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Bis[4′-(4-methylphenyl)-2,2′:6′,2″-terpyridine-κ^3N,N',N'']manganese(II) bis(perchlorate)

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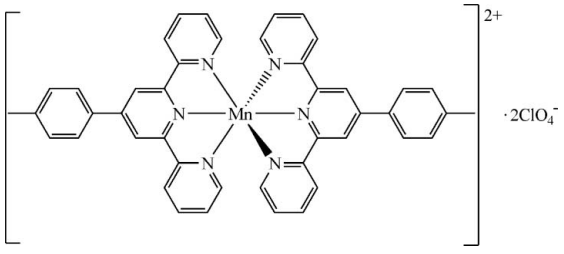
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.009 Å; disorder in solvent or counterion; R factor = 0.060; wR factor = 0.204; data-to-parameter ratio = 12.9.

In the title complex, $[Mn(C_{22}H_{17}N_3)_2](ClO_4)_2$, the MnN_6 coordination geometry is distorted octahedral, involving the six N atoms of two 4′-(4-methylphenyl)-2,2′:6′,2″-terpyridine (ttp) ligands. The two chelated ttp planes are almost perpendicular, with a dihedral angle of 89.1 (5)°. The packing involves intermolecular C—H···O hydrogen bonds between the ttp ligands and perchlorate anions. The latter are disordered over two positions, one with almost equal occupancy and the other in a ratio of *ca* 0.7:0.3.

Related literature

For related literature, see: Al-Noaimi, Yap & Crutchley (2004); Barigelletti *et al.* (2000); Chamchoumis & Potvin (1999); Collin *et al.* (1991); Duboc *et al.* (2006); Schubert *et al.* (2006); Steiner (1997); Uma *et al.* (2005); Wang *et al.* (2007); Wilkinson *et al.* (2004); Yucesan *et al.* (2005); Yutaka *et al.* (2005).



Experimental

Crystal data

$[Mn(C_{22}H_{17}N_3)_2](ClO_4)_2$
M_r = 900.61
Monoclinic, $P2_1/c$
a = 18.2372 (4) Å
b = 15.4778 (4) Å
c = 15.9465 (4) Å
β = 110.339 (2)°
V = 4220.60 (18) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.50 mm^{-1}
T = 293 (2) K
0.25 × 0.19 × 0.16 mm

Data collection

Bruker APEXII area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.885, T_{max} = 0.924
45630 measured reflections
8296 independent reflections
4836 reflections with $I > 2\sigma(I)$
R_{int} = 0.090

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.060
$wR(F^2)$ = 0.204
S = 0.98
8296 reflections
644 parameters
176 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.44 e Å^{-3}
$\Delta\rho_{min}$ = −0.46 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1···O3B	0.93	2.15	3.055 (15)	165
C3—H3···O6A^{i}	0.93	2.42	3.347 (9)	176
C13—H13···O5A^{ii}	0.93	2.52	3.400 (9)	158
C15—H15···O4B^{ii}	0.93	2.50	3.260 (16)	139
C22—H22C···O2B^{iii}	0.96	2.37	3.324 (14)	177
C23—H23···O6B	0.93	2.31	3.23 (2)	171
C34—H34···O3A^{iv}	0.93	2.55	3.458 (11)	167
C34—H34···O1B^{iv}	0.93	2.44	3.223 (12)	142
C37—H37···O8A^{v}	0.93	2.54	3.255 (9)	134
C37—H37···O7B^{v}	0.93	2.40	3.31 (2)	164
C39—H39···O2A^{ii}	0.93	2.49	3.341 (12)	152
C44—H44C···O8B^{vi}	0.96	2.41	3.30 (2)	153

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

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: GG2037).

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supplementary materials

Acta Cryst. (2007). E**63**, m2393-m2394 [**doi:10.1107/S1600536807040391**]

Bis[4'-(4-methylphenyl)-2,2':6',2''-terpyridine-κ^3N,N',N'']manganese(II) bis(perchlorate)

H.-G. Liu, Y.-C. Qiu and J.-Z. Wu

Comment

Terpyridines are a family of widely used ligands (Schubert *et al.* 2006). Whereas a large number of metal derivatives of terpyridine and its substituted derivatives have been reported, there are few examples of metal derivatives of 4'-(4-methylphenyl)-2,2':6',2''-terpyridine ligand (denoted as ttp), and examples of crystal structure reports are limited to those of ruthenium (Chamchoumis & Potvin, 1999; Barigelletti *et al.*, 2000; Al-Noaimi *et al.*, 2004), copper (Uma *et al.*, 2005; Yucesan *et al.*, 2005), iridium (Yutaka *et al.*, 2005; Wilkinson *et al.*, 2004) and manganese (Duboc *et al.*, 2006). The complex of Duboc *et al.* is $[Mn(ttp)Cl_2]$, in which Mn(II) is penta-coordinated. Here we report the title structure (I) from a hydrothermal reaction of manganese perchlorate and ttp.

