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A binuclear manganese(II) complex, decaaqua(μ-1,2,4,5-benzenetetracarboxylato-O^1:O^4)dimanganese(II) hydrate

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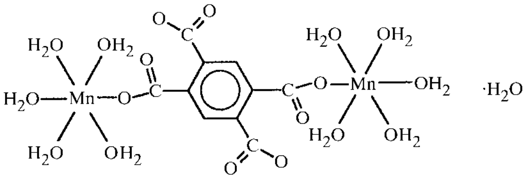
In the title Mn^{II} complex, $[Mn_2(C_{10}H_2O_8)(H_2O)_{10}]\cdot H_2O$, two independent binuclear molecules bridged by the 1,2,4,5-benzenetetracarboxyl anion exist in a unit cell, with each anion lying about an inversion centre. One of the Mn—O$_{water}$ distances [2.2922 (13) Å] is significantly longer than the Mn^{II}—O$_{water}$ distances reported so far for Mn^{II} complexes and very close to the Mn—O$_{water}$ distances found in the axial direction of Mn^{III} complexes.

Comment

As water coordination to manganese is an important step for oxygen evolution in the photosynthesis process, we are interested in the structural chemistry of manganese complexes. Some manganese complexes containing water ligands have been synthesized and their molecular structures have recently been determined in our laboratory (Yin *et al.*, 1999). We present here the structure of one such compound, namely decaaqua(μ-1,2,4,5-benzenetetracarboxylato-O^1:O^4)dimanganese(II) hydrate, (I).



(I)

The crystal structure of (I) (Fig. 1) is composed of two binuclear crystallographically independent complex molecules, 1 and 2, centred about 0,0,0 and 0,0,$\frac{1}{2}$, respectively. The benzenetetracarboxyl anion bridges two Mn^{II} atoms through carboxyl O atoms to form the binuclear molecule. Five water molecules, together with one carboxyl O atom, complete an octahedral coordination geometry around each Mn^{II} atom. There is no significant difference in the coordination distance between carboxyl and water O atoms. Most of the coordination bond distances in the present complex range from 2.1516 (14) to 2.216 (2) Å and are comparable to those reported previously, for example, 2.181 (1) in $[Mn(H_2O)_6]^{2+}\cdot ZnBr^{2-}$ (Villella *et al.*, 1986), 2.221 (6) in $[Mn(HC_4O_4)_2(H_2O)_4]$ (Yaghi *et al.*, 1995) and 2.247 (3) Å in $[Mn^{II}(Me_2PO_2)_2]\cdot 2H_2O$ (Cicha *et al.*, 1985). It is notable that the Mn1—O19 distance of 2.2922 (13) Å in the present Mn^{II} complex is significantly longer than the Mn^{II}—O$_{water}$ distances reported so far for Mn^{II} complexes and very close to the Mn—O$_{water}$ distances of 2.319 (3) (Horwitz *et al.*, 1995) and 2.287 (5) Å (Li *et al.*, 2000) found in the axial direction of two Mn^{III} complexes, both of which showed significant Jahn–Teller distortion. Jahn–Teller distortion is not expected in Mn^{II} complexes. Corresponding to the longer Mn1—O19 distance of 2.2922 (13) Å in molecule 1, there is a shorter Mn2—O29 distance of 2.1516 (14) Å in molecule 2. Both bonds are *para*

