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Dimethanoltetrakis[5,10,15,20-tetrakis-(2,6-dichlorophenyl)porphinato]manganese(III) hexacyanooctaselenidorhenate(III) tridecahydrate

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Key indicators

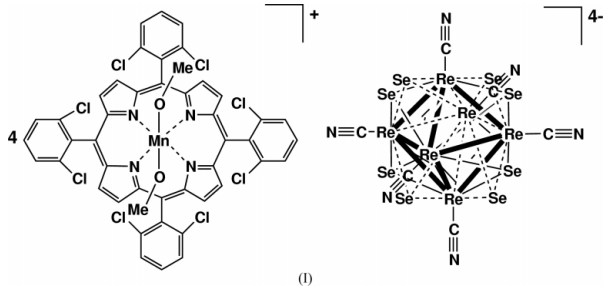
Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.017 Å
Some non-H atoms missing
Disorder in main residue
R factor = 0.071
wR factor = 0.196
Data-to-parameter ratio = 21.8

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

The crystal structure of the title compound, $[Mn(TDC)]_4[Re_6Se_8(CN)_6]\cdot 13H_2O$, contains discrete $[Re_6Se_8(CN)_6]^{4-}$ and $Mn(TDC)^+$ moieties [TDC is the tetrakis(2,6-dichlorophenyl)-porphinate dianion, $C_{44}H_{20}Cl_8N_4^{2-}$]. The anion as well as two of the cations lie on crystallographic centers of symmetry. Each $Mn(TDC)^+$ cation is octahedral with two axial methanol ligands. The coordinated methanol groups form O—H···O hydrogen bonds to solvent water molecules of crystallization in the lattice.

Comment

The reason that face-capped octahedral Re clusters, such as $Re_6Se_8(CN)_6^{4-}$, have been used as molecular building blocks is that there are six surrounding cyano groups which can link metal ions or metal complexes to obtain extended solid frameworks (Beauvais *et al.*, 1998; Beauvais *et al.*, 2000; Bennett *et al.*, 2000, 2001; Kim *et al.*, 2001; Kim, Choi *et al.*, 2002; Kim, Park & Kim, 2002; Naumov *et al.*, 1998, 2000, 2001; Shores *et al.*, 1999). Recently, we synthesized Re cluster-supported Mn^{III}–porphyrin complexes, which crystallize as discrete molecules (Kim, Choi *et al.*, 2002). For Mn(OEP) and Mn(TPP) (OEP = octaethylporphinato dianion; TPP = tetraphenylporphinato dianion), four and two cyano groups of the cyano–Re cluster were linked to the $Mn(OEP)^+$ and $Mn(TPP)^+$ units, respectively. In terms of a heterogeneous catalyst, the Mn(TPP)-containing Re cluster salt showed high catalytic activity in the epoxidation of olefins by iodosylbenzene (Kim, Choi *et al.*, 2002). This result encouraged us to try other Mn porphyrins, since the multinuclear metal clusters can be used as supporting matrices in the preparation of new heterogeneous catalysts. Here, we present the crystal structure of the Mn(TDC)-containing Re cluster salt in which four discrete $Mn(TDC)^+$ cations balance the charge of the $Re_6Te_8(CN)_6^{4-}$ anion, instead of bonding to the Re cluster through the CN groups.



(I)

In the formula unit, the $[Re_6Se_8(CN)_6]^{4-}$ anion as well as two of the $Mn(TDC)(CH_3OH)_2^+$ cations lie on crystal-

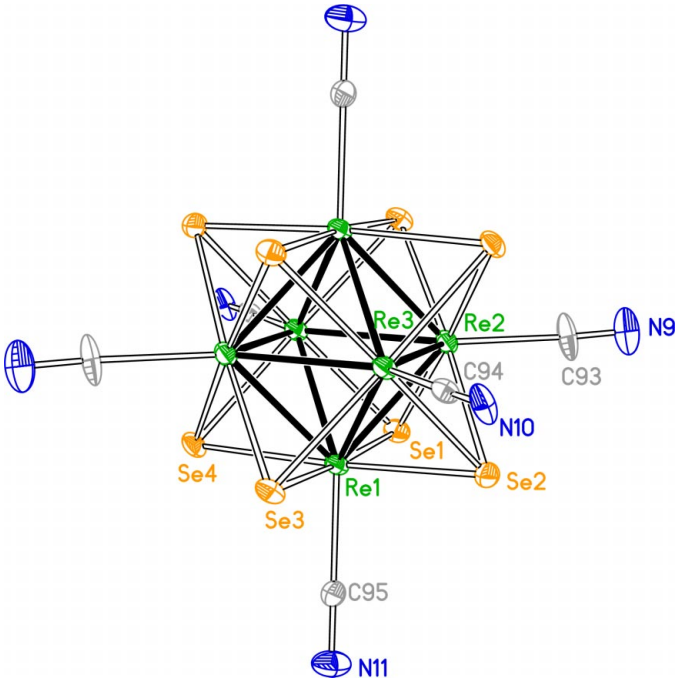


Figure 1
View of the anion, showing the atom-labeling scheme. Ellipsoids are drawn at the 30% probability level. Unlabeled atoms are generated by the symmetry code $(-x, 1-y, 1-z)$.

