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Di-μ-oxo-bis[bis(bipyridine-*N*,*N*′)-manganese(III,IV)] Triperchlorate Bis(nitrobenzene) Hemihydrate

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Abstract

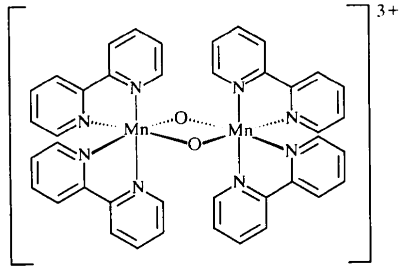
The title compound, $[Mn_2O_2(C_{10}H_8N_2)_4](ClO_4)_3.2C_6H_5NO_2.0.5H_2O$, retains a half water molecule and incorporates two nitrobenzene molecules in the structure when recrystallized from a mixture of nitrobenzene and nitromethane. The two manganese sites have differing geometries suggestive of oxidation states Mn^{III} and Mn^{IV}. The supposed d^4 configuration of Mn^{III} implies a Jahn–Teller distortion, which is observed.

Comment

Oxo-bridged mixed-valence manganese compounds provide important small molecule model compounds for the metalloenzyme OEC (oxygen evolving complex) of Photosystem II in photosynthesis; for a recent review, see Manchanda *et al.* (1995). The first experimental charge-density study of such a compound was recently carried out on the tetrafluoroborate salt of bis(μ-oxo)-tetrakis(2,2′-bipyridine)dimanganese(III,IV) (Jensen *et al.*, 1995) and revealed a substantial accumulation of charge density in a deformation map between the μ-O atoms in the Mn_2O_2 plane. The current study was undertaken to follow up this work with a combined X-ray and neutron study of the perchlorate salt of this cation. Different crystal growth media were tested with the aim of growing large crystals suitable for neutron work and resulted in the surprising incorporation of nitrobenzene molecules in the crystal.

The asymmetric unit contains one cation, three perchlorate anions, two nitrobenzene molecules and one half water molecule. All perchlorate ions were disordered. Two ions were modelled with all O atoms occupying two sites equally and one ion was modelled with only two of the O atoms occupying two sites. All groups were restrained to have tetrahedral geometry with a Cl—O bond length of 1.414 Å. The geometry around the metal sites determined at room temperature and at 200 K do not differ significantly. Details given in the text refer to the room-temperature results.

The cation, (I), has two crystallographically independent metal sites with clearly differing geometries suggestive of its description as a localized $Mn^{III}Mn^{IV}$ dimer. The Mn1—O bond lengths are longer relative to those of Mn2—O, which suggests that Mn1 may be assigned as the Mn^{III} site and Mn2 as Mn^{IV}. The Mn1—N(axial) bond lengths [average 2.170 (6) Å] are longer than the Mn1—N(equatorial) bond lengths [average 2.117 (6) Å], which may be explained as Jahn–Teller distortion of a d^4 Mn^{III} ion.



(I)

The distortion is probably reduced somewhat by the competing effect of the bridging O atoms resulting in an elongation of the equatorial Mn—N bonds. This same effect may explain the observed elongation of the Mn2—N(equatorial) bond lengths [average

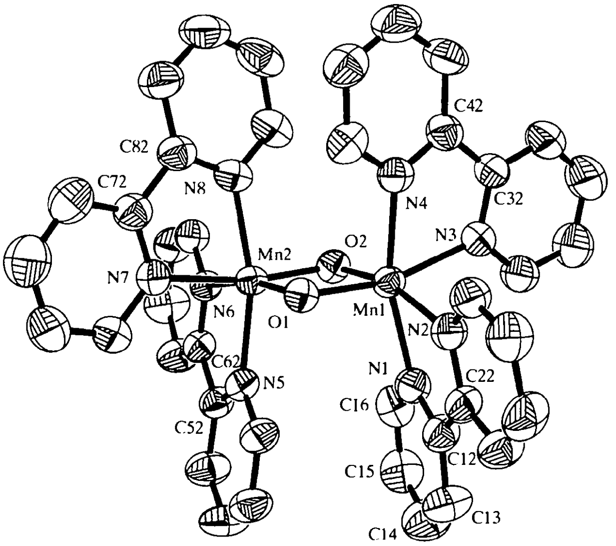


Fig. 1. Cation (I) drawn with atomic displacement parameters at the 50% probability level and showing the atom-labelling scheme.

2.099 (6) Å] relative to the Mn—N(axial) lengths [average 2.054 (6) Å], all of which would otherwise be expected to be equivalent for a d^3 Mn^{IV} ion.