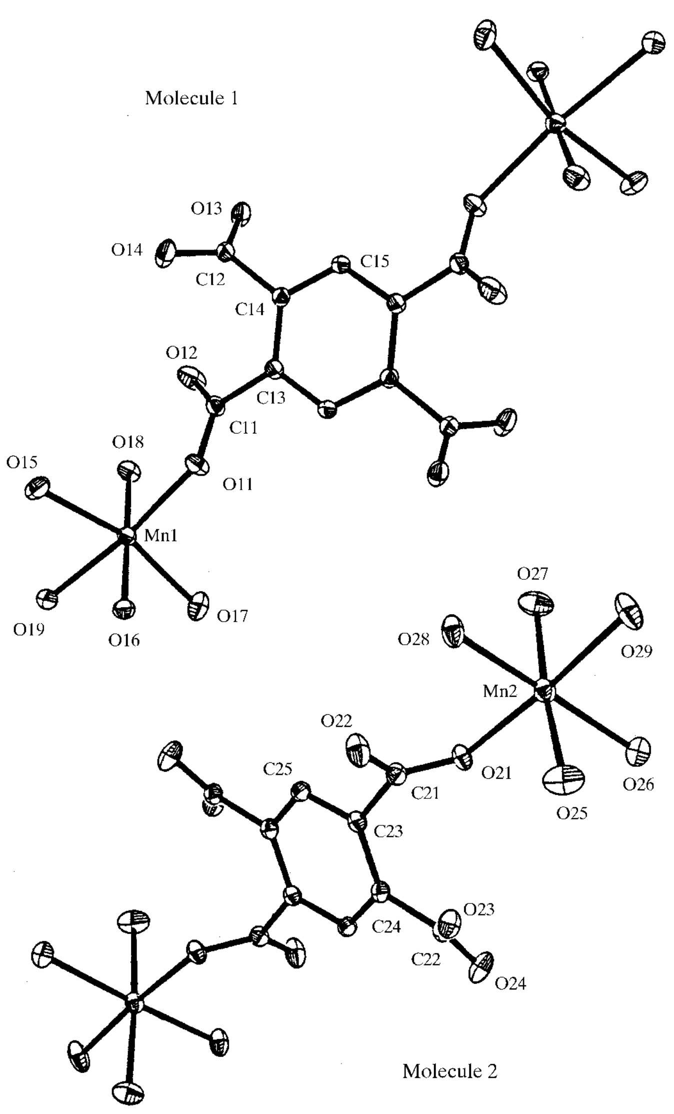


Figure 1
The molecular structures of the title complex showing 30% probability displacement ellipsoids, molecule 1 (top) and molecule 2 (bottom) being around the inversion centres at 0,0,0 and 0,0,$\frac{1}{2}$, respectively, in the unit cell. H atoms have been omitted for clarity.

with respect to the coordinated carboxyl groups and the difference in length of about 0.15 Å is one of the significant differences between the two molecules in the unit cell. The ranges for the O—Mn—O angles of the two molecules are normal. Another difference between the two molecules is the conformation of the carboxyl groups, *viz* the orientation of the uncoordinated O atom of the coordinated carboxyl group is the same as the carboxyl group in the *ortho* position for molecule 1, while it is opposite to that for molecule 2, as shown in Fig. 1.

There is an extensive network of hydrogen bonds between coordinated water molecules which includes hydration water linking the complex ions. O···O distances for these interactions range from 2.563 (12) to 2.881 (12) Å.

Experimental

About 5 mmol of 1,2,4,5-benzenetetracarboxylic acid was added slowly to an aqueous solution (20 ml) of NaOH (0.80 g, 20 mmol) with stirring at room temperature until the pH was close to 7.0. Manganese(II) acetate tetrahydrate (1.22 g, 5 mmol) was dissolved in water (10 ml). The two solutions were mixed and divided into three parts. The first part was maintained under the same conditions, methanol (0.5 ml) was added to the second part and acetonitrile (0.5 ml) was added to the last part. The above solutions were filtered, left to stand for 2 d, and only in the diluted methanol solution were well formed colourless single crystals obtained.

Crystal data

$[Mn_2(C_{10}H_2O_8)(H_2O)_{10}]\cdot H_2O$
$M_r = 558.17$
Triclinic, $P\overline{1}$
$a = 9.502$ (1) Å
$b = 10.286$ (1) Å
$c = 11.289$ (1) Å
$\alpha = 87.76$ (1)°
$\beta = 77.48$ (1)°
$\gamma = 69.85$ (1)°
$V = 1010.43$ (17) Å^3
$Z = 2$
$D_x = 1.835$ Mg m^{-3}

$D_m = 1.832$ (3) Mg m^{-3}
D_m measured by flotation in bromoform/octane
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10$–25°
$\mu = 1.343$ mm^{-1}
$T = 293$ (2) K
Hexagonal prism, colourless
0.50 × 0.48 × 0.45 mm

Data collection

Bruker AXS *P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical (*XPREP*; Siemens, 1996)
$T_{\min} = 0.476$, $T_{\max} = 0.546$
5471 measured reflections
4628 independent reflections
4045 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.017$
$\theta_{\max} = 27.5°$
$h = -12 \rightarrow 12$
$k = -13 \rightarrow 12$
$l = 0 \rightarrow 14$
3 standard reflections every 97 reflections intensity decay: 1.7%

Table 1
Selected geometric parameters (Å).

Mn1—O11	2.1610 (12)	Mn2—O21	2.1752 (12)
Mn1—O15	2.1616 (13)	Mn2—O25	2.216 (2)
Mn1—O16	2.1646 (12)	Mn2—O26	2.1941 (13)
Mn1—O17	2.1731 (14)	Mn2—O27	2.2071 (15)
Mn1—O18	2.1806 (13)	Mn2—O28	2.1707 (13)
Mn1—O19	2.2922 (13)	Mn2—O29	2.1516 (14)

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.086$
$S = 1.029$
4628 reflections
280 parameters
H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0505P)^2 + 0.2541P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.41$ e Å^{-3}
$\Delta\rho_{\min} = -0.32$ e Å^{-3}

Data collection was performed with a scan width of $\Delta\omega = (0.65 + 0.35\tan\theta)°$ and a scan rate of less than 5.6° min^{-1} in ω. The H-atom sites were obtained from the difference Fourier map and not refined.

Data collection, cell refinement and data reduction: *XSCANS* (Siemens, 1994); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Sheldrick, 1994).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1268). Services for accessing these data are described at the back of the journal.

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