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catena-Poly[[[aquabis(4-chlorobenzoato-κ^2O,O')manganese(II)]-μ-4,4′-bipyridine-$\kappa^2N:N'$]4,4′-bipyridine solvate]

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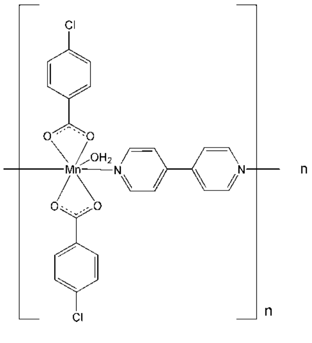
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.005 Å; R factor = 0.047; wR factor = 0.118; data-to-parameter ratio = 14.7.

The title compound, $\{[Mn(C_7H_4ClO_2)_2(C_{10}H_8N_2)(H_2O)]\cdot C_{10}H_8N_2\}_n$, is a manganese polymer constructed from 4-chlorobenzoate and 4,4′-bipyridine ligands. The Mn centre and coordinated water molecule lie on a twofold rotation axis. The Mn^{II} centre is in a distorted pentagonal–bipyramidal geometry, coordinated by four carboxylate O atoms from two symmetry-related 4-chlorobenzoate ligands, two N atoms from two symmetry-related 4,4′-bipyridine ligands (axial positions) and one water molecule. A polymeric structure results from the bridging character of the 4,4′-bipyridine ligands. A three-dimensional network is formed by these chains *via* O—H⋯O hydrogen bonds and π–π stacking interactions. The face-to-face and centroid–centroid distances between parallel 4-chlorobenzoic acids of neighboring complexes ($-x$, $-y$, $-z$) are 3.583 (3) and 3.703 (2) Å, respectively. The non-coordinated 4,4′-bipyridine molecule fills voids in the metal–organic framework, stabilizing the crystal structure.

Related literature

For related literature, see: Abrahams *et al.* (1999); Desiraju (2001); Dybtsev *et al.* (2004); Gu *et al.* (2004); Rodesiler *et al.* (1985); Tao *et al.* (2000); Yaghi *et al.* (1998).



Experimental

Crystal data

$[Mn(C_7H_4ClO_2)_2(C_{10}H_8N_2)(H_2O)]\cdot C_{10}H_8N_2$
M_r = 696.43
Monoclinic, $P2/n$
a = 11.6900 (3) Å
b = 6.1510 (2) Å
c = 22.5184 (6) Å
β = 102.369 (2)°
V = 1581.61 (8) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.64 mm^{-1}
T = 293 (2) K
0.25 × 0.19 × 0.18 mm

Data collection

Bruker APEX II diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.857, T_{max} = 0.894
16828 measured reflections
3115 independent reflections
2373 reflections with $I > 2\sigma(I)$
R_{int} = 0.056

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.118
S = 1.05
3115 reflections
212 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.61 e Å^{-3}
$\Delta\rho_{min}$ = −0.56 e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1W—H1W⋯O1^i	0.82 (3)	1.98 (3)	2.740 (3)	153 (3)
C8—H8⋯O1	0.93	2.55	3.181 (3)	125

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

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); 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, 2004); 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: BH2104).

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supplementary materials

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catena-Poly[[[aquabis(4-chlorobenzoato-κ^2O,O')manganese(II)]-μ-4,4'-bipyridine-$\kappa^2N:N'$]4,4'-bipyridine solvate]

D.-Y. Ma and **G.-H. Deng**

Comment

Increased attention is being focused on the design and synthesis of coordination networks or metal-organic frameworks (MOFs), owing to their attracting topologies and potential application in molecular recognition, gas storage, catalysis and luminescence (Yaghi *et al.*, 1998; Abrahams *et al.*, 1999; Desiraju, 2001). Some functional ligands, such as carboxylates, bipyridine or its derivatives, and mixtures of both carboxylate and bipyridine ligands have been successfully employed to construct MOFs (Dybtsev *et al.*, 2004; Tao *et al.*, 2000). To the best of our knowledge, hydrogen-bonding interactions between ligands are specific and directional, and have little dependence on the properties of metal ions, playing then a critical role in the structures and functions of the products. In this sense, 4-chlorobenzoic acid is an excellent candidate for the construction of supramolecular complexes, since it not only has multiple coordination modes but also can form regular hydrogen bonds, being both donor and acceptor (Gu *et al.*, 2004). In the paper, we report a novel Mn polymer, (I), which is a three-dimensional architecture with MOF.

