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The 1:2/3 adduct of manganese(II) terephthalate with *N,N*-dimethylformamide

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Key indicators

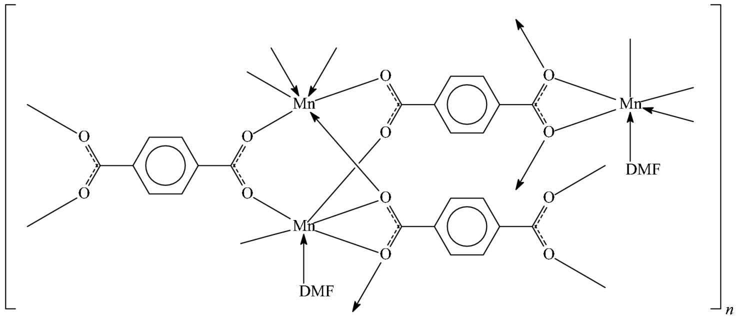
Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.005 Å
Disorder in main residue
R factor = 0.041
wR factor = 0.109
Data-to-parameter ratio = 15.6

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

Manganese(II) terephthalate crystallizes from *N*,*N*-dimethylformamide under solvothermal conditions as a $\frac{2}{3}$DMF adduct, $[Mn_3(C_8H_4O_4)_3(C_3H_7NO)_2]$; the compound is formally bis(*N*,*N*-dimethylformamide)tri-μ_5,μ_5,μ_4-terephthalato-trimanganese, which adopts a polymeric three-dimensional network structure. One of the tetraanions lies on a general position and binds to five Mn atoms, with one carboxyl group functioning as a μ_2-bridge and the other as a μ_3-bridge. The other lies on an inversion center, the dianion functioning in the μ_4-bridging mode. One Mn atom lies on a general position and is surrounded by six O atoms belonging to tetraanions. The other lies on a twofold axis and is also surrounded by six O atoms, one of which belongs to the DMF molecule.

Comment

This study continues the investigation on products of solvothermal reactions of metal salts with terephthalic acid in *N*,*N*-dimethylformamide solvent medium; the reaction with cobalt(II) nitrate gave the 1:1 adduct, $[Co(C_8H_4O_4)(C_3H_7NO)]_n$ (Fu *et al.*, 2004). The reaction with manganous chloride gave $[Mn(C_8H_4O_4)(C_3H_7NO)_{0.67}]_n$, but the compound is better regarded as bis(*N*,*N*-dimethylformamide)triterephthalatotrimanganese, which adopts a polymeric three-dimensional network structure (Fig. 1). One of the tetraanions lies on a general position and binds to five Mn atoms. One of its carboxyl groups binds to two Mn atoms; the other carboxy group chelates to an Mn atom, but both its O atoms also interact with two more so that this tetraanion is a μ_5-bridging terephthalate unit. The other tetraanion, which lies on an inversion center, functions in the μ_4-bridging mode.



(I)

A small number of adducts of manganese terephthalate have been characterized; these include the methylpyrazole (Hong & Do, 1997), 4,4′-bipyridine (Wang *et al.*, 2003), 1,10-phenanthroline (Cano *et al.*, 1994, 1997) and tris(2-pyridylmethyl)amine (Yang *et al.*, 2003) adducts, as well as two that are complexes of radical ligands coordinated through their N atoms (Li *et al.*, 2002, 2003).

Experimental

Manganese dichloride (0.198 g, 1.0 mmol), terephthalic acid (0.166, 1.0 mmol), *N*,*N*-dimethylformamide (7 ml) and 1,4-dioxane (4 ml) were sealed in a Teflon-lined stainless steel bomb, which was heated at 403 K for 6 d. Colorless crystals were obtained when the bomb was cooled slowly to room temperature. CH&N analysis. Found: C 45.10 H 2.44, N 3.48%; calc. for $C_{30}H_{26}N2_2O_{14}Mn_2$: C 45.19, H 2.53, N3.51%.

Crystal data

$[Mn_3(C_8H_4O_4)_3(C_3H_7NO)_2]$
$M_r = 803.35$
Monoclinic, $C2/c$
$a = 25.022$ (1) Å
$b = 9.5340$ (5) Å
$c = 17.923$ (1) Å
$\beta = 130.417$ (1)°
$V = 3255.2$ (3) Å^3
$Z = 4$
$D_x = 1.639$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4576 reflections
$\theta = 2.1$–27.0°
$\mu = 1.22$ mm^{-1}
$T = 295$ (2) K
Prism, colorless
0.16 × 0.14 × 0.14 mm

