metal-organic compounds

trans-Bis(cyano-κC)(1,4,8,11-tetraaza-cyclotetradecane-$\kappa^4 N$)manganese(III) perchlorate, a low-spin manganese(III) complex

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The crystal structure of the low-spin ($S = 1$) Mn[III] complex [Mn(CN)$_2$(C$_{10}$H$_{24}$N$_4$)]ClO$_4$, or *trans*-[Mn(CN)$_2$(cyclam)]-(ClO$_4$) (cyclam is the tetradentate amine ligand 1,4,8,11-tetraazacyclotetradecane), is reported. The structural parameters in the Mn(cyclam) moiety are found to be insensitive to both the spin and the oxidation state of the Mn ion. The difference between high- and low-spin Mn[III] complexes is that a pronounced tetragonal elongation of the coordination octahedron occurs in high-spin complexes and a slight tetragonal compression is seen in low-spin complexes, as in the title complex.

Comment

Few low-spin Mn[III] complexes are known; the classic examples are hexacyanomanganate (Griffith, 1975) and the related [(CN)$_5$MnOMn(CN)$_5$]$^{6-}$ complex anion (Ziolo *et al.*, 1974). Other known low-spin Mn[III] complexes are those with anionic organic ligands (Basu & Chakravorty, 1992; Ganguly *et al.*, 1997), and Mn[III] complexes of negatively charged porphyrin,

(I)
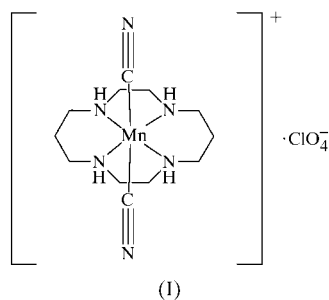
phthalocyanine and salen [salen is bis(salicylidene)imine] ligands with axially coordinated cyanide or imidazolate (Hansen & Goff, 1984; Landrum *et al.*, 1980; Matsumoto *et al.*,

1999; Sievertsen *et al.*, 1993), which have an equatorial coordination similar to the title compound, (I).

Compound (I) was first synthesized and characterized magnetically by Daugherty *et al.* (1991), but no structure was reported. The magnetic measurements showed that Mn in (I) is in a low-spin ground state. All other known monomeric Mn[III]–cyclam complexes are high-spin (Daugherty *et al.*, 1991; Mossin, Weihe, Glerup, Sørensen & Søtofte, 2002; Chan & Poon, 1976). Since good quality crystals of (I) have now been obtained, a structural comparison of this low-spin *trans*-Mn[III]–cyclam complex with the previously reported high-spin *trans*-Mn[III]–cyclam complexes can be performed.

In (I), the six metal–ligand distances are Mn—N 2.025 (4)–2.033 (3) Å and Mn—C 2.004 (4)–2.010 (4) Å, corresponding to a slightly tetragonally compressed octahedron. This indicates a low-spin $S = 1$ ground state, in agreement with the magnetic measurements of Daugherty *et al.* (1991). The cyclam ligand prefers the energetically most favourable conformation, which is denoted *trans*(III) by Bosnich *et al.* (1965). The cyanide groups are not coordinated linearly to Mn but are slightly bent, with Mn—C—N angles close to 176°.