As illustrated in Fig. 1, the Mn(II) centre is coordinated by six N atoms from two ttp ligands, and displays a distorted octahedral geometry. The tri-coordinating mode of the ttp ligands restricts the three pyridyl rings of each ttp and the central Mn(II) ion are very close to be coplanar. Such two planes are almost perpendicular with a dihedral angle of 89.1 (5)°. The two tolyl groups are twisted out of their connected terpyridyl moieties by 35.62 (4)° and 20.23 (6)°, respectively. Both perchlorate anions are disordered and were refined with two sets of disordered O atom positions for each. There are several C—H···O hydrogen bonds (Steiner, 1997) between the ttp ligand and the neighbouring perchloartes which involve the cations and counter-anions (Table 1).

Experimental

4'-(4-Methylphenyl)-2,2':6',2''-terpyridine (ttp) was prepared by an improved Kröhnke condensation method (Wang *et al.*, 2007; Collin *et al.*, 1991). A mixture of $Mn(ClO_4)_2{\cdot}6H_2O$ (1 mmol), ttp (2 mmol) and H_2O/MeOH (10 ml; 1:1) was placed in a 25 ml of Teflon-lined stainless steel vessel and heated under autogenous pressure at 432 K for 4 days, followed by cooling to room temperature at a rate of 5 K/h. Yellow block crystals of the title complex (I) were obtained in a yield of 38% based on Mn.

Refinement

Each of the two $[ClO_4]^-$ moieties was disordered and they were split into two sets of positions, with occupancy ratios of 0.505:0.495 and 0.738:0.262. The intra Cl—O and O—O distances were restrained to be 1.44 (1) and 2.35 (2) Å, respectively. Carbon-bound H atoms were placed at calculated positions and were treated as riding on the parent C atoms with C—H = 0.93 to 0.97 Å, with $U_{iso}(H) = 1.2$ or 1.5 $U_{eq}(C)$.

Figures

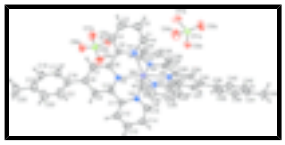


Fig. 1. The structure of (I), showing the numbering scheme and displacement ellipsoids drawn at the 20% probability level. Only one set of disordered positions for each perchlorate is displayed for clarity.

Bis[4'-(4-methylphenyl)-2,2':6',2''-terpyridine-κ^3N,N',N'']manganese(II) bis(perchlorate)

Crystal data

$[Mn(C_{22}H_{17}N_3)_2](ClO_4)_2$	F_{000} = 1852
M_r = 900.61	D_x = 1.417 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 8356 reflections
a = 18.2372 (4) Å	θ = 1.4–28.0º
b = 15.4778 (4) Å	μ = 0.50 mm^{-1}
c = 15.9465 (4) Å	T = 293 (2) K
β = 110.339 (2)º	Block, yellow
V = 4220.60 (18) Å^3	0.25 × 0.19 × 0.16 mm
Z = 4	

Data collection

Bruker APEXII area-detector diffractometer	8296 independent reflections
Radiation source: fine-focus sealed tube	4836 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.090
T = 293(2) K	θ_{max} = 26.0º
φ and ω scans	θ_{min} = 1.2º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	h = −22→22
T_{min} = 0.885, T_{max} = 0.924	k = −17→19
45630 measured reflections	l = −19→19

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.060	H-atom parameters constrained
$wR(F^2)$ = 0.204	$w = 1/[\sigma^2(F_o^2) + (0.1047P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 0.98	$(\Delta/\sigma)_{max}$ = 0.002
8296 reflections	$\Delta\rho_{max}$ = 0.44 e Å^{-3}

644 parameters
176 restraints
Primary atom site location: structure-invariant direct methods

$\Delta\rho_{min} = -0.45$ e Å^{-3}
Extinction correction: none

Special details

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 $F^2 > \sigma(F^2)$ 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)
C1	0.7202 (3)	0.6693 (3)	0.4596 (3)	0.0771 (15)	
H1	0.7742	0.6747	0.4759	0.092*	
C2	0.6874 (4)	0.6750 (4)	0.5240 (4)	0.0880 (17)	
H2	0.7185	0.6837	0.5835	0.106*	
C3	0.6072 (4)	0.6677 (4)	0.4998 (4)	0.0935 (18)	
H3	0.5835	0.6707	0.5428	0.112*	
C4	0.5628 (3)	0.6559 (4)	0.4110 (4)	0.0846 (17)	
H4	0.5087	0.6517	0.3935	0.102*	
C5	0.5989 (3)	0.6504 (3)	0.3479 (3)	0.0557 (12)	
C6	0.5569 (3)	0.6388 (3)	0.2515 (3)	0.0545 (11)	
C7	0.4766 (3)	0.6394 (3)	0.2116 (3)	0.0626 (13)	
H7	0.4456	0.6481	0.2465	0.075*	
C8	0.4413 (3)	0.6272 (3)	0.1198 (3)	0.0644 (13)	
C9	0.4919 (3)	0.6151 (3)	0.0721 (3)	0.0632 (13)	
H9	0.4712	0.6055	0.0108	0.076*	
C10	0.5717 (3)	0.6171 (3)	0.1141 (3)	0.0550 (12)	
C11	0.6290 (3)	0.6082 (3)	0.0682 (3)	0.0583 (12)	
C12	0.6073 (3)	0.5995 (3)	−0.0238 (3)	0.0698 (14)	
H12	0.5548	0.5968	−0.0596	0.084*	
C13	0.6650 (4)	0.5951 (4)	−0.0612 (3)	0.0809 (16)	
H13	0.6516	0.5887	−0.1227	0.097*	
C14	0.7417 (3)	0.6002 (4)	−0.0077 (4)	0.0814 (16)	
H14	0.7812	0.5977	−0.0319	0.098*	
C15	0.7593 (3)	0.6092 (3)	0.0832 (3)	0.0757 (15)	
H15	0.8116	0.6133	0.1195	0.091*	
C16	0.3552 (3)	0.6262 (3)	0.0749 (4)	0.0742 (15)	
C17	0.3057 (3)	0.6089 (3)	0.1227 (4)	0.0838 (17)	
H17	0.3266	0.6005	0.1842	0.101*	
C18	0.2248 (3)	0.6042 (4)	0.0786 (5)	0.096 (2)	