This pattern of geometry follows similar trends to those seen in the structures of other localized bis(μ-O)$Mn^{III}Mn^{IV}$ dimers (Plaksin *et al.*, 1972; Hagen *et al.*, 1988; Towle *et al.*, 1988; Brewer *et al.*, 1989; Jensen *et al.*, 1995). However, the differences between the geometries at the two metal sites are slightly less pronounced than those of the perchlorate salt of this cation without the incorporated nitrobenzene, perhaps suggesting a greater degree of delocalization.

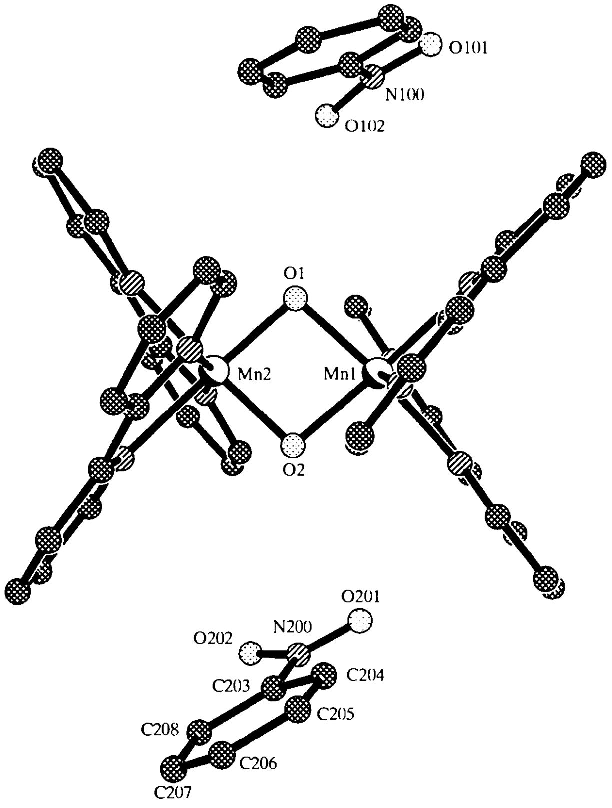


Fig. 2. View showing the relative positions of the nitrobenzene molecules and the cation in one asymmetric unit. Atoms are drawn as spheres with radii related to the atomic radii.

Experimental

The sample was synthesized according to Cooper & Calvin (1977), and was recrystallized from a mixture of nitrobenzene and nitromethane.

Crystal data

$[Mn_2O_2(C_{10}H_8N_2)_4](ClO_4)_3$.-
$2C_6H_5NO_2.0.5H_2O$
$M_r = 1320.19$
Monoclinic
$P2_1/n$
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 510 reflections
$\theta = 1.5$–29.6°
$a = 16.460 (3)$ Å
$b = 15.717 (3)$ Å
$c = 22.023 (4)$ Å
$\beta = 92.931 (5)°$
$V = 5689.9 (18)$ Å^3
$Z = 4$
$D_x = 1.541$ Mg m^{-3}
D_m not measured
$\mu = 0.666$ mm^{-1}
$T = 293 (2)$ K
Prism
0.42 × 0.36 × 0.24 mm
Green–black

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.665$, $T_{max} = 0.852$
35 661 measured reflections
14 216 independent reflections
7628 reflections with $I > 2\sigma(I)$
$R_{int} = 0.054$
$\theta_{max} = 29.67°$
$h = -15 \rightarrow 22$
$k = -20 \rightarrow 21$
$l = -25 \rightarrow 30$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.074$
$wR(F^2) = 0.152$
$S = 1.273$
13 364 reflections
707 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.001P)^2 + 5P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.10$ (for y coordinate of Mn1)
$\Delta\rho_{max} = 0.922$ e Å^{-3}
$\Delta\rho_{min} = -1.114$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Mn1—O1	1.840 (3)	Mn2—O1	1.788 (3)
Mn1—O2	1.829 (3)	Mn2—O2	1.787 (3)
Mn1—N1	2.185 (4)	Mn2—N5	2.052 (4)
Mn1—N2	2.107 (4)	Mn2—N6	2.097 (4)
Mn1—N3	2.126 (4)	Mn2—N7	2.101 (4)
Mn1—N4	2.155 (4)	Mn2—N8	2.056 (4)
Mn1···Mn2	2.7038 (10)		
O2—Mn1—O1	82.10 (13)	O2—Mn2—N5	100.81 (14)
O2—Mn1—N2	164.21 (14)	O1—Mn2—N5	90.39 (13)
O1—Mn1—N2	92.96 (14)	O2—Mn2—N8	91.66 (15)
O2—Mn1—N3	94.92 (14)	O1—Mn2—N8	99.46 (13)
O1—Mn1—N3	164.65 (14)	N5—Mn2—N8	164.80 (15)
N2—Mn1—N3	93.63 (15)	O2—Mn2—N6	92.20 (13)
O2—Mn1—N4	100.89 (13)	O1—Mn2—N6	167.36 (13)
O1—Mn1—N4	89.80 (14)	N5—Mn2—N6	78.12 (14)
N2—Mn1—N4	94.06 (14)	N8—Mn2—N6	92.87 (14)
N3—Mn1—N4	75.92 (15)	O2—Mn2—N7	168.16 (14)
O2—Mn1—N1	90.76 (14)	O1—Mn2—N7	92.08 (13)
O1—Mn1—N1	102.50 (14)	N5—Mn2—N7	90.60 (14)
N2—Mn1—N1	75.60 (14)	N8—Mn2—N7	77.59 (15)
N3—Mn1—N1	92.56 (15)	N6—Mn2—N7	93.26 (14)
N4—Mn1—N1	164.17 (14)	Mn2—O1—Mn1	96.34 (13)
O2—Mn2—O1	84.74 (13)	Mn2—O2—Mn1	96.79 (13)

