

Di- μ -oxido-bis{bis[*N,N'*-bis(2-pyridylmethyl)ethane-1,2-diamine]manganese(III,IV)} tris(perchlorate) hexahydrate: clarification of an order–disorder phase transition

Anne Nielsen, Christine J. McKenzie and Andrew D. Bond*

Department of Physics and Chemistry, University of Southern Denmark, Campusvej 55, 5230 Odense, Denmark

Correspondence e-mail: adb@chem.sdu.dk

Received 25 September 2009

Accepted 14 October 2009

Online 24 October 2009

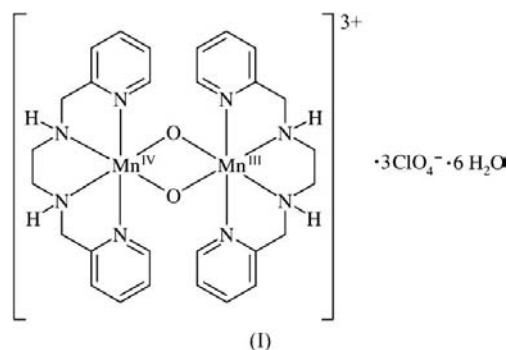
The title compound, $[\text{Mn}_2\text{O}_2(\text{C}_{14}\text{H}_{18}\text{N}_4)_2](\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$, contains a mixed-valent $\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}$ complex. In accordance with a previous report [Collins, Hodgson, Michelsen & Towle (1987). *J. Chem. Soc. Chem. Commun.* pp. 1659–1660], the structure at 295 K is best described in the space group $C2/c$, with the complex exhibiting twofold rotational symmetry, and with half site occupancy for one perchlorate anion and several solvent water molecules. At 180 K, the structure is ordered in the subgroup $P2_1/n$ and is clearly shown to be a hexahydrate, rather than the previously reported trihydrate. The origin of the order–disorder phase transition lies in the thermal motion of the perchlorate anions.

Comment

The crystal structure of the title compound, (I), at 295 K has been reported previously (Collins *et al.*, 1987). The compound was described as a trihydrate in the space group $C2/c$, with the $\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}$ complex lying on a twofold rotation axis passing through both of its Mn atoms. In that description, one perchlorate anion and one solvent water molecule have half site occupancy, which prompted Collins *et al.* to comment that there must be either ‘significant thermal motion or some disorder’ in the crystal structure. We have synthesized (I) in the course of our research on dinuclear Mn complexes (see, for example, Poulsen *et al.*, 2005) and have observed that the compound undergoes an order–disorder phase transition, adopting an ordered structure in the subgroup $P2_1/n$ at 180 K.

In the $P2_1/n$ description (referred to hereinafter as the LT structure), the $\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}$ complexes (Fig. 1) are sited on general positions and each perchlorate anion is fully occupied, although one exhibits rotational disorder typical for this pseudo-spherical anion. Six solvent water molecules are

clearly evident per formula unit, so that (I) should be described as a hexahydrate rather than as a trihydrate. In the $C2/c$ description (referred to hereinafter as the HT structure), the additional crystallographic twofold axes (running parallel to b) pass through both Mn atoms of each $\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}$ complex. The primitive lattice of the LT structure is indicated unambiguously by the X-ray data at 180 K, with 2388 out of 4520 unique $h+k$ odd reflections observed at the $3\sigma(I)$ level. For the same crystal at 295 K, only 98 such reflections are observed [mean $I/\sigma(I) = 0.6$], indicating that the $C2/c$ structure is appropriate at room temperature.



The origin of the disorder in the HT structure is clarified by comparison with the LT structure. The $\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}$ complexes are essentially indistinguishable at the two temperatures (Fig. 2), *i.e.* the complex maintains twofold rotational symmetry in the LT structure, but the twofold rotation axes are not operators of the $P2_1/n$ space group. The perchlorate anions containing atoms C11 and C12 in the LT structure correspond to atoms C12ⁱ and C12 in the HT structure

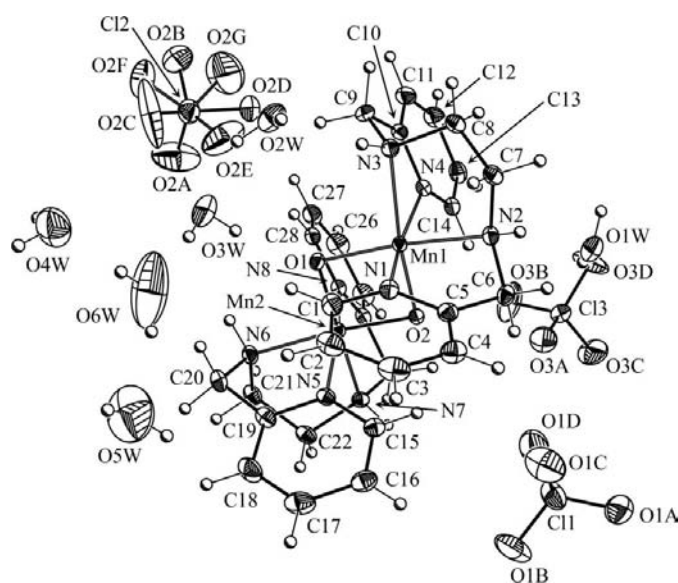


Figure 1

The asymmetric unit in the LT 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.