H18	0.1924	0.5940	0.1115	0.115*
C19	0.1920 (4)	0.6145 (4)	−0.0137 (6)	0.105 (2)
C20	0.2407 (4)	0.6317 (5)	−0.0603 (5)	0.125 (3)
H20	0.2196	0.6388	−0.1220	0.150*
C21	0.3212 (4)	0.6388 (4)	−0.0173 (5)	0.112 (2)
H21	0.3528	0.6522	−0.0504	0.134*
C22	0.1048 (4)	0.6031 (6)	−0.0606 (6)	0.164 (4)
H22A	0.0907	0.5443	−0.0545	0.247*
H22B	0.0913	0.6168	−0.1229	0.247*
H22C	0.0772	0.6410	−0.0342	0.247*
C23	0.7323 (3)	0.8362 (4)	0.2579 (3)	0.0607 (12)
H23	0.6790	0.8301	0.2466	0.073*
C24	0.7615 (3)	0.9169 (4)	0.2579 (3)	0.0695 (14)
H24	0.7287	0.9647	0.2473	0.083*
C25	0.8405 (3)	0.9271 (4)	0.2737 (4)	0.0836 (16)
H25	0.8618	0.9815	0.2730	0.100*
C26	0.8870 (3)	0.8537 (4)	0.2909 (4)	0.0765 (15)
H26	0.9405	0.8585	0.3024	0.092*
C27	0.8542 (3)	0.7738 (3)	0.2908 (3)	0.0526 (11)
C28	0.8998 (3)	0.6925 (3)	0.3100 (3)	0.0511 (11)
C29	0.9783 (3)	0.6870 (3)	0.3250 (3)	0.0569 (12)
H29	1.0057	0.7368	0.3214	0.068*
C30	1.0176 (3)	0.6093 (3)	0.3452 (3)	0.0576 (12)
C31	0.9733 (3)	0.5368 (3)	0.3503 (3)	0.0643 (13)
H31	0.9970	0.4829	0.3646	0.077*
C32	0.8946 (3)	0.5458 (3)	0.3341 (3)	0.0582 (12)
C33	0.8412 (3)	0.4725 (3)	0.3363 (3)	0.0661 (13)
C34	0.8671 (4)	0.3912 (4)	0.3655 (5)	0.097 (2)
H34	0.9202	0.3784	0.3847	0.117*
C35	0.8139 (4)	0.3288 (4)	0.3663 (5)	0.113 (2)
H35	0.8307	0.2731	0.3853	0.135*
C36	0.7364 (4)	0.3486 (4)	0.3390 (5)	0.105 (2)
H36	0.6997	0.3072	0.3397	0.126*
C37	0.7140 (3)	0.4313 (4)	0.3104 (4)	0.0926 (18)
H37	0.6611	0.4449	0.2911	0.111*
C38	1.1023 (3)	0.6038 (3)	0.3604 (3)	0.0613 (13)
C39	1.1345 (3)	0.6565 (3)	0.3126 (3)	0.0739 (15)
H39	1.1023	0.6930	0.2689	0.089*
C40	1.2146 (3)	0.6558 (4)	0.3292 (4)	0.0788 (15)
H40	1.2348	0.6917	0.2959	0.095*
C41	1.2643 (3)	0.6038 (4)	0.3929 (4)	0.0776 (15)
C42	1.2313 (3)	0.5503 (4)	0.4403 (4)	0.0874 (18)
H42	1.2636	0.5144	0.4846	0.105*
C43	1.1523 (3)	0.5490 (4)	0.4233 (3)	0.0802 (16)
H43	1.1318	0.5107	0.4544	0.096*
C44	1.3513 (3)	0.6065 (4)	0.4123 (4)	0.108 (2)
H44A	1.3619	0.6388	0.3664	0.162*
H44B	1.3708	0.5486	0.4137	0.162*
H44C	1.3767	0.6336	0.4692	0.162*