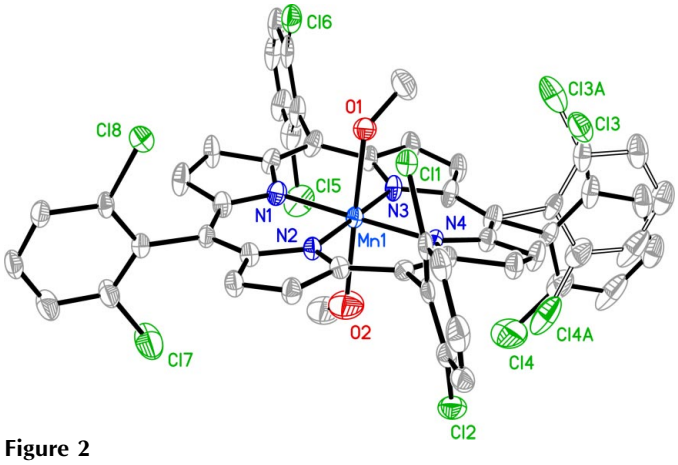


Figure 2
View of the cation containing Mn1, showing the atom-labeling scheme. Ellipsoids are drawn at the 30% probability level. All H atoms have been omitted for clarity and disordered atoms are joined with open bonds. C atoms are not labeled.

lographic centers of symmetry. In the anion, the Re—Re and Re—Se bond distances range from 2.6332 (5) to 2.6389 (5) Å and from 2.5133 (10) to 2.5249 (9) Å, respectively. The Re—C distances range from 2.106 (9) to 2.134 (10) Å, and the C—N distances range from 1.118 (14) to 1.161 (12) Å. In the cations, the Mn—N distances range from 1.999 (8) to 2.016 (9) Å, which are typical Mn—N bonding distances observed in coordination complexes. One of the dichlorophenyl rings is disordered over two sites (see *Experimental*). Each $Mn(TDC)^{+}$ has two axial methanol ligands and has octahedral coordination geometry (see Figs. 2, 3 and 4). The Mn—O(methanol)—C(methanol) angles range from 122.2 (11) to

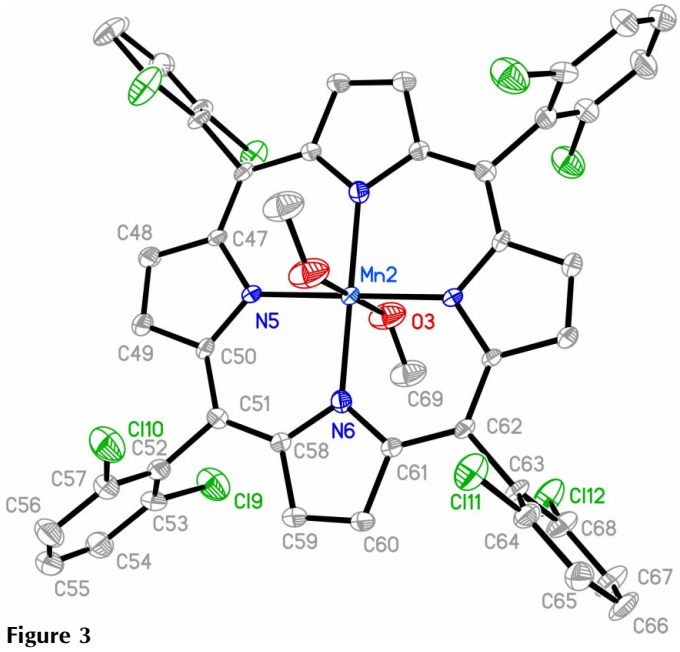


Figure 3
View of cation containig Mn2, showing the atom-labeling scheme. Ellipsoids are drawn at the 30% probability level. All H atoms have been omitted for clarity. Unlabeled atoms are gernerated by the symmetry code $(1-x, 1-y, 2-z)$.