As depicted in Fig. 1, The Mn1 and O1w water molecules lie on special positions (3/4, *y*, 3/4) in space group *P*2/*n*, corresponding to a twofold symmetry axis. The Mn^{II} centre presents a pentagonal-bipyramidal geometry, which is defined by four carboxylate O atoms from two 4-chlorobenzoate ligands, two N atoms from two 4,4'-bipyridine ligands and one water molecule (Table 1). The same situation was observed in the compound [Cd(py)$_2$(C$_7$H$_4$O$_2$Cl)$_2$(H$_2$O)] (C$_7$H$_4$O$_2$Cl = 4-chlorobenzoate, py = pyridine) (Rodesiler *et al.* 1985). The carboxylate groups of two opposite 4-chlorobenzoate ligands have a bidentate coordination mode to coordinate to the Mn atom, and the 4,4'-bipyiridine has a dihedral angle of 53.55 (3)° between two pyridine rings, and bridges Mn atoms along the [100] direction. The Mn···Mn separation along the chain is 11.690 (2) Å. The coordinated water molecules play an important role in the crystal packing: these one-dimensional chains are connected through O—H···O hydrogen bonds involving the water molecules as donors and the carboxylate O atoms as acceptors, forming a corrugated layer parallel to [100]. The shortest Mn···Mn separation is 6.151 (3) Å in the layer. Moreover these layers are assembled into a three-dimensional network *via* π–π stacking interactions which have dimensions of 12.252 × 8.367 Å^2 and accommodate 4,4'-bipyridine molecules (Fig. 2). The face-to-face and centroid-centroid distances between parallel 4-chlorobenzoate ligands of neighboring complexes are 3.583 (3) and 3.703 (2) Å, respectively. The free 4,4'-bipyridine molecule is stabilized through C—H···π interactions [C17—H17···$Cg1^i$ = 2.84 (2) Å; C14—H14···$Cg2^{ii}$ = 2.97 (2) Å. Symmetry codes: (*i*) *x*, *y*, *z*; (*ii*): 1 − *x*,1 − *y*, -*z; Cg*1 is the centroid of ring N1/C8···C12; *Cg*2 is the centroid of ring C2···C7].

Experimental

The title complex was prepared by addition of a stoichiometric amount of manganese acetate (20 mmol) and 4,4'-bipyridine (20 mmol) to a hot aqueous solution of 4-chlorobenzoic acid (20 mmol). The pH was then adjusted to 7.0–8.0 with NaOH

(30 mmol). The resulting solution was filtered, and yellow single crystals were obtained at room temperature by slow evaporation of the solvent over several days.

Refinement

Water H atom H1W was located in a difference map, while C-bonded H atoms were placed in calculated positions. All H atoms were refined using a riding model with constrained distances O—H = 0.82 Å, C—H = 0.93 Å and with U_{iso}(H) = 1.2U_{eq}(carrier atom).

Figures

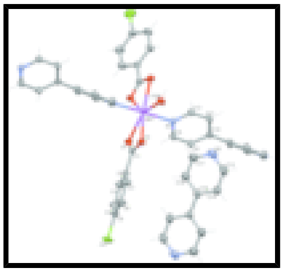

Fig. 1. The structure of (I), showing the atomic numbering scheme. Non-H atoms are shown with 30% probability displacement ellipsoids.

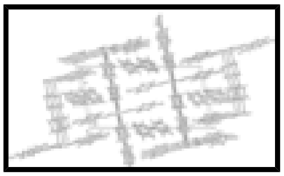

Fig. 2. A packing view of (I) viewed along the *b*-axis.