Mn1	0.73059 (4)	0.63041 (5)	0.26895 (4)	0.0557 (3)	
N1	0.6769 (2)	0.6561 (2)	0.3723 (2)	0.0605 (10)	
N2	0.6036 (2)	0.6273 (2)	0.2033 (2)	0.0541 (9)	
N3	0.7050 (2)	0.6124 (2)	0.1215 (2)	0.0605 (10)	
N4	0.7769 (2)	0.7645 (2)	0.2734 (2)	0.0548 (9)	
N5	0.8585 (2)	0.6222 (2)	0.3133 (2)	0.0542 (9)	
N6	0.7649 (2)	0.4934 (3)	0.3088 (3)	0.0692 (11)	
Cl1A	0.9435 (4)	0.7412 (4)	0.5646 (5)	0.103 (2)	0.505 (7)
Cl2A	0.50345 (19)	0.9028 (2)	0.1940 (2)	0.0725 (12)	0.739 (9)
O1A	0.8876 (6)	0.7478 (8)	0.6104 (6)	0.155 (4)	0.505 (7)
O2A	1.0179 (6)	0.7748 (10)	0.6119 (10)	0.200 (7)	0.505 (7)
O3A	0.9374 (5)	0.6574 (5)	0.5272 (6)	0.119 (4)	0.505 (7)
O4A	0.9015 (7)	0.8002 (7)	0.4925 (7)	0.164 (5)	0.505 (7)
O5A	0.5726 (3)	0.9584 (4)	0.2206 (5)	0.106 (2)	0.739 (9)
O6A	0.5221 (5)	0.8284 (4)	0.1549 (6)	0.131 (3)	0.739 (9)
O7A	0.4830 (5)	0.8790 (7)	0.2698 (5)	0.134 (3)	0.739 (9)
O8A	0.4411 (3)	0.9499 (5)	0.1343 (4)	0.121 (3)	0.739 (9)
Cl1B	0.9560 (5)	0.7580 (7)	0.5794 (7)	0.164 (4)	0.495 (7)
Cl2B	0.5018 (10)	0.8960 (11)	0.2035 (11)	0.167 (7)	0.261 (9)
O1B	0.9831 (7)	0.7036 (7)	0.6559 (6)	0.146 (4)	0.495 (7)
O2B	1.0134 (6)	0.7686 (8)	0.5385 (8)	0.151 (5)	0.495 (7)
O3B	0.8915 (9)	0.7227 (15)	0.5115 (11)	0.291 (9)	0.495 (7)
O4B	0.9392 (9)	0.8412 (9)	0.6074 (10)	0.228 (6)	0.495 (7)
O5B	0.5485 (16)	0.9575 (18)	0.1749 (18)	0.197 (10)	0.261 (9)
O6B	0.5510 (11)	0.8237 (12)	0.2409 (19)	0.168 (9)	0.261 (9)
O7B	0.4791 (13)	0.9387 (15)	0.2706 (14)	0.139 (8)	0.261 (9)
O8B	0.4373 (11)	0.867 (2)	0.1298 (13)	0.176 (9)	0.261 (9)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.087 (4)	0.077 (4)	0.063 (3)	0.000 (3)	0.021 (3)	0.004 (3)
C2	0.120 (5)	0.088 (4)	0.061 (3)	−0.009 (4)	0.037 (4)	0.001 (3)
C3	0.129 (6)	0.091 (5)	0.085 (4)	−0.001 (4)	0.069 (4)	0.002 (3)
C4	0.088 (4)	0.099 (5)	0.077 (4)	−0.006 (3)	0.041 (3)	−0.010 (3)
C5	0.062 (3)	0.053 (3)	0.060 (3)	−0.006 (2)	0.031 (2)	−0.001 (2)
C6	0.056 (3)	0.049 (3)	0.062 (3)	−0.001 (2)	0.026 (2)	0.000 (2)
C7	0.056 (3)	0.059 (3)	0.082 (3)	−0.005 (2)	0.036 (3)	0.003 (3)
C8	0.065 (3)	0.045 (3)	0.082 (3)	−0.004 (2)	0.023 (3)	0.004 (2)
C9	0.066 (3)	0.058 (3)	0.062 (3)	−0.009 (2)	0.019 (2)	−0.005 (2)
C10	0.060 (3)	0.050 (3)	0.056 (3)	−0.012 (2)	0.021 (2)	−0.006 (2)
C11	0.070 (3)	0.055 (3)	0.057 (3)	−0.014 (2)	0.031 (2)	−0.005 (2)
C12	0.076 (3)	0.071 (4)	0.068 (3)	−0.021 (3)	0.032 (3)	−0.013 (3)
C13	0.108 (5)	0.082 (4)	0.066 (3)	−0.021 (3)	0.046 (3)	−0.017 (3)
C14	0.095 (4)	0.083 (4)	0.085 (4)	−0.019 (3)	0.056 (3)	−0.022 (3)
C15	0.073 (3)	0.092 (4)	0.073 (3)	−0.010 (3)	0.039 (3)	−0.015 (3)
C16	0.059 (3)	0.057 (3)	0.096 (4)	−0.004 (3)	0.014 (3)	0.011 (3)
C17	0.059 (3)	0.080 (4)	0.115 (4)	−0.001 (3)	0.034 (3)	−0.006 (3)