The other Mn[III]–cyclam complexes are, as noted above, high-spin d^4 systems ($S = 2$). The Mn—N$_{cyclam}$ distances [2.03 (1) Å] and the N—Mn—N angles [94 (1) and 86 (1)°] found in the high-spin complexes are the same as in the low-spin complex, (I), to within two s.u.'s. The axial Mn–ligand distances in the high-spin complexes (Daugherty *et al.*, 1991; Mossin, Weihe, Glerup, Sørensen & Søtofte, 2002; Létumier *et al.*, 1998; Meyer *et al.*, 1998) are all considerably longer than the equatorial distances, leading to a pronounced tetragonal elongation of these complexes (Table 3).
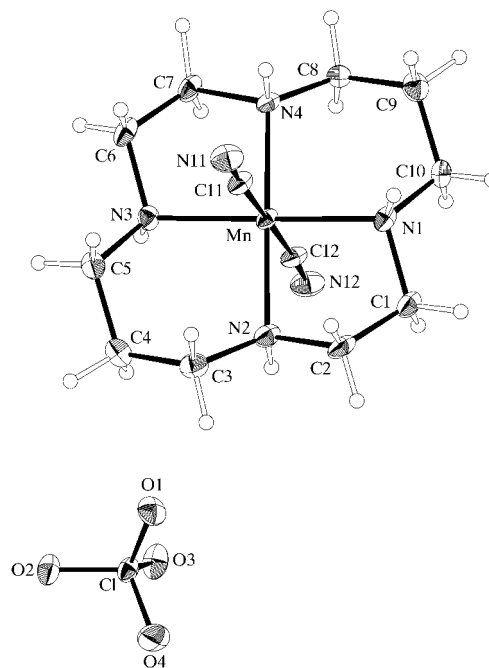

Figure 1
A view of the molecular structure of (I) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

The geometric parameters in the Mn(cyclam) moiety of (I) are not only rather insensitive to the spin state of the central Mn ion, but also to the oxidation state of Mn. This is seen by comparison with cyclam complexes of Mn in other oxidation states (IV or V; Mossin, Weihe, Glerup & Sørensen, 2002; Meyer *et al.*, 1998).

The reported Mn–ligand distances in (I) are in agreement with the findings for other monomeric low-spin Mn^{III} complexes, which are in the range 1.91–2.02 Å. We observe a slight tetragonal compression in (I), as occurs in two of the three monomeric low-spin Mn^{III} complexes (Table 3). It is not possible to distinguish the axial and equatorial Mn–ligand distances in the last complex in Table 3, *i.e. trans*-[Mn(tpp)(CN)$_2$]$^-$ (tpp is tetraphenylporphyrin), because of the high s.u. values.

The fact that compound (I), which is not a chiral species, crystallizes in the non-centrosymmetric space group $P2_12_12_1$ can be explained by the stabilization of the crystal packing *via* an extended hydrogen-bond pattern in two directions. The N4—H4N···N12 and N2—H2N···N11 hydrogen bonds stabilize the packing of the cations along the *a* axis. Furthermore, two weaker hydrogen bonds are found, linking the cations and perchlorate anions along the *c* axis. Hydrogen-bond distances are given in Table 2.

Experimental

trans-[Mn(cyclam)(H$_2$O)$_2$](CF$_3$SO$_3$)$_3$·H$_2$O was prepared according to the method of Mossin, Weihe, Glerup, Sørensen & Søtofte (2002) and was dissolved (50 mg) in acetonitrile (1 ml) in a 3 ml test tube. NaCN (6 mg) and NaClO$_4$·H$_2$O (15 mg) were dissolved in water (0.5 ml) and the aqueous solution was added very carefully to the bottom of the test tube using a glass pipette. A few crystals of (I) appeared at the water–acetonitrile junction within 20 min. The crystals were removed using a pipette, placed on filter paper and air dried.

Crystal data

[Mn(CN)$_2$(C$_{10}$H$_{24}$N$_4$)]ClO$_4$
$M_r = 406.76$
Orthorhombic, $P2_12_12_1$
$a = 6.7599\ (3)$ Å
$b = 13.3609\ (8)$ Å
$c = 19.0240\ (5)$ Å
$V = 1718.22\ (14)$ Å^3
$Z = 4$
$D_x = 1.572$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 474 reflections
$\theta = 4.4$–$31.0°$
$\mu = 0.95$ mm^{-1}
$T = 122\ (1)$ K
Needle, yellow
$0.22 \times 0.08 \times 0.04$ mm

Table 1
Selected geometric parameters (Å, °).