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Crystal data

$[Mn(C_7H_4ClO_2)_2(C_{10}H_8N_2)(H_2O)]\cdot C_{10}H_8N_2$

M_r = 696.43

Monoclinic, *P*2/*n*

Hall symbol: -P 2yac

a = 11.6900 (3) Å

b = 6.1510 (2) Å

c = 22.5184 (6) Å

β = 102.369 (2)°

V = 1581.61 (8) Å^3

Z = 2

F_{000} = 714

D_x = 1.462 Mg m^{-3}

Mo *K*α radiation
λ = 0.71073 Å

Cell parameters from 2376 reflections

θ = 2.2–28.0°

μ = 0.64 mm^{-1}

T = 293 (2) K

Block, yellow

0.25 × 0.19 × 0.18 mm

Data collection

Bruker APEXII
diffractometer

Radiation source: fine-focus sealed tube

3115 independent reflections

2373 reflections with *I* > 2σ(*I*)

Monochromator: graphite	$R_{\text{int}} = 0.056$
$T = 293(2)$ K	$\theta_{\max} = 26.0°$
φ and ω scans	$\theta_{\min} = 3.0°$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -14 \rightarrow 14$
$T_{\min} = 0.857$, $T_{\max} = 0.894$	$k = -7 \rightarrow 7$
16828 measured reflections	$l = -27 \rightarrow 27$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.047$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.118$	$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 1.3366P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{\max} = 0.001$
3115 reflections	$\Delta\rho_{\max} = 0.61$ e Å^{-3}
212 parameters	$\Delta\rho_{\min} = -0.56$ 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}
C1	0.7981 (2)	0.7343 (5)	0.86400 (12)	0.0350 (6)
C2	0.8244 (2)	0.8210 (5)	0.92758 (12)	0.0338 (6)
C3	0.7973 (3)	1.0318 (5)	0.93992 (14)	0.0508 (8)
H3	0.7643	1.1241	0.9081	0.061*
C4	0.8186 (3)	1.1078 (6)	0.99910 (15)	0.0587 (9)
H4	0.7979	1.2489	1.0073	0.070*
C5	0.8706 (3)	0.9728 (6)	1.04552 (14)	0.0490 (8)
C6	0.8995 (3)	0.7654 (6)	1.03456 (14)	0.0604 (9)
H6	0.9350	0.6756	1.0664	0.072*
C7	0.8755 (3)	0.6890 (5)	0.97564 (13)	0.0484 (8)
H7	0.8942	0.5461	0.9681	0.058*
C8	0.5015 (2)	0.7563 (5)	0.76962 (13)	0.0399 (7)
H8	0.5481	0.8737	0.7858	0.048*
C9	0.3844 (2)	0.7609 (5)	0.77142 (13)	0.0401 (7)
H9	0.3534	0.8803	0.7878	0.048*
C10	0.3131 (2)	0.5870 (5)	0.74867 (12)	0.0344 (6)
C11	0.3641 (2)	0.4174 (5)	0.72347 (14)	0.0427 (7)
H11	0.3195	0.2978	0.7072	0.051*
C12	0.4821 (2)	0.4272 (5)	0.72261 (14)	0.0419 (7)
H12	0.5146	0.3127	0.7049	0.050*
C13	0.4107 (5)	0.1163 (10)	0.9169 (3)	0.142 (3)
H13	0.3605	−0.0024	0.9138	0.171*