C18	0.059 (4)	0.074 (4)	0.155 (6)	0.002 (3)	0.038 (4)	−0.012 (4)
C19	0.061 (4)	0.084 (5)	0.147 (6)	0.005 (3)	0.009 (4)	0.013 (4)
C20	0.076 (5)	0.131 (7)	0.136 (6)	−0.001 (4)	−0.004 (4)	0.050 (5)
C21	0.073 (4)	0.121 (6)	0.126 (5)	−0.006 (4)	0.015 (4)	0.047 (4)
C22	0.065 (4)	0.175 (9)	0.206 (9)	0.011 (5)	−0.014 (5)	0.010 (7)
C23	0.066 (3)	0.062 (4)	0.063 (3)	0.010 (3)	0.034 (2)	0.003 (2)
C24	0.074 (4)	0.061 (4)	0.082 (3)	0.019 (3)	0.038 (3)	0.011 (3)
C25	0.089 (4)	0.049 (4)	0.126 (5)	0.004 (3)	0.054 (4)	0.007 (3)
C26	0.055 (3)	0.062 (4)	0.116 (4)	0.002 (3)	0.034 (3)	0.007 (3)
C27	0.053 (3)	0.053 (3)	0.056 (3)	−0.001 (2)	0.025 (2)	−0.001 (2)
C28	0.054 (3)	0.050 (3)	0.051 (2)	0.001 (2)	0.021 (2)	−0.001 (2)
C29	0.054 (3)	0.053 (3)	0.066 (3)	−0.002 (2)	0.024 (2)	0.003 (2)
C30	0.059 (3)	0.057 (3)	0.059 (3)	0.003 (2)	0.022 (2)	−0.001 (2)
C31	0.060 (3)	0.055 (3)	0.080 (3)	0.011 (3)	0.026 (2)	0.003 (3)
C32	0.060 (3)	0.053 (3)	0.065 (3)	0.002 (2)	0.025 (2)	0.000 (2)
C33	0.059 (3)	0.058 (4)	0.084 (3)	0.000 (3)	0.030 (3)	0.001 (3)
C34	0.083 (4)	0.054 (4)	0.160 (6)	0.010 (3)	0.050 (4)	0.015 (4)
C35	0.111 (6)	0.059 (4)	0.175 (7)	−0.007 (4)	0.059 (5)	0.019 (4)
C36	0.088 (5)	0.069 (5)	0.167 (6)	−0.015 (4)	0.058 (4)	0.009 (4)
C37	0.072 (4)	0.067 (4)	0.147 (5)	−0.011 (3)	0.049 (4)	0.010 (4)
C38	0.054 (3)	0.064 (3)	0.069 (3)	0.003 (2)	0.025 (2)	−0.003 (3)
C39	0.057 (3)	0.079 (4)	0.089 (4)	0.007 (3)	0.029 (3)	0.014 (3)
C40	0.062 (3)	0.087 (4)	0.089 (4)	0.000 (3)	0.029 (3)	0.007 (3)
C41	0.054 (3)	0.090 (4)	0.089 (4)	0.000 (3)	0.026 (3)	−0.010 (3)
C42	0.065 (4)	0.107 (5)	0.082 (4)	0.026 (3)	0.015 (3)	0.012 (3)
C43	0.068 (4)	0.092 (4)	0.081 (3)	0.016 (3)	0.028 (3)	0.016 (3)
C44	0.057 (4)	0.144 (6)	0.125 (5)	0.005 (4)	0.033 (3)	−0.009 (4)
Mn1	0.0487 (4)	0.0608 (5)	0.0601 (4)	−0.0020 (3)	0.0222 (3)	−0.0027 (3)
N1	0.067 (3)	0.061 (3)	0.057 (2)	−0.003 (2)	0.025 (2)	0.0038 (19)
N2	0.059 (2)	0.054 (2)	0.054 (2)	−0.0068 (18)	0.0249 (18)	−0.0054 (17)
N3	0.059 (2)	0.067 (3)	0.060 (2)	−0.010 (2)	0.027 (2)	−0.0097 (19)
N4	0.053 (2)	0.059 (3)	0.058 (2)	0.0064 (19)	0.0251 (17)	−0.0008 (18)
N5	0.059 (2)	0.046 (3)	0.061 (2)	−0.001 (2)	0.0239 (18)	−0.0036 (18)
N6	0.063 (3)	0.056 (3)	0.095 (3)	−0.007 (2)	0.037 (2)	0.003 (2)
Cl1A	0.064 (3)	0.143 (4)	0.086 (3)	0.013 (3)	0.006 (2)	−0.028 (3)
Cl2A	0.065 (2)	0.077 (2)	0.0813 (19)	0.0177 (15)	0.0326 (15)	0.0062 (14)
O1A	0.154 (8)	0.206 (11)	0.118 (7)	0.024 (8)	0.065 (6)	−0.052 (7)
O2A	0.100 (7)	0.234 (13)	0.211 (13)	−0.002 (8)	−0.017 (7)	−0.091 (11)
O3A	0.098 (6)	0.144 (7)	0.096 (6)	0.034 (5)	0.008 (5)	−0.042 (5)
O4A	0.158 (9)	0.174 (9)	0.138 (8)	0.041 (8)	0.025 (6)	0.035 (7)
O5A	0.082 (4)	0.100 (5)	0.127 (5)	−0.011 (3)	0.024 (3)	−0.002 (4)
O6A	0.168 (7)	0.068 (4)	0.194 (7)	0.002 (4)	0.111 (6)	−0.016 (4)
O7A	0.110 (5)	0.213 (10)	0.094 (4)	0.014 (6)	0.056 (4)	0.030 (5)
O8A	0.094 (4)	0.132 (6)	0.115 (4)	0.031 (4)	0.010 (3)	0.026 (4)
Cl1B	0.086 (5)	0.301 (10)	0.098 (4)	0.035 (5)	0.024 (4)	−0.063 (5)
Cl2B	0.116 (12)	0.184 (15)	0.182 (14)	0.005 (9)	0.029 (9)	−0.003 (11)
O1B	0.160 (9)	0.198 (10)	0.123 (7)	−0.022 (7)	0.104 (6)	−0.049 (6)
O2B	0.128 (8)	0.193 (11)	0.157 (9)	0.048 (7)	0.079 (7)	0.047 (8)
O3B	0.176 (11)	0.421 (19)	0.226 (13)	−0.096 (14)	0.006 (10)	−0.041 (13)

