (4)
C7—C8	1.521 (5)	C37—C41	1.436 (5)
C7—H7A	0.9700	C38—C39	1.327 (6)
C7—H7B	0.9700	C38—H38	0.9300
C8—O1	1.234 (4)	C39—C40	1.429 (5)
C8—O2	1.256 (4)	C39—H39	0.9300
C9—O10	1.358 (5)	C40—C41	1.400 (5)
C9—C14	1.378 (5)	C40—C42	1.425 (5)
C9—C10	1.402 (5)	C41—N2	1.347 (4)
C10—C11	1.379 (5)	C42—C43	1.358 (6)
C10—H10	0.9300	C42—H42	0.9300
C11—C12	1.356 (5)	C43—C44	1.382 (5)
C11—H11	0.9300	C43—H43	0.9300
C12—C13	1.390 (5)	C44—N2	1.332 (5)
C12—H12	0.9300	C44—H44	0.9300
C13—C14	1.391 (5)	C45—N3	1.327 (5)
C13—H13	0.9300	C45—C46	1.396 (5)
C14—H14	0.9300	C45—H45	0.9300
C15—O10	1.418 (4)	C46—C47	1.374 (6)
C15—C16	1.533 (5)	C46—H46	0.9300
C15—H15A	0.9700	C47—C48	1.397 (7)
C15—H15B	0.9700	C47—H47	0.9300
C16—O4	1.247 (4)	C48—C56	1.401 (5)
C16—O3	1.254 (4)	C48—C49	1.452 (6)
C17—C22	1.364 (6)	C49—C50	1.315 (6)
C17—O11	1.371 (4)	C49—H49	0.9300
C17—C18	1.408 (5)	C50—C51	1.422 (5)
C18—C19	1.354 (5)	C50—H50	0.9300
C18—H18	0.9300	C51—C52	1.405 (6)
C19—C20	1.364 (6)	C51—C55	1.421 (5)
C19—H19	0.9300	C52—C53	1.385 (5)
C20—C21	1.361 (6)	C52—H52	0.9300
C20—H20	0.9300	C53—C54	1.405 (5)
C21—C22	1.369 (6)	C53—H53	0.9300

C21—H21	0.9300	C54—N4	1.324 (5)
C22—H22	0.9300	C54—H54	0.9300
C23—O11	1.419 (4)	C55—N4	1.373 (5)
C23—C24	1.532 (5)	C55—C56	1.421 (6)
C23—H23A	0.9700	C56—N3	1.365 (5)
C23—H23B	0.9700	C57—O13	1.465 (10)
C24—O5	1.227 (4)	C57—H57A	0.9600
C24—O6	1.257 (4)	C57—H57B	0.9600
C25—O12	1.366 (5)	C57—H57C	0.9600
C25—C26	1.385 (6)	Mn1—O1	2.250 (3)
C25—C30	1.397 (6)	Mn1—O3	2.094 (2)
C26—C27	1.386 (5)	Mn1—O5	2.289 (2)
C26—H26	0.9300	Mn1—O7	2.112 (3)
C27—C28	1.388 (5)	Mn1—N1	2.299 (3)
C27—H27	0.9300	Mn1—N2	2.302 (3)
C28—C29	1.382 (6)	Mn2—O2	2.087 (2)
C28—H28	0.9300	Mn2—O4	2.227 (3)
C29—C30	1.369 (5)	Mn2—O6	2.102 (2)
C29—H29	0.9300	Mn2—O8	2.351 (3)
C30—H30	0.9300	Mn2—N3	2.327 (3)
C31—O12	1.417 (4)	Mn2—N4	2.299 (3)
C31—C32	1.515 (5)	O13—H13A	0.8200
C31—H31A	0.9700		
O9—C1—C2	115.15 (19)	N1—C37—C41	117.6 (3)
O9—C1—C6	124.84 (19)	C36—C37—C41	120.0 (3)
C2—C1—C6	120.0	C39—C38—C36	121.3 (4)
C3—C2—C1	120.0	C39—C38—H38	119.3
C3—C2—H2	120.0	C36—C38—H38	119.3
C1—C2—H2	120.0	C38—C39—C40	121.4 (3)
C2—C3—C4	120.0	C38—C39—H39	119.3
C2—C3—H3	120.0	C40—C39—H39	119.3
C4—C3—H3	120.0	C41—C40—C42	116.6 (3)
C3—C4—C5	120.0	C41—C40—C39	120.0 (4)
C3—C4—H4	120.0	C42—C40—C39	123.4 (3)
C5—C4—H4	120.0	N2—C41—C40	123.4 (3)
C6—C5—C4	120.0	N2—C41—C37	117.9 (3)
C6—C5—H5	120.0	C40—C41—C37	118.7 (3)
C4—C5—H5	120.0	C43—C42—C40	119.3 (3)
C5—C6—C1	120.0	C43—C42—H42	120.4
C5—C6—H6	120.0	C40—C42—H42	120.4
C1—C6—H6	120.0	C42—C43—C44	119.6 (4)
O9—C7—C8	111.8 (3)	C42—C43—H43	120.2
O9—C7—H7A	109.3	C44—C43—H43	120.2
C8—C7—H7A	109.3	N2—C44—C43	123.3 (4)
O9—C7—H7B	109.3	N2—C44—H44	118.3
C8—C7—H7B	109.3	C43—C44—H44	118.3
H7A—C7—H7B	107.9	N3—C45—C46	123.8 (4)
O1—C8—O2	127.6 (3)	N3—C45—H45	118.1
O1—C8—C7	120.6 (3)	C46—C45—H45	118.1