C14	0.4212 (5)	0.2464 (10)	0.9674 (3)	0.131 (3)
H14	0.3802	0.2129	0.9973	0.157*
C15	0.4926 (3)	0.4267 (6)	0.97334 (16)	0.0558 (9)
C16	0.5512 (3)	0.4561 (6)	0.92726 (16)	0.0666 (10)
H16	0.6021	0.5732	0.9287	0.080*
C17	0.5357 (4)	0.3148 (7)	0.87917 (17)	0.0723 (11)
H17	0.5775	0.3405	0.8491	0.087*
Cl1	0.90101 (10)	1.0741 (2)	1.11973 (4)	0.0800 (3)
Mn1	0.7500	0.58733 (9)	0.7500	0.02869 (17)
N1	0.55156 (17)	0.5918 (4)	0.74588 (10)	0.0339 (5)
N2	0.4661 (3)	0.1464 (6)	0.87269 (16)	0.0844 (11)
O1	0.77094 (16)	0.8643 (3)	0.81989 (8)	0.0410 (5)
O2	0.80153 (18)	0.5331 (3)	0.85538 (9)	0.0449 (5)
O1W	0.7500	0.2327 (5)	0.7500	0.0453 (8)
H1W	0.739 (3)	0.153 (5)	0.7201 (14)	0.054*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0252 (13)	0.0471 (18)	0.0325 (15)	−0.0041 (12)	0.0061 (10)	0.0015 (13)
C2	0.0314 (14)	0.0372 (15)	0.0324 (15)	−0.0050 (11)	0.0062 (11)	0.0013 (12)
C3	0.073 (2)	0.0406 (19)	0.0382 (17)	0.0020 (16)	0.0098 (15)	0.0038 (14)
C4	0.086 (3)	0.0425 (19)	0.051 (2)	−0.0058 (18)	0.0204 (18)	−0.0099 (16)
C5	0.0518 (19)	0.061 (2)	0.0335 (16)	−0.0141 (16)	0.0079 (13)	−0.0091 (15)
C6	0.071 (2)	0.072 (3)	0.0329 (17)	0.0150 (19)	0.0013 (15)	0.0040 (17)
C7	0.0569 (19)	0.0455 (18)	0.0403 (17)	0.0102 (15)	0.0047 (14)	0.0033 (15)
C8	0.0296 (14)	0.0384 (16)	0.0508 (17)	−0.0034 (12)	0.0066 (12)	−0.0081 (14)
C9	0.0288 (14)	0.0401 (16)	0.0510 (18)	0.0019 (12)	0.0079 (12)	−0.0091 (14)
C10	0.0255 (13)	0.0436 (16)	0.0334 (14)	0.0010 (12)	0.0050 (10)	0.0016 (13)
C11	0.0306 (14)	0.0416 (16)	0.0547 (18)	−0.0064 (13)	0.0062 (12)	−0.0160 (15)
C12	0.0318 (14)	0.0459 (17)	0.0485 (17)	−0.0020 (13)	0.0099 (12)	−0.0146 (15)
C13	0.133 (5)	0.159 (6)	0.162 (5)	−0.102 (4)	0.090 (4)	−0.105 (5)
C14	0.128 (4)	0.155 (5)	0.141 (5)	−0.097 (4)	0.095 (4)	−0.095 (4)
C15	0.0409 (17)	0.065 (2)	0.062 (2)	−0.0090 (16)	0.0118 (15)	−0.0146 (18)
C16	0.082 (3)	0.065 (2)	0.054 (2)	−0.023 (2)	0.0162 (18)	−0.0051 (19)
C17	0.090 (3)	0.077 (3)	0.052 (2)	−0.011 (2)	0.020 (2)	−0.006 (2)
Cl1	0.0960 (8)	0.1026 (8)	0.0397 (5)	−0.0174 (6)	0.0111 (5)	−0.0241 (5)
Mn1	0.0237 (3)	0.0308 (3)	0.0316 (3)	0.000	0.0060 (2)	0.000
N1	0.0239 (11)	0.0406 (13)	0.0376 (12)	−0.0009 (10)	0.0072 (9)	−0.0041 (11)
N2	0.081 (2)	0.095 (3)	0.079 (2)	−0.022 (2)	0.0222 (19)	−0.036 (2)
O1	0.0445 (11)	0.0465 (12)	0.0293 (10)	0.0002 (9)	0.0021 (8)	0.0052 (9)
O2	0.0595 (13)	0.0372 (12)	0.0389 (11)	−0.0051 (9)	0.0128 (9)	−0.0038 (9)
O1W	0.068 (2)	0.0307 (16)	0.0358 (17)	0.000	0.0072 (15)	0.000

Geometric parameters (Å, °)