O4B	0.201 (12)	0.299 (13)	0.179 (11)	0.104 (11)	0.060 (9)	−0.021 (9)
O5B	0.177 (19)	0.208 (19)	0.20 (2)	−0.025 (15)	0.061 (14)	0.009 (16)
O6B	0.111 (13)	0.149 (15)	0.215 (19)	0.007 (10)	0.020 (12)	−0.020 (13)
O7B	0.105 (13)	0.121 (16)	0.167 (15)	−0.005 (11)	0.018 (10)	−0.009 (12)
O8B	0.126 (14)	0.22 (2)	0.152 (15)	0.008 (13)	0.017 (11)	−0.020 (14)

Geometric parameters (Å, °)

C1—N1	1.357 (6)	C28—N5	1.334 (5)
C1—C2	1.359 (7)	C28—C29	1.370 (6)
C1—H1	0.9300	C29—C30	1.380 (6)
C2—C3	1.382 (7)	C29—H29	0.9300
C2—H2	0.9300	C30—C31	1.403 (6)
C3—C4	1.377 (7)	C30—C38	1.480 (6)
C3—H3	0.9300	C31—C32	1.373 (6)
C4—C5	1.383 (7)	C31—H31	0.9300
C4—H4	0.9300	C32—N5	1.339 (5)
C5—N1	1.341 (5)	C32—C33	1.503 (6)
C5—C6	1.472 (6)	C33—N6	1.346 (6)
C6—N2	1.343 (5)	C33—C34	1.368 (7)
C6—C7	1.379 (6)	C34—C35	1.373 (8)
C7—C8	1.392 (7)	C34—H34	0.9300
C7—H7	0.9300	C35—C36	1.360 (8)
C8—C9	1.398 (7)	C35—H35	0.9300
C8—C16	1.481 (7)	C36—C37	1.372 (8)
C9—C10	1.374 (6)	C36—H36	0.9300
C9—H9	0.9300	C37—N6	1.342 (6)
C10—N2	1.346 (5)	C37—H37	0.9300
C10—C11	1.476 (6)	C38—C39	1.379 (7)
C11—N3	1.352 (6)	C38—C43	1.386 (6)
C11—C12	1.386 (6)	C39—C40	1.391 (6)
C12—C13	1.380 (7)	C39—H39	0.9300
C12—H12	0.9300	C40—C41	1.364 (7)
C13—C14	1.365 (7)	C40—H40	0.9300
C13—H13	0.9300	C41—C42	1.391 (8)
C14—C15	1.377 (7)	C41—C44	1.508 (7)
C14—H14	0.9300	C42—C43	1.371 (7)
C15—N3	1.333 (6)	C42—H42	0.9300
C15—H15	0.9300	C43—H43	0.9300
C16—C17	1.395 (7)	C44—H44A	0.9600
C16—C21	1.397 (8)	C44—H44B	0.9600
C17—C18	1.397 (7)	C44—H44C	0.9600
C17—H17	0.9300	Mn1—N2	2.185 (4)
C18—C19	1.392 (9)	Mn1—N5	2.193 (4)
C18—H18	0.9300	Mn1—N1	2.225 (4)
C19—C20	1.368 (10)	Mn1—N4	2.233 (4)
C19—C22	1.514 (8)	Mn1—N6	2.240 (4)
C20—C21	1.392 (8)	Mn1—N3	2.250 (4)
C20—H20	0.9300	Cl1A—O2A	1.404 (8)

