metal-organic papers

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Key indicators

A polymorph of cis-dichlorobis(phenanthroline-κ²N,N′)manganese(II)

In the title compound, [MnCl$_2$(C$_{12}$H$_8$N$_2$)$_2$], the Mn^{II} complex displays a distorted octahedral coordination geometry formed by two phenanthroline ligands and two Cl$^-$ anions. The crystal structure is different from that reported previously for the same compound [McCann, McCann, Casey, Jackman, Devereux & McKee (1998). *Inorg. Chim. Acta*, **279**, 24–29].

Comment

Recently, π–π stacking between aromatic rings has attracted much attention because it is correlated with the electron transfer process in some biological systems (Deisenhofer & Michel, 1989). As part of an ongoing investigation of π–π stacking in metal complexes, we tried to prepare a Mn^{II} complex of phenanthroline (phen) with thiodiacetate as the second ligand, but X-ray structure analysis showed that the product was the title complex, (I). A search of the Cambridge Structural Database (November 2003 update; Allen, 2002) indicated that the structure of the complex has been reported four times (Malinowski *et al.*, 1996; Zhou *et al.*, 1997; McCann *et al.*, 1998; Che *et al.*, 2001); all of these authors report essentially the same crystal structure. However, the crystal structure of (I) is different from those reported previously. We present here the structure of (I) to show the new crystalline form of this complex.

(I)
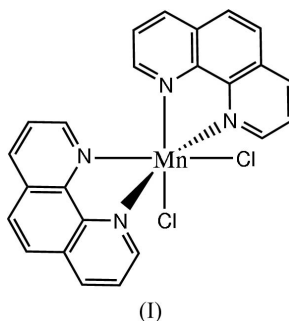
The structure of (I) is shown in Fig. 1. The Mn^{II} atom is coordinated by two phen ligands and two Cl$^-$ anions with a distorted octahedral geometry (Table 1). The Mn—N bond located in the *trans* position relative to the Mn—Cl bond is significantly longer than the other Mn—N bond to the same phen ligand. The dihedral angle between the two phen mean planes is 70.86 (6)°. The large Cl1—Mn—Cl2 bond angle of 102.97 (6)° may be a result of the repulsion between the neighboring Cl$^-$ anions.

The cell parameters and space group for (I) are different from those for the previously reported structures [*e.g.* a = 9.461 (5) Å, b = 15.200 (10) Å, c = 14.514 (2) Å, β = 98.82 (3)°,
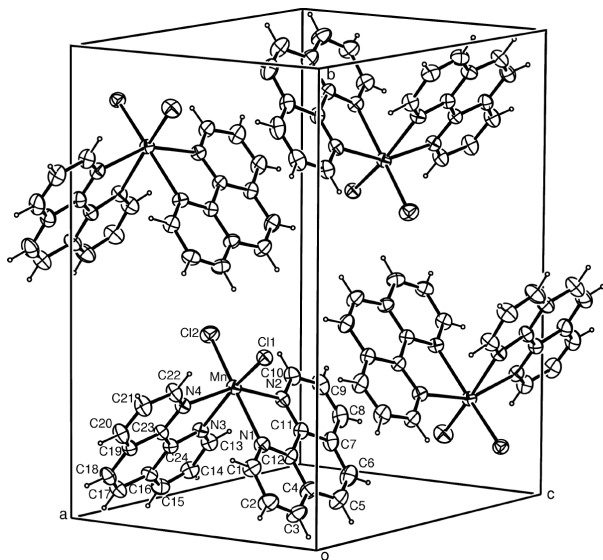
Figure 1
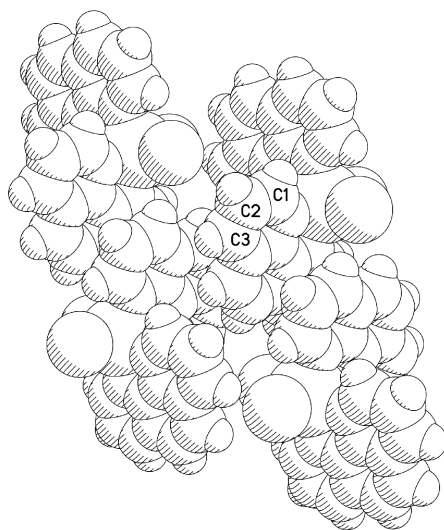The unit cell contents of (I). The atomic displacement ellipsoids are plotted at the 30% probability level.

Figure 2
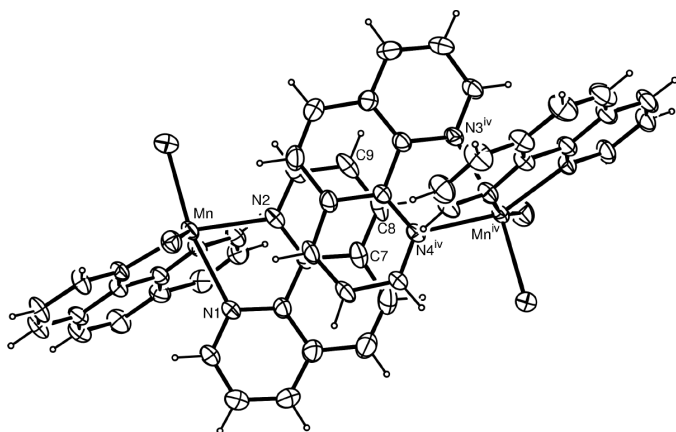A space filling model, showing the voids occurring in the crystal structure of (I).