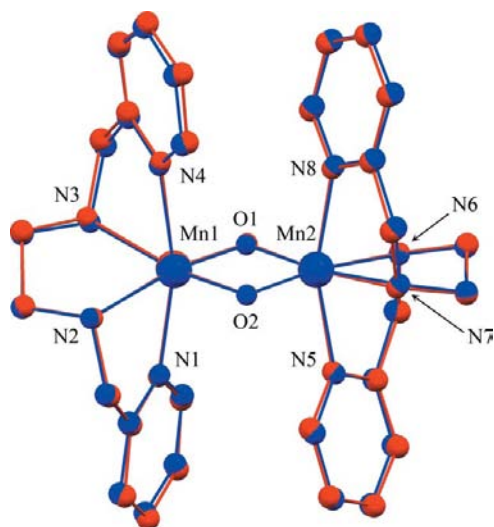


Figure 2
Least-squares overlay of the Mn^{III}/Mn^{IV} complexes in the LT (dark; blue in the electronic version of the paper) and HT (light; red in the electronic version of the paper) structures. The r.m.s. deviation is 0.10 Å for overlay of all 40 non-H atoms. Atom labels refer to the LT structure.

[symmetry code: (i) $-x + 1, y, -z + \frac{1}{2}$; Fig. 3]. The anion containing atom Cl3 in the LT structure corresponds to atom Cl3 in the HT structure. However, the symmetry-generated atom Cl3ⁱ in the HT structure has no corresponding anion in the LT structure. Hence, the perchlorate anion containing atom Cl3 must have half-occupancy in the $C2/c$ description.

In their work, Collins *et al.* (1987) located only some of the solvent water molecules. Atoms O1W and O2W in the LT structure correspond to the full-occupancy water molecule in the Collins HT structure, while atom O5W in the LT structure corresponds to the half-occupancy water molecule. The remainder of the solvent water molecules are situated around the site of the 'missing' perchlorate anion in the LT structure [close to (0.254, 0.310, 0.399)], which would correspond to the site of atom Cl3ⁱ in the HT structure. Thus, these water molecules appear in the asymmetric unit of the HT structure as partial atoms in the vicinity of the perchlorate anion containing atom Cl3. Under these circumstances, it is understandable that they were not included by Collins *et al.* In our 295 K data, all of the O atoms identified in the LT structure are evident in difference Fourier maps, with the exception of atom O6W, which lies close to the Cl3—O3B bond (*ca* 0.7 Å from atom Cl3; Fig. 3). We note, however, that our interpretation of the HT Fourier maps to identify these water molecules could only be made with knowledge of the LT structure. The positions of the solvent water molecules in the final refined HT structure closely resemble those in the LT structure, suggesting that the O—H...O hydrogen-bond network (Table 1) remains comparable at 180 and 295 K.

As implied by the statement of Collins *et al.* (1987), averaging of the LT structure to give the HT structure could in principle originate from static disorder of perchlorate anion Cl3 and several of the water molecules. However, the fact that the same single crystal displays the order–disorder transition,