O2—C8—C7	111.9 (3)	C47—C46—C45	117.6 (4)
O10—C9—C14	125.8 (3)	C47—C46—H46	121.2
O10—C9—C10	115.7 (3)	C45—C46—H46	121.2
C14—C9—C10	118.4 (3)	C46—C47—C48	121.3 (4)
C11—C10—C9	120.0 (3)	C46—C47—H47	119.4
C11—C10—H10	120.0	C48—C47—H47	119.4
C9—C10—H10	120.0	C47—C48—C56	116.6 (4)
C12—C11—C10	121.3 (4)	C47—C48—C49	124.4 (4)
C12—C11—H11	119.3	C56—C48—C49	119.0 (4)
C10—C11—H11	119.3	C50—C49—C48	121.5 (4)
C11—C12—C13	119.6 (3)	C50—C49—H49	119.2
C11—C12—H12	120.2	C48—C49—H49	119.2
C13—C12—H12	120.2	C49—C50—C51	121.2 (4)
C12—C13—C14	119.7 (4)	C49—C50—H50	119.4
C12—C13—H13	120.2	C51—C50—H50	119.4
C14—C13—H13	120.2	C52—C51—C55	117.8 (3)
C9—C14—C13	120.9 (4)	C52—C51—C50	123.0 (3)
C9—C14—H14	119.6	C55—C51—C50	119.2 (4)
C13—C14—H14	119.6	C53—C52—C51	119.7 (3)
O10—C15—C16	115.2 (3)	C53—C52—H52	120.1
O10—C15—H15A	108.5	C51—C52—H52	120.1
C16—C15—H15A	108.5	C52—C53—C54	118.9 (4)
O10—C15—H15B	108.5	C52—C53—H53	120.6
C16—C15—H15B	108.5	C54—C53—H53	120.6
H15A—C15—H15B	107.5	N4—C54—C53	123.0 (4)
O4—C16—O3	127.3 (3)	N4—C54—H54	118.5
O4—C16—C15	119.7 (3)	C53—C54—H54	118.5
O3—C16—C15	113.0 (3)	N4—C55—C56	118.6 (3)
C22—C17—O11	116.7 (3)	N4—C55—C51	121.6 (4)
C22—C17—C18	119.2 (4)	C56—C55—C51	119.8 (3)
O11—C17—C18	124.1 (3)	N3—C56—C48	123.1 (4)
C19—C18—C17	118.3 (4)	N3—C56—C55	117.7 (3)
C19—C18—H18	120.8	C48—C56—C55	119.2 (4)
C17—C18—H18	120.8	O13—C57—H57A	109.5
C18—C19—C20	122.9 (3)	O13—C57—H57B	109.5
C18—C19—H19	118.6	H57A—C57—H57B	109.5
C20—C19—H19	118.6	O13—C57—H57C	109.5
C21—C20—C19	117.9 (4)	H57A—C57—H57C	109.5
C21—C20—H20	121.1	H57B—C57—H57C	109.5
C19—C20—H20	121.1	O3—Mn1—O7	165.10 (9)
C20—C21—C22	121.6 (4)	O3—Mn1—O1	89.02 (10)
C20—C21—H21	119.2	O7—Mn1—O1	85.90 (10)
C22—C21—H21	119.2	O3—Mn1—O5	85.75 (10)
C17—C22—C21	120.0 (4)	O7—Mn1—O5	85.38 (10)
C17—C22—H22	120.0	O1—Mn1—O5	123.41 (9)
C21—C22—H22	120.0	O3—Mn1—N1	91.36 (10)
O11—C23—C24	110.2 (3)	O7—Mn1—N1	99.24 (10)
O11—C23—H23A	109.6	O1—Mn1—N1	154.47 (10)
C24—C23—H23A	109.6	O5—Mn1—N1	82.06 (9)