Figure 3
A π–π stacking diagram. [Symmetry code: (iv) $x - \frac{1}{2}, \frac{1}{2} - y, z + \frac{1}{2}$].

$V = 2062.5$ (8) Å^3 and space group $P2_1/c$ at room temperature (Zhou *et al.*, 1997); $a = 9.420$ (1) Å, $b = 15.193$ (2) Å, $c = 14.354$ (2) Å, $\beta = 98.62$ (2)°, $V = 2031.1$ (5) Å^3 and space group $P2_1/c$ at 153 K (McCann *et al.*, 1998)]. The molecular packing (Fig. 1) is completely different from that observed in the previously reported structures.

A *PLATON* analysis (Spek, 2003) indicates that the crystal structure of (I) contains solvent-accessible voids at two locations in the unit cell, each with a volume of 31 Å^3, which is smaller than the expected volume of 40 Å^3 for a water molecule. The center of one void is located at $(\frac{1}{2}, 0, 0)$, and the distances to the neighboring non-H atoms are 2.93 (C2) and 3.20 Å (C1) (Fig. 2). The total void volume of 62 Å^3 is about 3% of the cell volume of (I). The voids lead to the larger cell volume and smaller crystal density for (I) compared with those for the previously reported structures [1.56 Mg m^{-3} at room temperature (Zhou *et al.*, 1997) and 1.59 Mg m^{-3} at 153 K (McCann *et al.*, 1998)].

There is an intermolecular C—H···Cl short contact (Table 2), and a parallel or nearly parallel arrangement between the neighboring phen rings is observed. The distance of 3.621 (11) Å between parallel N1-phen and N2^{iii}-phen planes suggests no π–π stacking between them [symmetry code: (iii) $1 - x, -y, 1 - z$]. However, overlapped displacement (Fig. 3) and a shorter centroid-to-centroid distance [of 3.594 (3) Å] are observed between nearly parallel N1-phen and N4^{iv}-phen rings [dihedral angle 3.96 (17)°; symmetry code: (iv) $x - \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$], and the distances of atoms C7, C8 and C9 from the N4^{iv}-phen plane are 3.402 (6)–3.448 (6) Å. These findings suggest π–π interaction between the N1-phen and N4^{iv}-phen rings.

Experimental

MnCl$_2$·2H$_2$O (0.16 g, 1 mmol) was dissolved in an aqueous solution (10 ml) containing thiodiacetic acid (0.15 g, 1 mmol) and NaOH (0.08 g, 2 mmol). The solution was refluxed for 10 min, then an ethanol solution (10 ml) of phen (0.36 g, 2 mmol) was added to the above solution with continuous stirring. The mixture was refluxed for a further 2 h. After cooling to room temperature, the solution was filtered. Yellow crystals of (I) were obtained from the filtrate after one week.

Crystal data

[MnCl$_2$(C$_{24}$H$_{16}$N$_4$)]	$D_x = 1.499$ Mg m^{-3}
$M_r = 486.25$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 8668
$a = 10.1597$ (18) Å	reflections
$b = 17.105$ (2) Å	$\theta = 2.5$–$24.0°$
$c = 12.593$ (2) Å	$\mu = 0.88$ mm^{-1}
$\beta = 100.178$ (4)°	$T = 295$ (2) K
$V = 2154.1$ (6) Å^3	Prism, yellow
$Z = 4$	$0.40 \times 0.21 \times 0.16$ mm

Data collection

Rigaku R-AXIS RAPID	3724 independent reflections
diffractometer	2669 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.095$
Absorption correction: multi-scan	$\theta_{max} = 25.0°$
(*ABSCOR*; Higashi, 1995)	$h = -12 \rightarrow 12$
$T_{min} = 0.700$, $T_{max} = 0.870$	$k = -20 \rightarrow 19$
10 079 measured reflections	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.132P)^2 + 1.1079P]$
$R[F^2 > 2\sigma(F^2)] = 0.075$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.221$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.04$	$\Delta\rho_{max} = 0.72$ e Å^{-3}
3724 reflections	$\Delta\rho_{min} = -0.61$ e Å^{-3}
280 parameters	Extinction correction: none
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Mn—Cl1	2.4804 (14)	Mn—N2	2.264 (4)
Mn—Cl2	2.4167 (15)	Mn—N3	2.355 (4)
Mn—N1	2.369 (4)	Mn—N4	2.259 (4)
Cl1—Mn—Cl2	102.97 (6)	N1—Mn—Cl2	165.27 (10)
N4—Mn—N2	151.63 (15)	N3—Mn—Cl1	160.51 (9)

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C15—H15⋯Cl1^i	0.93	2.69	3.616 (6)	175

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

H atoms were placed in calculated positions, with C—H = 0.93 Å, and included in the final cycles of refinement in riding mode, with $U_{iso}(H) = 1.2U_{eq}$(carrier atom).

Data collection: *PROCESS-AUTO* (Rigaku Corporation, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC & Rigaku Corporation, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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