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cis-Dichlorobis(4,5-diazafluoren-9-one-κ^2N,N')-manganese(II) ethanol solvate

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Key indicators

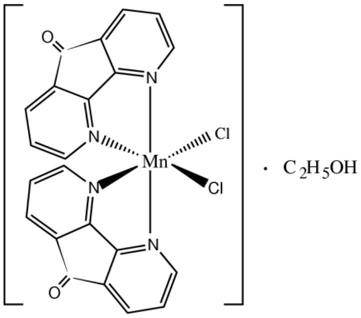
Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.004 Å
H-atom completeness 67%
Disorder in solvent or counterion
R factor = 0.030
wR factor = 0.073
Data-to-parameter ratio = 17.3

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

In the title compound, $[MnCl_2(C_{11}H_6N_2O)_2]\cdot C_2H_5OH$, the Mn atom is located on a twofold axis and chelated by two diazafluorenone (dafone) ligands. Two *cis* Cl^- anions coordinate to the Mn atom to complete the octahedral coordination. The long Mn—N bond distances [2.323 (2) and 2.445 (2) Å] observed may be due to the large N···N separation within dafone.

Comment

4,5-Diazafluoren-9-one (dafone) is structurally similar to 1,10-phenanthroline (phen) and has been used as a chelating reagent to prepare metal complexes. Some metal complexes with the chelating dafone ligand have been reported in the past decade (Menon & Rajasekharan, 1997; Wang *et al.*, 1995; Shi *et al.*, 1994). However, dafone does not usually chelate to a metal ion, as the longer N···N distance in dafone, relative to phen, reduces the overlap of metal–N atomic orbitals (Henderson *et al.*, 1984). Recently, we tried to prepare dafone-chelating complexes with metal ions such as Co^{II}, Fe^{II}, Cu^{I}, Zn^{II}, Hg^{II} and Mn^{II}, and found that the dafone molecule did not coordinate to the metal ion except in the title Mn^{II} complex, (I) (Wu *et al.*, 2002, 2004).



(I)

The molecular structure of (I) is illustrated in Fig. 1. The Mn^{II} atom is located on a twofold axis and has a distorted octahedral coordination geometry. While two Cl^- anions coordinate to the Mn^{II} atom in *cis* positions, two planar dafone ligands chelate to the Mn^{II} atom with their mean planes nearly perpendicular to each other [dihedral angle = 86.19 (4)°].

The molecular structure of the dafone complex is similar to a phen complex, dichlorobis(phenanthroline)manganese(II), which was determined at room temperature by Zhou *et al.* (1997) and at 153 K by McCann *et al.* (1998). The Mn—Cl bond of 2.4257 (7) Å in this complex is shorter than the values of 2.4470 (14) (McCann *et al.*, 1998) and 2.4426 (16) Å (Zhou *et al.*, 1997) in the phen complex; however, the average Mn—N(dafone) bond distance [2.384 (2) Å] is appreciably longer

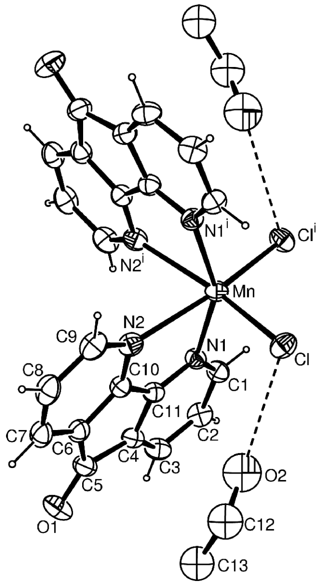


Figure 1
The molecular structure of (I), with 30% probability displacement ellipsoids. Only one component of the disordered ethanol molecule is shown. Dashed lines indicate hydrogen bonds. [Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.]

than the average Mn—N(phen) bond distance [2.323 (4) (McCann *et al.*, 1998) and 2.323 (5) Å (Zhou *et al.*, 1997)]. This may indicate the poor overlap of metal–nitrogen orbitals in this dafone-chelating complex.

The N···N distance of 2.933 (3) Å in the dafone complex is much longer than the N···N distances of 2.713 (3) and 2.711 (5) Å found in the above phen complex and may explain the longer Mn—N(dafone) bonds. On the other hand, the N···N distance of 2.933 (3) Å is significantly shorter than the values of 3.075 (4) and 3.064 (4) Å found in crystal structures containing uncoordinated dafone (Wu *et al.*, 2002, 2004). This may suggest a constraint in the chelating dafone ring and indicate the weaker chelating ability of dafone than phen.