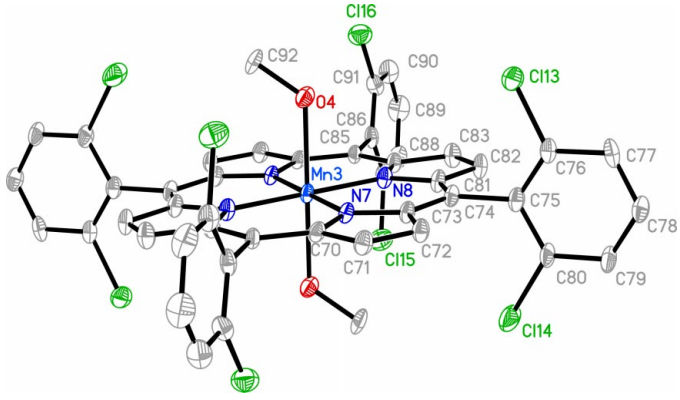


Figure 4
View of the cation containing Mn3, showing the atom-labeling scheme. Ellipsoids are drawn at the 30% probability level. All H atoms have been omitted for clarity. Unlabeled atoms are generated by the symmetry code $(1-x, 2-y, 1-z)$.

130.1 (8)°. The O(methanol)—Mn—O(methanol) angle for the cation on a general position is 178.5 (4)° and, by virtue of the inversion center, the other two O(methanol)—Mn—O(methanol) angles are exactly 180°. The methanol ligands form O—H···O hydrogen bonds with water molecules of crystallization (see Table 2 and *Experimental*). The dichlorophenyl rings are tilted from the porphyrinate plane with torsion angles, for Mn1, −76.2 (1), 82.5 (1), 79.01 (2), and −89.7 (1)° for C4—C5—C6—C7, C15—C16—C17—C22, C26—C27—C28—C29, and C37—C38—C39—C40, respectively; for Mn2, 87.1 (1) and −88.2 (1)° for C50—C51—C52—C53 and C61—C62—C63—C64, respectively; for Mn3, 80.4 (1) and −91.3 (1)° for C73—C74—C75—C80 and C84—C85—C86—C91, respectively. In contrast to previous cluster-

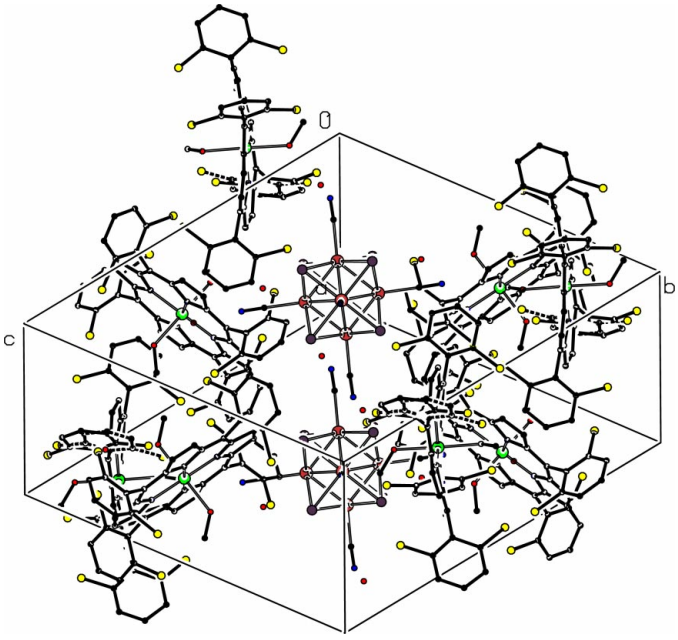


Figure 5
Packing diagram (Spek, 2003).

supported manganese porphyrins [Mn(TPP)$^+$ and Mn(OEP)$^+$], the Mn(TDC)$^+$ complex was used as a counter-cation for the title compound, without any interaction with an Re cluster anion.

Experimental

The title compound was prepared by a direct diffusion technique in which a methanol–water (*v*/*v*, 70/30) solution of $Na_4[Re_6Se_8(CN)_6]$ was carefully layered with a methanol solution of Mn(TDC)Cl. Plate-shaped crystals of compound (I), suitable for X-ray data collection, were obtained after a few days.

Crystal data

$[Mn(CH_4O)_2(C_{44}H_{20}Cl_8N_4)]_4$-$[Re_6Se_8(CN)_6]\cdot 13H_2O$
M_r = 6168.26
Triclinic, $P\overline{1}$
a = 18.4091 (2) Å
b = 18.6585 (2) Å
c = 19.8406 (3) Å
α = 114.329 (7)°
β = 93.926 (7)°
γ = 95.828 (7)°
V = 6131.8 (4) Å^3
Z = 1
D_x = 1.670 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 149247 reflections
θ = 2.6–27.6°
μ = 4.74 mm^{-1}
T = 150 (1) K
Purple, plate
0.27 × 0.25 × 0.04 mm

Data collection

Nonius KappaCCD diffractometer
φ scans and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
T_{min} = 0.320, T_{max} = 0.530
71313 measured reflections
27876 independent reflections
20976 reflections with $I > 2\sigma(I)$
R_{int} = 0.074
θ_{max} = 27.5°
$h = -23 \rightarrow 23$
$k = -24 \rightarrow 23$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.071
$wR(F^2)$ = 0.196
S = 1.03
27876 reflections
1276 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0721P)^2 + 88.9226P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 4.39 e Å^{-3}
$\Delta\rho_{min}$ = −3.56 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00120 (9)

Table 1
Selected geometric parameters (Å, °).