Data collection

Bruker SMART APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
$T_{min} = 0.748$, $T_{max} = 0.848$
17473 measured reflections
3722 independent reflections
3116 reflections with $I > 2\sigma(I)$
$R_{int} = 0.035$
$\theta_{max} = 27.5°$
$h = -32 \rightarrow 31$
$k = -12 \rightarrow 12$
$l = -22 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.109$
$S = 1.03$
3722 reflections
238 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0614P)^2 + 3.4074P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.58$ e Å^{-3}
$\Delta\rho_{min} = -0.50$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mn1—O1	2.128 (2)	Mn2—O6	2.166 (2)
Mn1—O3^i	2.291 (2)	Mn2—O7	2.127 (3)
Mn1—O5	2.159 (2)	Mn2—O4^i	2.289 (2)
Mn2—O2	2.107 (2)	Mn2—O4^{ii}	2.175 (2)
Mn2—O3^i	2.394 (2)		
O1—Mn1—O1^{iii}	95.2 (1)	O2—Mn2—O3^i	84.7 (1)
O1—Mn1—O3^i	96.4 (1)	O2—Mn2—O4^i	89.8 (1)
O1—Mn1—O3^{iv}	91.4 (1)	O2—Mn2—O4^{ii}	93.1 (1)
O1—Mn1—O5	88.6 (1)	O2—Mn2—O6	89.5 (1)
O1—Mn1—O5^{iii}	173.2 (1)	O2—Mn2—O7	172.5 (1)
O1^{iii}—Mn1—O3^i	91.4 (1)	O3^i—Mn2—O4^i	55.4 (1)
O1^{iii}—Mn1—O3^{iv}	96.4 (1)	O3^i—Mn2—O4^{ii}	133.5 (1)
O1^{iii}—Mn1—O5	173.2 (1)	O3^i—Mn2—O6	126.0 (1)
O1^{iii}—Mn1—O5^{iii}	88.6 (1)	O3^i—Mn2—O7	89.1 (1)
O3^i—Mn1—O3^{iv}	168.5 (1)	O4^i—Mn2—O4^{ii}	78.1 (1)
O3^i—Mn1—O5	82.5 (1)	O4^i—Mn2—O6	178.4 (1)
O3^i—Mn1—O5^{iii}	89.2 (1)	O4^i—Mn2—O7	90.1 (1)
O3^{iv}—Mn1—O5	89.2 (1)	O4^{ii}—Mn2—O6	100.5 (1)
O3^{iv}—Mn1—O5^{iii}	82.5 (1)	O4^{ii}—Mn2—O7	94.3 (1)
O5—Mn1—O5^{iii}	88.3 (1)	O6—Mn2—O7	90.8 (1)

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

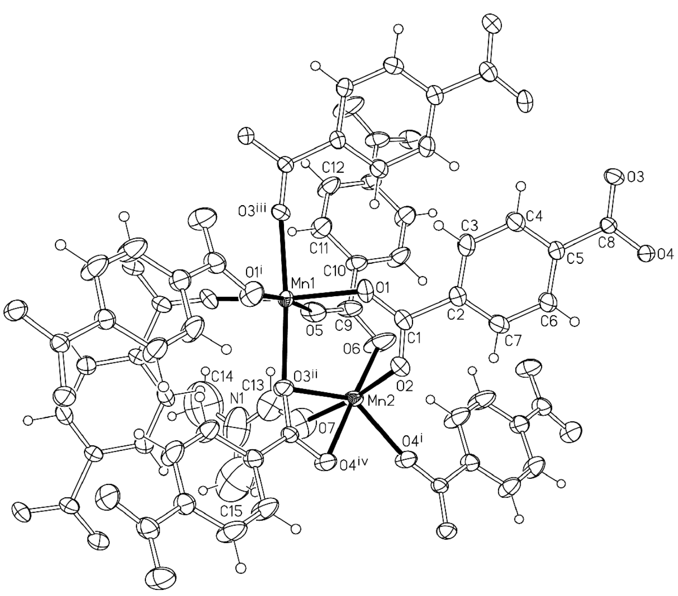


Figure 1
*ORTEP*II (Johnson, 1976) plot of a portion of polymeric structure of (I). Displacement ellipsoids are drawn at the 50% probability level. H atoms are drawn as spheres of arbitrary radii. [Symmetry codes: (i) $1-x, y, \frac{3}{2}-z$; (ii) $x, 2-y, \frac{1}{2}+z$; (iii) $1-x, 2-y, 1-z$; (iv) $\frac{3}{2}-x, y-\frac{1}{2}, \frac{3}{2}-1z$.]

The DMF molecule is disordered over two positions, with the two components (unprimed and primed atom numbers) sharing a common O atom; the disorder is such that the two components are approximately related by a rotation along the Mn2—O7 vector. The two carbonyl distances were restrained to be within ±0.01 Å of each other. The six N—C distances were restrained to be similar. The displacement parameters of the primed atoms were made to equal those of the unprimed atoms. Additionally, the vibration of these atoms were restrained to approximately isotropic displacements, and each component was restrained to be approximately planar. As the disorder refined to almost 50:50, the occupancy of each component was fixed as exactly 0.5. H atoms were placed at calculated positions (C—H = 0.93 Å for the sp^2-hybridized parent C atoms and 0.96 Å for the methyl C atoms) and were included in the refinement in the riding-model approximation, with $U_{iso}(H) = 1.2U_{eq}$ for the aromatic H atoms and $1.5U_{eq}$ for the methyl H atoms. The two methyl groups were rotated so as to fit the electron density.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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