Experimental

Dafone was prepared according to a previously reported method (Henderson *et al.*, 1984). $MnCl_2{\cdot}4H_2O$ (0.050 g, 0.25 mmol), thiourea (0.038 g, 0.5 mmol) and dafone (0.091 g, 0.5 mmol) were dissolved in absolute ethanol (15 ml). The solution was refluxed for 4 h and filtered. Absolute ethanol (5 ml) was then added to the filtrate. The solution was kept in a thermostat at 318 K. Yellow crystals were obtained after 2 d. Analysis calculated for $C_{24}H_{18}Cl_2MnN_4O_3$: C 53.75, H 3.38, N 10.45%; found: C 53.33, H 3.46, N 10.28%.

Crystal data

$[MnCl_2(C_{11}H_6N_2O)_2]{\cdot}C_2H_6O$
$M_r = 530.26$
Orthorhombic, $C222_1$
$a = 7.7376$ (2) Å
$b = 13.5917$ (4) Å
$c = 22.3338$ (8) Å
$V = 2348.78$ (12) Å^3
$Z = 4$
$D_x = 1.517$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 20 reflections
$\theta = 3.5$–8.8°
$\mu = 0.82$ mm^{-1}
$T = 295$ (2) K
Prism, yellow
0.46 × 0.42 × 0.36 mm

Data collection

Rigaku AFC-7*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.685$, $T_{\max} = 0.735$
2649 measured reflections
2649 independent reflections
2161 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 27.4°$
$h = -9 \rightarrow 10$
$k = -16 \rightarrow 17$
$l = -28 \rightarrow 28$
3 standard reflections every 150 reflections intensity decay: 0.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.073$
$S = 0.99$
2649 reflections
153 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0364P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.33$ e Å^{-3}
$\Delta\rho_{\min} = -0.20$ e Å^{-3}
Absolute structure: Flack (1983); 1136 Friedel pairs
Flack parameter = 0.02 (3)

Table 1
Selected geometric parameters (Å, °).

Mn—N1	2.323 (2)	Mn—N2	2.445 (2)
Mn—Cl	2.4257 (7)		
N1—Mn—N1^i	154.42 (9)	Cl^i—Mn—N2	164.27 (5)
N1—Mn—Cl^i	93.38 (5)	Cl—Mn—N2	90.37 (5)
N1—Mn—Cl	102.46 (5)	N1—Mn—N2^i	84.22 (7)
Cl^i—Mn—Cl	103.29 (3)	N2—Mn—N2^i	77.34 (10)
N1—Mn—N2	75.82 (7)		

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

The ethanol solvent molecule is disordered over a crystallographic twofold axis and its atoms were isotropically refined, but its H atoms were not located. H atoms on dafone were placed in calculated positions, with C—H = 0.93 Å, and were included in the final cycles of refinement in riding mode, with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$ of the carrier atoms.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1985); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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References

Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Henderson, L. J. Jr, Fronczek, F. R. & Cherry, W. R. (1984). *J. Am. Chem. Soc.* **106**, 5876–5879.
McCann, S., McCann, M., Casey, M. T., Jackman, M., Devereux, M. & McKee, V. (1998). *Inorg. Chim. Acta*, **279**, 24–28.
Menon, S. & Rajasekharan, M. V. (1997). *Inorg. Chem.* **36**, 4983–4987.
Molecular Structure Corporation (1985). *TEXSAN*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1992). *MSC/AFC Diffractometer Control Software*. Version 5.32. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Shi, X.-H., You, X.-Z., Li, C., Xiong, R.-G. & Yu, K.-B. (1994). *Transition Met. Chem.* **20**, 191–194.

Wang, Y.-X., Jackman, D. C., Woods, C. & Rillema, D. P. (1995). *J. Chem. Crystallogr.* **25**, 549–553.

Wu, Z.-Y., Xu, D.-J., Wu, J.-Y. & Chiang, M. Y. (2002). *Acta Cryst.* C**58**, m374–m376.

Wu, Z.-Y., Xu, D.-J. & Yin, K.-L. (2004). *Acta Cryst.* E**60**, m514–m516.

Zhou, K.-J., Zhang, C.-G., Xu, D.-J. & Xu, Y.-Z. (1997). *Chin. J. Struct. Chem.* **16**, 20–23.