C1—O2	1.254 (4)	C11—H11	0.9300
C1—O1	1.262 (3)	C12—N1	1.333 (3)
C1—C2	1.497 (4)	C12—H12	0.9300

C2—C3	1.377 (4)	C13—N2	1.311 (6)
C2—C7	1.382 (4)	C13—C14	1.375 (6)
C3—C4	1.383 (4)	C13—H13	0.9300
C3—H3	0.9300	C14—C15	1.378 (5)
C4—C5	1.371 (5)	C14—H14	0.9300
C4—H4	0.9300	C15—C16	1.372 (5)
C5—C6	1.356 (5)	C15—C15^{ii}	1.482 (7)
C5—Cl1	1.747 (3)	C16—C17	1.370 (5)
C6—C7	1.378 (4)	C16—H16	0.9300
C6—H6	0.9300	C17—N2	1.306 (5)
C7—H7	0.9300	C17—H17	0.9300
C8—N1	1.336 (3)	Mn1—O1W	2.181 (3)
C8—C9	1.378 (4)	Mn1—O1	2.297 (2)
C8—H8	0.9300	Mn1—O1^{iii}	2.297 (2)
C9—C10	1.385 (4)	Mn1—N1	2.302 (2)
C9—H9	0.9300	Mn1—N1^{iii}	2.302 (2)
C10—C11	1.382 (4)	Mn1—O2^{iii}	2.344 (2)
C10—C10^{i}	1.490 (5)	Mn1—O2	2.344 (2)
C11—C12	1.385 (4)	O1W—H1W	0.82 (3)

O2—C1—O1	121.0 (3)	C13—C14—H14	120.2
O2—C1—C2	119.5 (3)	C15—C14—H14	120.2
O1—C1—C2	119.5 (3)	C16—C15—C14	115.0 (3)
C3—C2—C7	118.3 (3)	C16—C15—C15^{ii}	122.8 (4)
C3—C2—C1	121.3 (3)	C14—C15—C15^{ii}	122.1 (4)
C7—C2—C1	120.3 (3)	C17—C16—C15	120.7 (4)
C2—C3—C4	120.7 (3)	C17—C16—H16	119.6
C2—C3—H3	119.6	C15—C16—H16	119.6
C4—C3—H3	119.6	N2—C17—C16	124.4 (4)
C5—C4—C3	119.3 (3)	N2—C17—H17	117.8
C5—C4—H4	120.4	C16—C17—H17	117.8
C3—C4—H4	120.4	O1W—Mn1—O1	137.89 (5)
C6—C5—C4	121.2 (3)	O1W—Mn1—O1^{iii}	137.89 (5)
C6—C5—Cl1	120.2 (3)	O1—Mn1—O1^{iii}	84.22 (10)
C4—C5—Cl1	118.6 (3)	O1W—Mn1—N1	90.69 (6)
C5—C6—C7	119.3 (3)	O1—Mn1—N1	88.70 (7)
C5—C6—H6	120.4	O1^{iii}—Mn1—N1	90.28 (7)
C7—C6—H6	120.4	O1W—Mn1—N1^{iii}	90.69 (6)
C6—C7—C2	121.2 (3)	O1—Mn1—N1^{iii}	90.28 (8)
C6—C7—H7	119.4	O1^{iii}—Mn1—N1^{iii}	88.70 (7)
C2—C7—H7	119.4	N1—Mn1—N1^{iii}	178.62 (12)
N1—C8—C9	123.4 (3)	O1W—Mn1—O2^{iii}	81.82 (5)
N1—C8—H8	118.3	O1—Mn1—O2^{iii}	139.99 (7)
C9—C8—H8	118.3	O1^{iii}—Mn1—O2^{iii}	56.30 (7)
C8—C9—C10	119.7 (3)	N1—Mn1—O2^{iii}	85.56 (7)
C8—C9—H9	120.1	N1^{iii}—Mn1—O2^{iii}	94.63 (7)