C21—H21	0.9300	Cl1A—O3A	1.416 (8)
C22—H22A	0.9600	Cl1A—O1A	1.448 (8)
C22—H22B	0.9600	Cl1A—O4A	1.459 (8)
C22—H22C	0.9600	Cl2A—O6A	1.406 (6)
C23—N4	1.347 (6)	Cl2A—O8A	1.407 (5)
C23—C24	1.358 (7)	Cl2A—O7A	1.431 (6)
C23—H23	0.9300	Cl2A—O5A	1.462 (5)
C24—C25	1.382 (7)	Cl1B—O3B	1.403 (9)
C24—H24	0.9300	Cl1B—O1B	1.422 (9)
C25—C26	1.388 (7)	Cl1B—O2B	1.423 (9)
C25—H25	0.9300	Cl1B—O4B	1.430 (9)
C26—C27	1.373 (6)	Cl2B—O8B	1.416 (10)
C26—H26	0.9300	Cl2B—O6B	1.430 (10)
C27—N4	1.347 (5)	Cl2B—O7B	1.435 (10)
C27—C28	1.481 (6)	Cl2B—O5B	1.452 (10)
N1—C1—C2	122.2 (5)	C31—C32—C33	124.2 (4)
N1—C1—H1	118.9	N6—C33—C34	121.8 (5)
C2—C1—H1	118.9	N6—C33—C32	114.7 (4)
C1—C2—C3	119.0 (5)	C34—C33—C32	123.5 (5)
C1—C2—H2	120.5	C33—C34—C35	119.3 (6)
C3—C2—H2	120.5	C33—C34—H34	120.3
C4—C3—C2	119.0 (5)	C35—C34—H34	120.3
C4—C3—H3	120.5	C36—C35—C34	119.8 (6)
C2—C3—H3	120.5	C36—C35—H35	120.1
C3—C4—C5	119.9 (5)	C34—C35—H35	120.1
C3—C4—H4	120.1	C35—C36—C37	118.2 (6)
C5—C4—H4	120.1	C35—C36—H36	120.9
N1—C5—C4	120.7 (4)	C37—C36—H36	120.9
N1—C5—C6	115.2 (4)	N6—C37—C36	123.1 (5)
C4—C5—C6	124.1 (5)	N6—C37—H37	118.4
N2—C6—C7	121.3 (4)	C36—C37—H37	118.4
N2—C6—C5	114.2 (4)	C39—C38—C43	117.6 (5)
C7—C6—C5	124.4 (4)	C39—C38—C30	119.7 (4)
C6—C7—C8	120.9 (5)	C43—C38—C30	122.7 (5)
C6—C7—H7	119.5	C38—C39—C40	120.7 (5)
C8—C7—H7	119.5	C38—C39—H39	119.6
C7—C8—C9	116.0 (4)	C40—C39—H39	119.6
C7—C8—C16	122.3 (5)	C41—C40—C39	121.9 (5)
C9—C8—C16	121.7 (5)	C41—C40—H40	119.0
C10—C9—C8	121.3 (4)	C39—C40—H40	119.0
C10—C9—H9	119.3	C40—C41—C42	117.0 (5)
C8—C9—H9	119.3	C40—C41—C44	121.1 (6)
N2—C10—C9	120.8 (4)	C42—C41—C44	121.9 (5)
N2—C10—C11	114.5 (4)	C43—C42—C41	121.6 (5)
C9—C10—C11	124.7 (4)	C43—C42—H42	119.2
N3—C11—C12	121.6 (4)	C41—C42—H42	119.2
N3—C11—C10	115.6 (4)	C42—C43—C38	121.1 (5)
C12—C11—C10	122.8 (4)	C42—C43—H43	119.5
C13—C12—C11	118.8 (5)	C38—C43—H43	119.5

C13—C12—H12	120.6	N2—Mn1—N5	169.82 (13)
C11—C12—H12	120.6	N2—Mn1—N1	72.13 (13)
C14—C13—C12	119.7 (5)	N5—Mn1—N1	117.65 (13)
C14—C13—H13	120.1	N2—Mn1—N4	111.21 (13)
C12—C13—H13	120.1	N5—Mn1—N4	72.26 (14)
C13—C14—C15	118.5 (5)	N1—Mn1—N4	94.00 (13)
C13—C14—H14	120.7	N2—Mn1—N6	105.07 (14)
C15—C14—H14	120.7	N5—Mn1—N6	72.12 (14)
N3—C15—C14	123.2 (5)	N1—Mn1—N6	96.33 (14)
N3—C15—H15	118.4	N4—Mn1—N6	143.71 (14)
C14—C15—H15	118.4	N2—Mn1—N3	72.32 (14)
C17—C16—C21	117.8 (5)	N5—Mn1—N3	98.07 (14)
C17—C16—C8	121.1 (5)	N1—Mn1—N3	144.22 (14)
C21—C16—C8	121.0 (6)	N4—Mn1—N3	94.98 (13)
C16—C17—C18	120.4 (6)	N6—Mn1—N3	96.61 (14)
C16—C17—H17	119.8	C5—N1—C1	119.2 (4)
C18—C17—H17	119.8	C5—N1—Mn1	118.0 (3)
C19—C18—C17	121.1 (6)	C1—N1—Mn1	122.5 (3)
C19—C18—H18	119.5	C6—N2—C10	119.5 (4)
C17—C18—H18	119.5	C6—N2—Mn1	120.0 (3)
C20—C19—C18	118.4 (6)	C10—N2—Mn1	120.4 (3)
C20—C19—C22	121.5 (7)	C15—N3—C11	118.1 (4)
C18—C19—C22	120.1 (7)	C15—N3—Mn1	124.6 (3)
C19—C20—C21	121.3 (7)	C11—N3—Mn1	117.3 (3)
C19—C20—H20	119.3	C27—N4—C23	118.2 (4)
C21—C20—H20	119.3	C27—N4—Mn1	117.6 (3)
C20—C21—C16	120.9 (7)	C23—N4—Mn1	124.2 (3)
C20—C21—H21	119.5	C28—N5—C32	119.6 (4)
C16—C21—H21	119.5	C28—N5—Mn1	119.5 (3)
N4—C23—C24	123.1 (5)	C32—N5—Mn1	120.5 (3)
N4—C23—H23	118.5	C37—N6—C33	117.7 (5)
C24—C23—H23	118.5	C37—N6—Mn1	123.9 (4)
C23—C24—C25	119.3 (5)	C33—N6—Mn1	118.3 (3)
C23—C24—H24	120.4	O2A—Cl1A—O3A	119.0 (8)
C25—C24—H24	120.4	O2A—Cl1A—O1A	114.9 (9)
C24—C25—C26	118.0 (5)	O3A—Cl1A—O1A	108.1 (7)
C24—C25—H25	121.0	O2A—Cl1A—O4A	109.7 (9)
C26—C25—H25	121.0	O3A—Cl1A—O4A	107.5 (8)
C27—C26—C25	120.0 (5)	O1A—Cl1A—O4A	94.8 (7)
C27—C26—H26	120.0	O6A—Cl2A—O8A	112.8 (5)
C25—C26—H26	120.0	O6A—Cl2A—O7A	109.8 (5)
N4—C27—C26	121.4 (4)	O8A—Cl2A—O7A	108.6 (5)
N4—C27—C28	115.0 (4)	O6A—Cl2A—O5A	107.1 (4)
C26—C27—C28	123.5 (4)	O8A—Cl2A—O5A	107.7 (4)
N5—C28—C29	120.9 (4)	O7A—Cl2A—O5A	111.0 (5)
N5—C28—C27	114.7 (4)	O3B—Cl1B—O1B	112.3 (12)
C29—C28—C27	124.4 (4)	O3B—Cl1B—O2B	104.1 (10)
C28—C29—C30	121.4 (4)	O1B—Cl1B—O2B	111.7 (8)
C28—C29—H29	119.3	O3B—Cl1B—O4B	112.2 (11)