Mn—C11	2.010 (4)	Mn—N3	2.033 (3)
Mn—C12	2.004 (4)	Mn—N4	2.025 (4)
Mn—N1	2.029 (3)	C11—N11	1.154 (6)
Mn—N2	2.029 (4)	C12—N12	1.154 (6)
C11—Mn—N1	89.19 (16)	N1—Mn—N2	86.42 (15)
C11—Mn—N2	90.68 (17)	N1—Mn—N3	179.32 (15)
C11—Mn—N3	90.62 (16)	N2—Mn—N3	94.24 (15)
C11—Mn—N4	89.73 (16)	N4—Mn—N1	93.18 (14)
C12—Mn—C11	178.88 (19)	N4—Mn—N3	179.43 (17)
C12—Mn—N1	90.86 (16)	N4—Mn—N3	86.16 (14)
C12—Mn—N2	88.21 (16)	N11—C11—Mn	175.9 (4)
C12—Mn—N3	89.35 (16)	N12—C12—Mn	175.7 (4)
C12—Mn—N4	91.39 (16)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N···O2^i	0.92 (5)	2.24 (6)	3.078 (5)	151 (5)
N2—H2N···N11^{ii}	0.90 (6)	2.13 (6)	2.961 (6)	153 (5)
N3—H3N···O4	0.84 (6)	2.21 (6)	2.999 (5)	155 (5)
N4—H4N···N12^{iii}	0.98 (6)	2.03 (6)	2.938 (5)	152 (5)

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

Table 3
Comparison of structural parameters for a selection of Mn(cyclam) complexes (Å).

L_{eq} denotes the four equatorial ligands and L_{ax} the two axial ligands in a tetragonally distorted octahedron. Uncertainties for the averaged Mn—L distances are given as root-mean-square deviations (r.m.s.d.). If only a single parameter is available or the s.u. is larger than the r.m.s.d., the s.u. is given.

Complex	Spin state	Ligating atoms	Average Mn—L_{eq}	Average Mn—L_{ax}
trans-[Mn(cyclam)(CN)$_2$]$^{+\ a}$	ls	4 N, 2 C	2.029 (4)	2.007 (4)
trans-[Mn(cyclam)Cl$_2$]$^{+\ b,c}$	hs	4 N, 2 Cl	2.035 (3)	2.527 (1)
trans-[Mn(cyclam)Br$_2$]$^{+\ b}$	hs	4 N, 2 Br	2.029 (6)	2.689 (1)
trans-[Mn(cyclam)I$_2$]$^{+\ d}$	hs	4 N, 2 I	2.028 (2)	2.9416 (2)
trans-[Mn(cyclam)(NCS)$_2$]$^{+\ b}$	hs	6 N	2.038 (4)	2.166 (17)
trans-[Mn(cyclam)(NO$_3$)$_2$]$^{+\ b}$	hs	4 N, 2 O	2.036 (7)	2.221 (4)
trans-[Mn(cyclam)(N$_3$)$_2$]$^{+\ e}$	hs	6 N	2.041 (3)	2.175 (3)
[Mn(CN)$_6$]$^{3-\ f}$	ls	6 C	2.024 (2)	2.013 (2)
[Mn(PhL)$_2$]$^{-\ g}$	ls	4 N, 2 O	1.940 (15)	1.906 (7)
trans-[Mn(tpp)(CN)$_2$]$^{-\ h}$	ls	4 N, 2 C	2.00 (2)	2.02 (2)

Notes: (a) present work; (b) Daugherty *et al.* (1991); (c) Létumier *et al.* (1998); (d) Mossin, Weihe, Glerup, Sørensen & Søtofte (2002); (e) Meyer *et al.* (1998); (f) Buschmann *et al.* (1999); (g) PhL is [(2-carboxylatophenyl)azo]benzaldoxime, Ganguly *et al.* (1997); (h) Galich *et al.* (1998).