C10—C9—H9	120.1	O1W—Mn1—O2	81.82 (5)
C11—C10—C9	117.2 (2)	O1—Mn1—O2	56.30 (7)
C11—C10—C10^{i}	122.29 (19)	O1^{iii}—Mn1—O2	139.99 (7)
C9—C10—C10^{i}	120.50 (19)	N1—Mn1—O2	94.63 (7)
C10—C11—C12	119.4 (3)	N1^{iii}—Mn1—O2	85.56 (7)
C10—C11—H11	120.3	O2^{iii}—Mn1—O2	163.65 (10)
C12—C11—H11	120.3	C12—N1—C8	116.8 (2)
N1—C12—C11	123.5 (3)	C12—N1—Mn1	122.04 (18)
N1—C12—H12	118.2	C8—N1—Mn1	121.13 (18)
C11—C12—H12	118.2	C17—N2—C13	115.1 (4)
N2—C13—C14	125.1 (4)	C1—O1—Mn1	92.36 (17)
N2—C13—H13	117.5	C1—O2—Mn1	90.38 (16)
C14—C13—H13	117.5	Mn1—O1W—H1W	127 (2)
C13—C14—C15	119.6 (4)		

Symmetry codes: (i) $-x+1/2, y, -z+3/2$; (ii) $-x+1, -y+1, -z+2$; (iii) $-x+3/2, y, -z+3/2$.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1W—H1W···O1^{iv}	0.82 (3)	1.98 (3)	2.740 (3)	153 (3)
C8—H8···O1	0.93	2.55	3.181 (3)	125

Symmetry codes: (iv) $-x+3/2, y-1, -z+3/2$.

Fig. 1

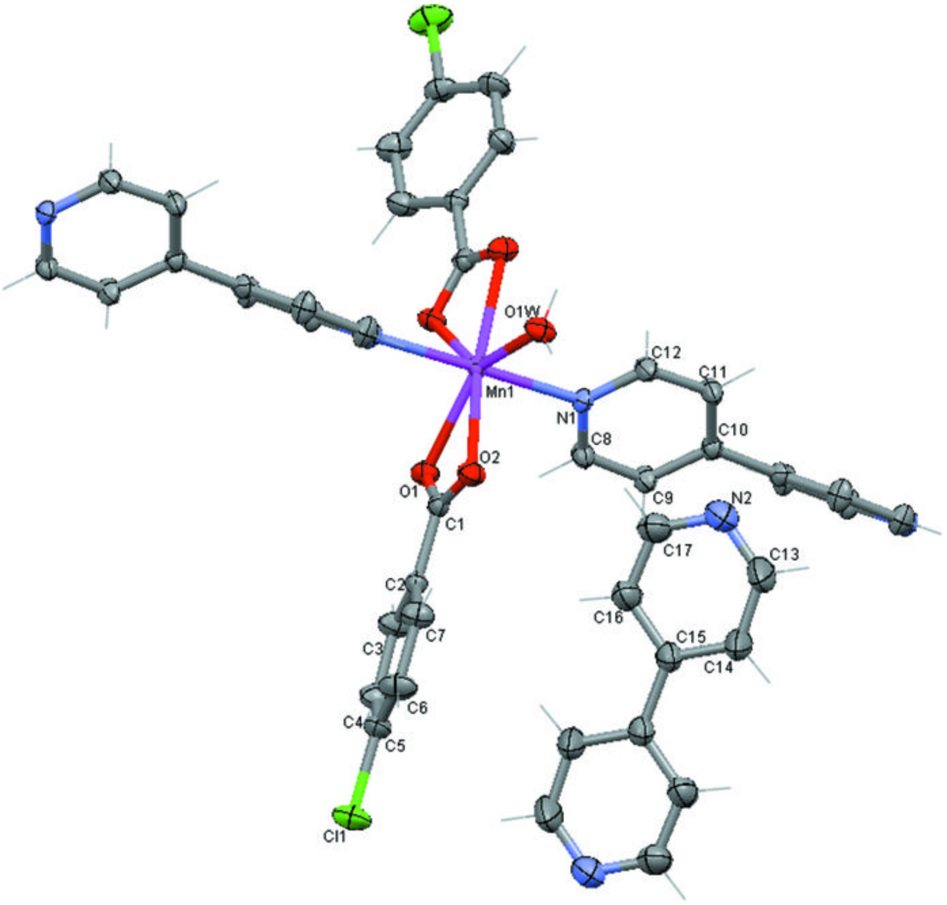
O1W
Mn1
N1
C12
C11
C10
C8
C9
O2
O1
C1
N2
C13
C17
C2
C16
C15
C14
C3
C7
C6
C4
C5
Cl1

Fig. 2