Frames were measured covering a hemisphere of data to 0.72 Å^{-1}. ω scans were measured with 40 s per scan. Data were 88% complete to $2\theta = 61.5°$. The structure was solved by direct methods, which showed the positions of all non-H atoms. H atoms were placed in calculated positions and with isotropic atomic displacement parameters (a.d.p.'s) 20% larger than the equivalent isotropic a.d.p. of the parent atom. Anisotropic a.d.p.'s were refined for all non-H atoms, except for the O atoms of the perchlorate anions, for which a common $U_{\rm iso}$ was refined for each molecule, and the water O atom. After initial room-temperature investigation of crystal quality, accurate low-temperature data collection was planned for a charge–density study. The crystal was cooled to 9 K using a Displex closed-cycle He cryostat mounted on a Huber diffractometer (Henriksen *et al.*, 1986). However, some effect causes reversible splitting of most intensity profiles below 200 K. A data set was therefore collected at 200 K. Disappointingly, the higher-order reflections were generally very weak and as further cooling was not considered helpful given the peak broadening effect, data were collected only to a 2θ limit of 43°. The structure was solved and a satisfactory refinement was obtained using these data. However, the 2θ limit was deemed to be unacceptably low and a further data set was therefore collected. The first attempt at collecting a new data set showed the original batch of crystals, which had been exposed to the atmosphere, to be polycrystalline despite retaining the appearance of single crystals, *i.e.* hard well formed with shiny faces. Data were therefore collected on a crystal from a second batch of crystals which had not been open to air. Data were collected at room temperature so as not to damage the crystal. Although there was obviously a similar problem with a rapid drop in intensity with increasing 2θ values, especially given the higher temperature, the use of an area detector allowed the collection of many more significant higher-order data in a reasonable length of time.

Data collection: *SMART* (Siemens, 1994); *MAD* (Allibon, 1995) for 200 K data. Cell refinement: *SMART*. Data reduction: *SORTAV* (Blessing, 1997) and *SAINT* (Siemens, 1994); *KRYSTAL* (Hazell, 1995) for 200 K data. Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXTL* (Sheldrick, 1994). Molecular graphics: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1015). Services for accessing these data are described at the back of the journal.

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N—H···N, N—H···O and N—H···$\pi_{\rm CO}$ Hydrogen Bonding in [*N*,*N*-Bis(2-aminoethyl)-2-aminoethyl]ammonium Tetracarbonylcobaltate(1−)

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Abstract

In the title compound, $(C_6H_{19}N_4)[Co(CO)_4]$, the cations are linked *via* N—H···N hydrogen bonds in a two-dimensional (2D) grid that takes the form of a buckled sheet. Channels between sheets are occupied by the $[Co(CO)_4]^-$ anions, which are linked to the cation network *via* N—H···O and N—H···$\pi_{\rm CO}$ hydrogen bonds. Both types of cation–anion hydrogen bond are uncommon. Indeed, this is the first report of a structurally characterized N—H···$\pi_{\rm CO}$ hydrogen bond.

Comment

Organometallic compounds are rich sources of hydrogen-bonding interactions. In some cases, hydrogen bonds between ligands can be similar to those found in the organic analogs (Braga *et al.*, 1994; Biradha *et al.*, 1996). However, in other cases, the metal can induce electronic changes in ligands such as halogens (Aullón *et al.*, 1998; Mareque Rivas & Brammer, 1998*c*), carbonyls (Braga *et al.*, 1995; Braga & Grepioni, 1997) and alkynyls (Müller *et al.*, 1994) *via* metal–ligand bonding interactions, which enhance interactions that are uncommon or weaker in organic compounds. Moreover,