Re1—C95	2.111 (9)	O2—C46	1.433 (13)
Re2—C93	2.134 (10)	Mn2—N6	2.006 (8)
Re3—C94	2.106 (9)	Mn2—N5	2.013 (7)
Mn1—N2	1.999 (8)	Mn2—O3	2.240 (9)
Mn1—N3	2.006 (9)	O3—C69	1.376 (15)
Mn1—N4	2.008 (8)	Mn3—N8	2.006 (7)
Mn1—N1	2.016 (9)	Mn3—N7	2.011 (7)
Mn1—O1	2.184 (8)	Mn3—O4	2.258 (7)
Mn1—O2	2.249 (11)	O4—C92	1.412 (13)
O1—C45	1.432 (13)		
N9—C93—Re2	174.7 (14)	O3—Mn2—O3^{i}	180.00
N10—C94—Re3	178.8 (8)	C69—O3—Mn2	130.1 (8)
N11—C95—Re1	179.6 (9)	N8^{ii}—Mn3—N8	180.00
O1—Mn1—O2	178.5 (4)	O4^{ii}—Mn3—O4	180.00
C45—O1—Mn1	126.8 (8)	C92—O4—Mn3	125.0 (7)
C46—O2—Mn1	122.2 (11)		

Symmetry codes: (i) $1-x, 1-y, 2-z$; (ii) $1-x, 2-y, 1-z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O1*W*	0.84	1.94	2.582 (11)	132
O2—H2···O2*W*	0.84	2.09	2.864 (17)	154
O3—H3A···O3*W*	0.84	1.87	2.682 (15)	164
O4—H4···O4*W*	0.84	2.04	2.688 (14)	133
O1*W*—H1*WA*···N10^{iii}	0.84	1.91	2.753 (9)	180
O1*W*—H1*WB*···Cl12^{iv}	0.84	2.55	3.392 (3)	180
O2*W*—H2*WA*···Cl2	0.84	2.86	3.670 (4)	163
O3*W*—H3*WA*···Cl10^{i}	0.84	2.80	3.636 (4)	179
O3*W*—H3*WB*···Cl11^{i}	0.84	2.74	3.581 (3)	179
O4*W*—H4*WA*···Cl16	0.84	2.68	3.518 (3)	179
O4*W*—H4*WB*···Cl13	0.84	2.92	3.764 (3)	179

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

All H atoms were included in calculated positions, with C—H distances of 0.95–0.98 Å and 0.84 Å for O—H. They were included in the refinement in riding motion approximation, with $U_{iso} = 1.2U_{eq}$ ($U_{iso} = 1.5U_{eq}$ for hydroxyl) of the carrier atom. The dichlorophenyl group consisting of atoms C16/C17/C18/C19/C20/C21/C22/Cl3/Cl4 is disordered over two sites with refined occupancies of 0.575 (13) and 0.425 (13). In the final cycles of least-squares refinement, the largest peaks in a difference Fourier map were located in positions that were not close to the anion or cations. These residual electron-density peaks (as large as 5 e Å^{-3}) were interpreted as disordered water molecules residing in lattice voids. These discrete electron-density peaks were difficult to model as O atoms of water. Therefore, before the last cycles of least-squares refinement the electron-density contribution from these peaks was removed from the Fourier using SQUEEZE in *PLATON* (Spek, 2003). A total of 52 electrons were removed, which is a good approximation of the electron count from five water molecules. The five additional water molecules were included in the empirical formula to adjust the molecular weight, density and absorption coefficient accordingly. On the other hand, four density peaks that were located within hydrogen-bonding distance from the coordinated methanol molecules were included in the refinement as water molecules (giving the hydrogen-bonding geometry described in Table 2). The H atoms of the water molecules were placed in calculated positions so as to form probable O—

H···acceptor ineractions. The O—H bonds that do not have notable donor–acceptor relationships are probably hydrogen bonded to the unrefined (and subsequently removed) water molecules within the large voids in the lattice. The largest peaks in the final difference Fourier are in the vicinity of the Re_6Se_8 moiety.

Data collection: *COLLECT* (Nonius, 1997–2002); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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