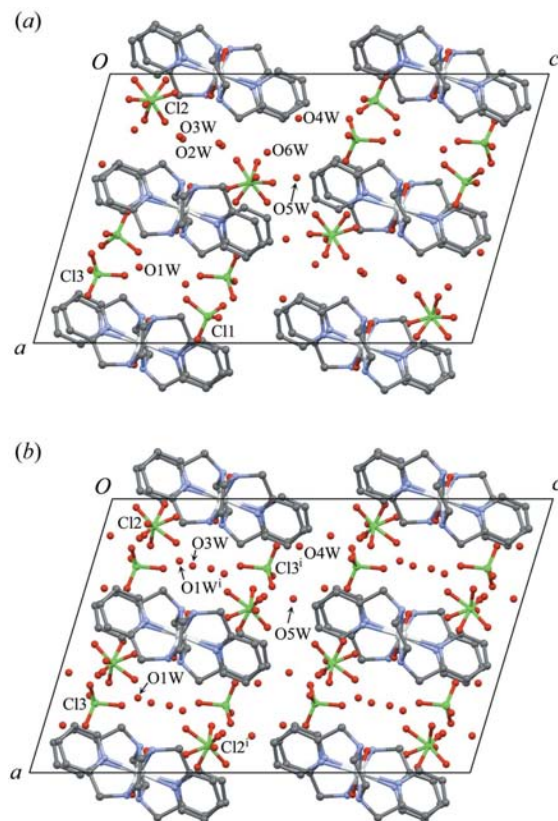


Figure 3
Unit-cell contents, viewed along the *b* axis, showing the correspondence between (a) the LT structure and (b) the HT structure. The LT structure is fully ordered. In the HT structure, perchlorate anion Cl3 and water molecules O3W, O4W and O5W have half site occupancy. H atoms have been omitted for clarity. [Symmetry code: (i) $-x + 1, y, -z + \frac{1}{2}$]

and that it is reversible, shows that the averaging must be a result of thermal motion. Since the geometry of the Mn^{III}/Mn^{IV} complex does not change significantly from 180 to 295 K, and the positions of the solvent water molecules also appear to be comparable at the two temperatures, the significant factor must be the thermal motion of the perchlorate anions. For the anions containing atoms Cl1 and Cl2, which are inequivalent in the LT structure but become equivalent in the HT structure, the movement required for this is very slight. The most important group in the system is the perchlorate anion containing atom Cl3. In principle, this continues to break the $C2/c$ symmetry in the HT structure, but its influence is apparently diminished by the scattering contributions of solvent water molecules O3W, O4W, O5W and O6W in the symmetry-related site near to (0.254, 0.310, 0.399). At 180 K, the difference between these two sites is detectable. At 295 K, where the thermal motion of both the perchlorate anions and the solvent water molecules is greater, the sites appear from the X-ray data to be effectively equivalent.

Experimental

N,N'-Di-2-picolylethylenediamine (bispicene) was prepared according to literature procedures (Glerup *et al.*, 1994; Goodwin & Lions, 1960). Manganese(II) perchlorate hexahydrate (747 mg, 2 mmol) in

water (1 ml) was then added to bispicene (501 mg, 2 mmol) in water (2 ml). The initially pale-yellow solution turned green, and black crystals of (I) were deposited overnight.

Compound (I) at 180 K

Crystal data

$[\text{Mn}_2\text{O}_2(\text{C}_{14}\text{H}_{18}\text{N}_4)_2](\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$	$V = 4207.4 (5) \text{ \AA}^3$
$M_r = 1032.97$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 15.1204 (9) \text{ \AA}$	$\mu = 0.88 \text{ mm}^{-1}$
$b = 12.2337 (7) \text{ \AA}$	$T = 180 \text{ K}$
$c = 23.6514 (16) \text{ \AA}$	$0.25 \times 0.20 \times 0.05 \text{ mm}$
$\beta = 105.912 (2)^\circ$	

Data collection

Bruker–Nonius X8 APEXII CCD area-detector diffractometer	82186 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	8600 independent reflections
$T_{\min} = 0.874$, $T_{\max} = 0.957$	6203 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.036$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.051$	57 restraints
$wR(F^2) = 0.158$	H-atom parameters constrained
$S = 1.09$	$\Delta\rho_{\text{max}} = 1.19 \text{ e \AA}^{-3}$
8600 reflections	$\Delta\rho_{\text{min}} = -0.83 \text{ e \AA}^{-3}$
578 parameters	

Compound (I) at 295 K

Crystal data

$[\text{Mn}_2\text{O}_2(\text{C}_{14}\text{H}_{18}\text{N}_4)_2](\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$	$V = 4312.1 (3) \text{ \AA}^3$
$M_r = 1032.97$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 15.4488 (7) \text{ \AA}$	$\mu = 0.86 \text{ mm}^{-1}$
$b = 12.2792 (5) \text{ \AA}$	$T = 295 \text{ K}$
$c = 23.7512 (10) \text{ \AA}$	$0.25 \times 0.20 \times 0.05 \text{ mm}$
$\beta = 106.852 (2)^\circ$	

Data collection

Bruker–Nonius X8 APEXII CCD area-detector diffractometer	34341 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	4424 independent reflections
$T_{\min} = 0.832$, $T_{\max} = 0.958$	3026 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.069$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.067$	30 restraints
$wR(F^2) = 0.235$	H-atom parameters constrained
$S = 1.07$	$\Delta\rho_{\text{max}} = 0.92 \text{ e \AA}^{-3}$
4424 reflections	$\Delta\rho_{\text{min}} = -0.70 \text{ e \AA}^{-3}$
298 parameters	