O11—C23—H23B	109.6	O3—Mn1—N2	96.27 (9)
C24—C23—H23B	109.6	O7—Mn1—N2	96.98 (10)
H23A—C23—H23B	108.1	O1—Mn1—N2	82.86 (10)
O5—C24—O6	127.7 (3)	O5—Mn1—N2	153.72 (10)
O5—C24—C23	119.8 (3)	N1—Mn1—N2	71.72 (10)
O6—C24—C23	112.5 (3)	O2—Mn2—O6	164.69 (10)
O12—C25—C26	125.1 (4)	O2—Mn2—O4	90.14 (10)
O12—C25—C30	115.6 (4)	O6—Mn2—O4	88.70 (10)
C26—C25—C30	119.2 (4)	O2—Mn2—N4	95.76 (10)
C25—C26—C27	120.1 (4)	O6—Mn2—N4	92.14 (10)
C25—C26—H26	120.0	O4—Mn2—N4	153.09 (11)
C27—C26—H26	120.0	O2—Mn2—N3	101.55 (10)
C26—C27—C28	120.2 (4)	O6—Mn2—N3	93.36 (10)
C26—C27—H27	119.9	O4—Mn2—N3	81.30 (10)
C28—C27—H27	119.9	N4—Mn2—N3	71.79 (11)
C29—C28—C27	119.4 (3)	O2—Mn2—O8	84.33 (10)
C29—C28—H28	120.3	O6—Mn2—O8	83.89 (10)
C27—C28—H28	120.3	O4—Mn2—O8	125.25 (9)
C30—C29—C28	120.7 (4)	N4—Mn2—O8	81.54 (10)
C30—C29—H29	119.6	N3—Mn2—O8	153.09 (10)
C28—C29—H29	119.6	C33—N1—C37	117.5 (3)
C29—C30—C25	120.3 (4)	C33—N1—Mn1	126.4 (2)
C29—C30—H30	119.9	C37—N1—Mn1	116.1 (2)
C25—C30—H30	119.9	C44—N2—C41	117.7 (3)
O12—C31—C32	112.3 (3)	C44—N2—Mn1	125.9 (2)
O12—C31—H31A	109.1	C41—N2—Mn1	116.4 (2)
C32—C31—H31A	109.1	C45—N3—C56	117.7 (3)
O12—C31—H31B	109.1	C45—N3—Mn2	126.5 (2)
C32—C31—H31B	109.1	C56—N3—Mn2	115.7 (3)
H31A—C31—H31B	107.9	C54—N4—C55	118.9 (3)
O8—C32—O7	127.1 (3)	C54—N4—Mn2	125.1 (2)
O8—C32—C31	122.1 (3)	C55—N4—Mn2	116.0 (3)
O7—C32—C31	110.8 (3)	C8—O1—Mn1	143.6 (2)
N1—C33—C34	123.9 (3)	C8—O2—Mn2	123.9 (2)
N1—C33—H33	118.0	C16—O3—Mn1	121.8 (2)
C34—C33—H33	118.0	C16—O4—Mn2	144.6 (2)
C35—C34—C33	118.8 (4)	C24—O5—Mn1	148.5 (2)
C35—C34—H34	120.6	C24—O6—Mn2	117.4 (2)
C33—C34—H34	120.6	C32—O7—Mn1	121.6 (2)
C34—C35—C36	119.4 (3)	C32—O8—Mn2	145.0 (2)
C34—C35—H35	120.3	C1—O9—C7	116.4 (3)
C36—C35—H35	120.3	C9—O10—C15	116.7 (3)
C35—C36—C37	118.0 (3)	C17—O11—C23	117.4 (3)
C35—C36—C38	123.4 (3)	C25—O12—C31	116.4 (3)
C37—C36—C38	118.6 (4)	C57—O13—H13A	109.5
N1—C37—C36	122.3 (3)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C20—H20···O10^{i}	0.93	2.70	3.627 (5)	175

Symmetry codes: (i) *x*, *y*+1, *z*.

