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Tris(1,10-phenanthroline-$\kappa N,N'$)manganese(II) bis(perchlorate) chloroform disolvate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.008 Å
R factor = 0.073
wR factor = 0.205
Data-to-parameter ratio = 14.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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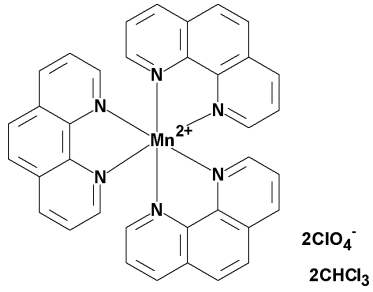
In the title compound, $[Mn(C_{12}H_8N_6)_3](ClO_4)_2\cdot 2CHCl_3$, the Mn^{II} ion is chelated by three 1,10-phenanthroline molecules in a twisted octahedral coordination geometry. In the crystal structure, there are intermolecular π–π interactions between adjacent phenanthroline rings.

Comment

There has been increasing interest in the mechanism of the racemization of tris-phenanthroline metal complexes in solid and solution phases (Gillard & Mitchell, 1988; Fujiwara & Yamamoto, 1980). In considering such mechanisms, a fundamental requirement is knowledge of the crystal structure. With these compounds, some basic information as to phase identification and a proper understanding of the role played by water in determining the structure have been reported (Gillard *et al.*, 1989). Here, we report the structure of the title complex, $[Mn(L)_3](ClO_4)_2\cdot 2CHCl_3$, (I), where L is 1,10-phenanthroline. This complex probably offers some useful information on the mechanism of the racemization of tris-phenanthroline metal complexes lacking water of crystallization.



(I)

X-ray structure analysis reveals that (I) is an ionic monomeric Mn^{II} complex (Fig. 1) with solvent chloroform molecules. The coordination geometry around the Mn^{II} centre is twisted (from trigonal prismatic towards regular octahedral) about the quasi-C_3 axis, approaching the octahedral extreme. The Mn—N bond distances lie in a narrow range from 2.277 (4) to 2.293 (3) Å.

In addition, there are π–π interactions between the centroids of adjacent phenanthroline rings. For *Cg*1 (the centroid of ring C16–C24) and *Cg*1*A* (ring C16*A*–C24*A*) [symmetry code (*A*): $-x$, $-y$, $1-z$], the centroid–centroid distance is 3.739 (3) Å and the dihedral angle is 18.41 (3)°. For *Cg*2 (C28–C36) and *Cg*2*B* (C28*B*–C36*B*) [symmetry code (*B*): $1-x$, $-y$, $-z$], the centroid–centroid distance is 3.758 (3) Å and the dihedral angle is 18.61 (3)°.

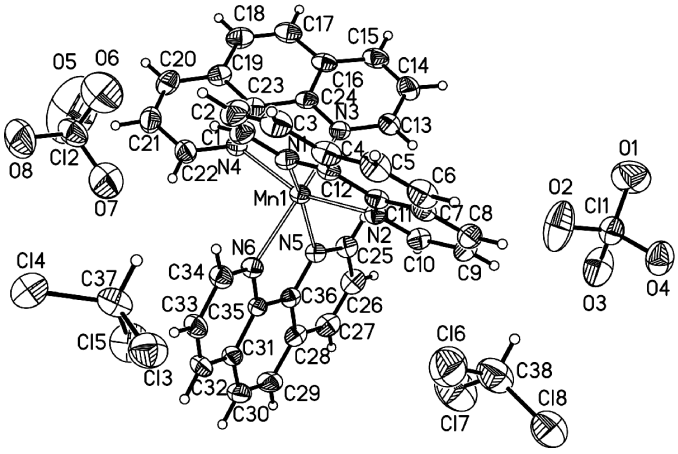


Figure 1
The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

Experimental

Complex (I) was prepared by reacting $Mn(ClO_4)_2\cdot 6H_2O$ (0.361 g, 1 mmol) and 1,10-phenanthroline (0.593 g, 3 mmol) in a methanol–chloroform (1:1) solution. The mixture was stirred at room temperature for 30 min and then filtered. Pale-yellow block crystals of (I) were obtained from the filtrate after 10 d. Yield 0.216 g, 21% (based on Mn).

Crystal data

$[Mn(C_{12}H_8N_6)_3](ClO_4)_2\cdot 2CHCl_3$
$M_r = 1033.19$
Triclinic, $P\overline{1}$
$a = 12.642$ (3) Å
$b = 12.987$ (3) Å
$c = 14.501$ (3) Å
$\alpha = 86.15$ (3)°
$\beta = 75.77$ (3)°
$\gamma = 70.17$ (3)°
$V = 2170.4$ (9) Å^3
$Z = 2$
$D_x = 1.581$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3351 reflections
$\theta = 6.7$–$54.2°$
$\mu = 0.86$ mm^{-1}
$T = 293$ (2) K
Block, yellow
0.28 × 0.28 × 0.26 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.796$, $T_{max} = 0.808$
13 078 measured reflections
7909 independent reflections
4953 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$
$\theta_{max} = 25.5°$
$h = -15 \rightarrow 15$
$k = -15 \rightarrow 15$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.073$
$wR(F^2) = 0.205$
$S = 1.00$
7909 reflections
550 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1288P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.67$ e Å^{-3}
$\Delta\rho_{min} = -0.64$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mn1—N1	2.292 (4)	Mn1—N4	2.277 (4)
Mn1—N2	2.284 (4)	Mn1—N5	2.293 (3)
Mn1—N3	2.291 (3)	Mn1—N6	2.282 (3)
N1—Mn1—N5	158.9 (1)	N4—Mn1—N3	73.4 (1)
N2—Mn1—N1	73.8 (1)	N4—Mn1—N5	102.5 (1)
N2—Mn1—N3	93.0 (1)	N4—Mn1—N6	99.2 (1)
N2—Mn1—N5	94.4 (1)	N6—Mn1—N1	91.3 (1)
N3—Mn1—N1	105.4 (1)	N6—Mn1—N2	98.3 (1)
N3—Mn1—N5	92.4 (1)	N6—Mn1—N3	162.0 (1)
N4—Mn1—N1	93.6 (1)	N6—Mn1—N5	72.8 (1)
N4—Mn1—N2	158.6 (1)		

All H atoms were placed in calculated positions and included in the final cycles of refinement in the riding model. For aromatic H atoms, C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. For chloroform H atoms, C—H = 0.98 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXL97*; software used to prepare material for publication: *SHELXL97*.

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