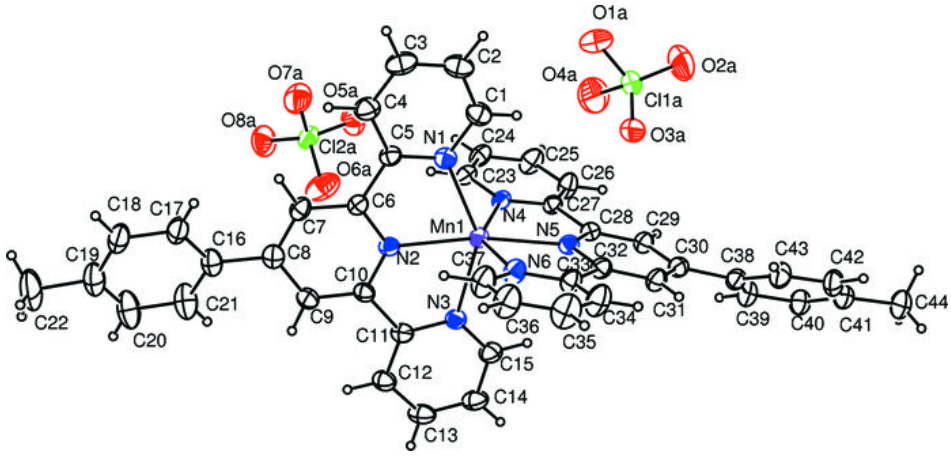
C30—C29—H29	119.3	O1B—Cl1B—O4B	108.3 (9)
C29—C30—C31	116.6 (4)	O2B—Cl1B—O4B	108.1 (10)
C29—C30—C38	121.1 (4)	O8B—Cl2B—O6B	108.5 (13)
C31—C30—C38	122.3 (4)	O8B—Cl2B—O7B	113.2 (13)
C32—C31—C30	119.6 (4)	O6B—Cl2B—O7B	110.5 (13)
C32—C31—H31	120.2	O8B—Cl2B—O5B	110.9 (14)
C30—C31—H31	120.2	O6B—Cl2B—O5B	106.9 (13)
N5—C32—C31	121.9 (4)	O7B—Cl2B—O5B	106.6 (13)
N5—C32—C33	113.9 (4)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···O3B	0.93	2.15	3.055 (15)	165
C3—H3···O6A^{i}	0.93	2.42	3.347 (9)	176
C13—H13···O5A^{ii}	0.93	2.52	3.400 (9)	158
C15—H15···O4B^{ii}	0.93	2.50	3.260 (16)	139
C22—H22C···O2B^{iii}	0.96	2.37	3.324 (14)	177
C23—H23···O6B	0.93	2.31	3.23 (2)	171
C34—H34···O3A^{iv}	0.93	2.55	3.458 (11)	167
C34—H34···O1B^{iv}	0.93	2.44	3.223 (12)	142
C37—H37···O8A^{v}	0.93	2.54	3.255 (9)	134
C37—H37···O7B^{v}	0.93	2.40	3.31 (2)	164
C39—H39···O2A^{ii}	0.93	2.49	3.341 (12)	152
C44—H44C···O8B^{vi}	0.96	2.41	3.30 (2)	153

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

Fig. 1


O1a
O2a
O4a
Cl1a
O3a
C3
C2
O7a
O5a
C4
C1
O8a
Cl2a
C5
N1
C24
C25
O6a
C23
C26
C6
N4
C27
C18
C17
C7
Mn1
N5
C28
C29
C19
C16
C8
N2
C37
N6
C33
C32
C30
C38
C43
C42
C10
C31
C34
C39
C40
C41
C44
C22
C21
C9
N3
C36
C35
C20
C11
C15
C12
C14
C13