For both structures, H atoms bound to C or N atoms were placed in calculated positions and allowed to ride during subsequent refinement, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$. At 180 K, C–H = 0.95 Å for Csp^2 or 0.99 Å for Csp^3 and N–H = 0.93 Å. At 295 K, C–H = 0.93 Å for Csp^2 or 0.97 Å for Csp^3 and N–H = 0.91 Å. In the LT structure, the H atoms of the water molecules were placed so as to form a reasonable hydrogen-bond network, with O–H = 0.85 Å, and then allowed to ride on their parent O atoms, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. In the HT structure, the H atoms of the water molecules were placed by comparison with the LT structure, and then refined in the same way. One water molecule site is omitted from the HT structure (corre-

Table 1

Hydrogen-bond geometry (Å, °) for (I) at 180 K.

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
N2–H2B···O1W	0.93	2.05	2.952 (4)	162
N3–H3B···O2W	0.93	2.09	2.964 (4)	155
N6–H6C···O2W ⁱ	0.93	2.00	2.882 (4)	158
N7–H7C···O1W ⁱⁱ	0.93	2.05	2.901 (4)	151
O1W–H2···O3A	0.85	2.35	3.094 (4)	147
O1W–H2···O3D	0.85	2.29	3.075 (6)	153
O1W–H1···O1B ⁱⁱⁱ	0.85	2.23	3.047 (6)	161
O1W–H1···O1D ⁱⁱⁱ	0.85	2.33	2.990 (5)	135
O2W–H4···O3W	0.85	2.19	2.858 (6)	136
O2W–H3···O2A ^{iv}	0.85	2.05	2.852 (6)	157
O3W–H6···O6W	0.85	1.87	2.716 (9)	175
O3W–H5···O1	0.85	1.97	2.806 (4)	167
O4W–H7···O1A ^v	0.85	2.24	2.918 (5)	137
O4W–H8···O3B ^{vi}	0.85	2.08	2.899 (5)	161
O5W–H9···O3C ^{vi}	0.85	2.13	2.977 (7)	177
O5W–H10···O2G ^{vii}	0.85	2.32	3.129 (15)	160
O6W–H12···O4W	0.85	1.87	2.717 (8)	177
O6W–H11···O5W	0.85	1.72	2.548 (12)	164

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

sponding to O6W in the LT structure), so that the atom count sums to four water molecules per unit cell less than the stated formula. All perchlorate anions were refined with their Cl–O distances restrained to a common refined value and O···O distances restrained to be 1.633 times that value. At 180 K, perchlorate anion Cl2 is modelled as disordered over two orientations with equal site occupancy, with atom O2A common to both orientations. The O atoms of this anion were refined with anisotropic displacement parameters restrained to resemble isotropic behaviour. For some of these atoms (particularly O2C), the anisotropic displacement parameters are nonetheless elongated, but this was considered to be acceptable in the context of the rotational disorder. At 295 K, perchlorate anion Cl2 was modelled as rotationally disordered over two orientations. In this case, all O atoms were given a common refined isotropic displacement parameter. At 180 K, the highest peak in the difference density is located in the vicinity of the solvent water molecules, *ca* 1.65 Å from atom H4. At 295 K, the highest residual peak is associated with the rotationally disordered Cl2 perchlorate anion.

For both structures, data collection: APEX2 (Bruker–Nonius, 2004); cell refinement: SAINT (Bruker, 2003); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

The authors are grateful to the Danish Natural Science Research Council (SNF) and Carlsbergfondet (Denmark) for provision of the X-ray equipment.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3119). Services for accessing these data are described at the back of the journal.

References

- Bruker (2003). SAINT. Version 7.06a. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker–Nonius (2004). APEX2. Version 1.0-22. Bruker–Nonius BV, Delft, The Netherlands.
- Collins, M. A., Hodgson, D. J., Michelsen, K. & Towle, D. K. (1987). *J. Chem. Soc. Chem. Commun.* pp. 1659–1660.

metal-organic compounds

- Glerup, J., Goodson, P. A., Hazell, A., Hazell, R., Hodgson, D. J., McKenzie, C. J., Michelsen, K., Rychlewska, U. & Toftlund, H. (1994). *Inorg. Chem.* **33**, 4105–4111.
- Goodwin, H. A. & Lions, F. (1960). *J. Am. Chem. Soc.* **82**, 5013–5023.
- Poulsen, A. K., Rompel, A. & McKenzie, C. J. (2005). *Angew. Chem. Int. Ed.* **44**, 6916–6920.
- Sheldrick, G. M. (2003). *SADABS*. Version 2.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.