Fig. 1

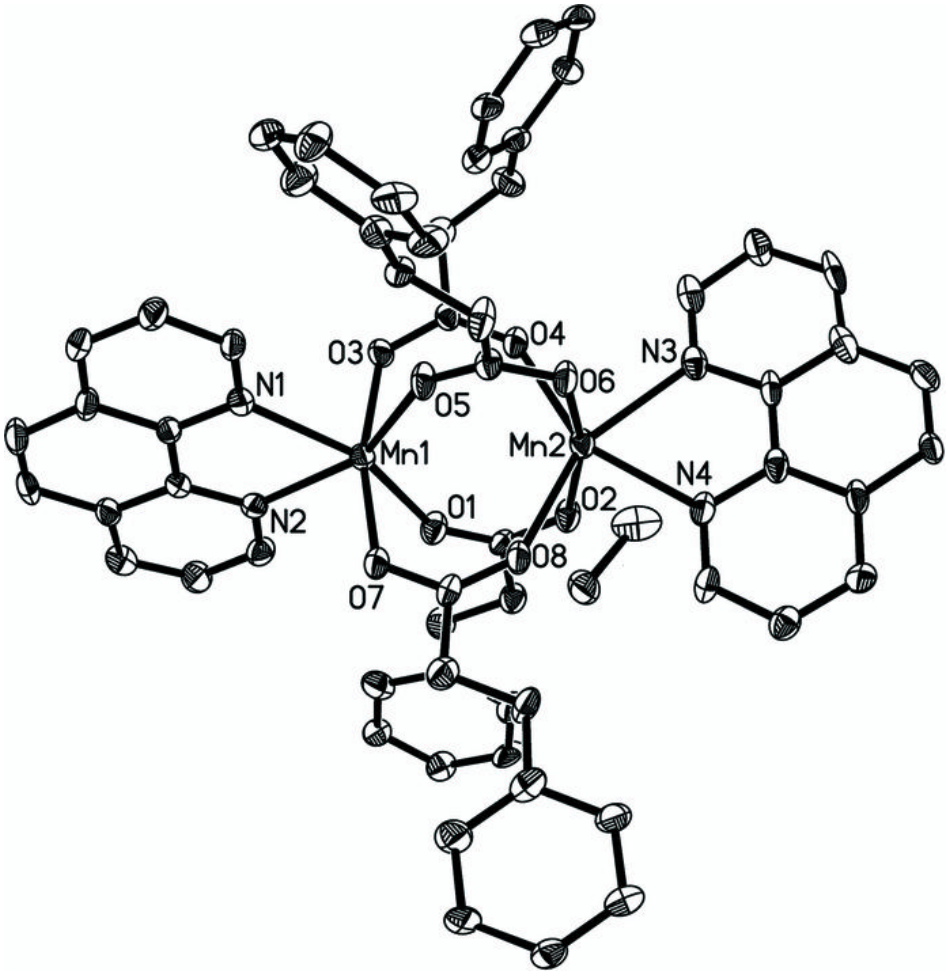

Fig. 2

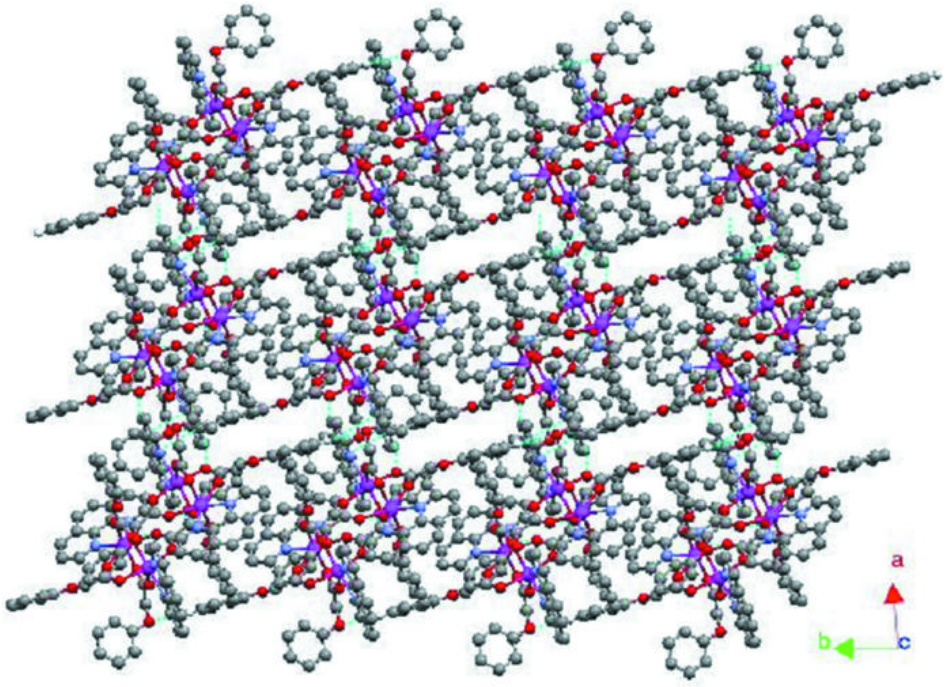

Fig. 3