Data collection

Nonius KappaCCD area-detector diffractometer
ω and φ scans
Absorption correction: by integration (Coppens, 1970)
  $T_{min} = 0.840$, $T_{max} = 0.967$
39 637 measured reflections

2897 independent reflections (plus 2180 Friedel-related reflections)
4366 reflections with $I > 2\sigma(I)$
$R_{int} = 0.064$
$\theta_{max} = 30.3°$
$h = -9 \rightarrow 9$
$k = -18 \rightarrow 18$
$l = -26 \rightarrow 26$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.159$
$S = 1.07$
5077 reflections
290 parameters
Only coordinates of H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.0705P)^2 + 5.3702P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.51$ e Å^{-3}
$\Delta\rho_{min} = -0.94$ e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = 0.57 (3)

Space group $P2_12_12_1$ was determined from the analysis of the systematically absent reflections. H atoms were found in a difference Fourier map and were included in the refinement with their isotropic displacement parameters constrained to $1.2U_{eq}$ of the parent atom. All atomic positions were refined freely; the C—H distances were in the range 0.89 (6)–1.06 (6) Å and the N—H distances in the range 0.84 (6)–0.98 (6) Å. Refinement of the Flack parameter (Flack, 1983) showed that the crystal was a racemic twin (Flack & Bernardinelli, 1999), with a twin fraction of 0.57 (3).

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DIRAX* (Duisenberg, 1992); data reduction: *EvalCCD* (Duisenberg, 1998) and *DREAD* (Blessing, 1987); program(s) used to solve

metal-organic compounds

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.

Basu, P. & Chakravorty, A. (1992). *Inorg. Chem.* **31**, 4980–4986.

Blessing, R. H. (1987). *Crystallogr. Rev.* **1**, 3–58.

Bosnich, B., Poon, C. K. & Tobe, M. L. (1965). *Inorg. Chem.* **4**, 1102–1108.

Buschmann, W. E., Liable-Sands, L., Rheingold, A. L. & Miller, J. S. (1999). *Inorg. Chim. Acta*, **284**, 175–179.

Chan, P.-K. & Poon, C.-K. (1976). *J. Chem. Soc. Dalton Trans.* pp. 858–862.

Coppens, P. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 255–270. Copenhagen: Munksgaard.

Daugherty, P. A., Glerup, J., Goodson, P. A., Hodgson, D. J. & Michelsen, K. (1991). *Acta Chem. Scand.* **45**, 244–253.

Duisenberg, A. J. M. (1992). *J. Appl. Cryst.* **25**, 92–96.

Duisenberg, A. J. M. (1998). PhD thesis, University of Utrecht, The Netherlands.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Flack, H. D. & Bernardinelli, G. (1999). *Acta Cryst.* A**55**, 908–915.

Galich, L., Häckstädt, H. & Homborg, H. J. (1998). *Porphyrins Phthalocyanines*, **2**, 79–87.

Ganguly, S., Karmakar, S. & Chakravorty, A. (1997). *Inorg. Chem.* **36**, 116–118.

Griffith, W. P. (1975). *Coord. Chem. Rev.* **17**, 177–247.

Hansen, A. P. & Goff, H. M. (1984). *Inorg. Chem.* **23**, 4519–4525.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Landrum, J. T., Hatano, K., Scheidt, R. & Reed, C. A. (1980). *J. Am. Chem. Soc.* **102**, 6729–6735.

Létumier, F., Broeker, G., Barbe, J., Guilard, R., Lucas, D., Dahaoui-Gindrey, V., Lecomte, C., Thouin, L. & Amatore, C. (1998). *J. Chem. Soc. Dalton Trans.* pp. 2233–2239.

Matsumoto, N., Sunatsuki, Y., Miyasaka, H., Hashimoto, Y., Luneau, D. & Tuchagues, J.-P. (1999). *Angew. Chem. Int. Ed.* **38**, 171–173.

Meyer, K., Bendix, J., Metzler-Nolte, N., Weyhermüller, T. & Wieghardt, K. (1998). *J. Am. Chem. Soc.* **120**, 7260–7270.

Mossin, S., Weihe, H., Glerup, J. & Sørensen, H. O. (2002). In preparation.

Mossin, S., Weihe, H., Glerup, J., Sørensen, H. O. & Søtofte, I. (2002). In preparation.

Nonius (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.

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

Sievertsen, S., Grunewald, H. & Homborg, H. (1993). *Z. Anorg. Allg. Chem.* **619**, 1729–1737.

Ziolo, R. F., Stanford, R. H., Rossman, G. R. & Gray, H. B. (1974). *J. Am. Chem. Soc.* **96**, 7910–7915.