C35	−0.1790 (4)	0.8652 (3)	0.1118 (3)	0.0891 (11)
C41	−0.2202 (4)	0.7031 (3)	−0.1835 (2)	0.0706 (8)
C42	−0.3697 (4)	0.6788 (4)	−0.1917 (2)	0.0797 (9)
C43	−0.4135 (5)	0.8047 (5)	−0.1885 (3)	0.0978 (13)
C44	−0.2943 (5)	0.8992 (4)	−0.1807 (3)	0.1002 (13)
C45	−0.1735 (4)	0.8391 (4)	−0.1771 (3)	0.1015 (13)

Table 2. *Selected geometric parameters (Å, °)*

*Cg*1, *Cg*2, *Cg*3 and *Cg*4 are the centroids of the four cyclopentadienyl rings, calculated from the positions of the constituent atoms.

Fe1—*Cg*1	1.644 (2)	Fe2—*Cg*4	1.645 (2)
Fe1—*Cg*2	1.654 (2)	O1—C1	1.440 (2)
Fe2—*Cg*3	1.641 (2)	O1—C4	1.435 (3)
*Cg*1—Fe1—*Cg*2	177.9 (1)	C1—O1—C4	115.7 (2)
*Cg*3—Fe2—*Cg*4	177.7 (1)		
C4—O1—C1—C11	−69.9 (2)	O1—C4—C5—C6	−60.0 (3)
C4—O1—C1—C2	166.4 (2)	C31—C4—C5—C6	178.6 (2)
O1—C1—C2—C3	−59.3 (3)	O1—C1—C11—C12	−70.2 (3)
C11—C1—C2—C3	−179.8 (2)	C2—C1—C11—C12	47.9 (3)
C1—O1—C4—C31	−65.6 (2)	O1—C4—C31—C32	−70.9 (3)
C1—O1—C4—C5	170.1 (2)	C5—C4—C31—C32	47.9 (3)

Examination of the structure with *PLATON* (Spek, 1995*a*) showed that there were no solvent-accessible voids in the crystal lattice.

Data collection: *CAD-4-PC* (Enraf–Nonius, 1992). Cell refinement: *SET*4 and *CELDIM* (Enraf–Nonius, 1991). Data reduction: *DATRD*2 in *NRCVAX*94 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SOLVER* in *NRCVAX*94. Program(s) used to refine structure: *NRCVAX*94 and *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *NRCVAX*94, *PLATON* (Spek, 1995*a*) and *PLUTON* (Spek, 1995*b*). Software used to prepare material for publication: *NRCVAX*94 and *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1047). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 777–779

[$Mn_4^{III}(\mu_3$-$O)_2(\mu$-$O_2CMe)_7$(2,2′-bipyridine)$_2$]ClO_4

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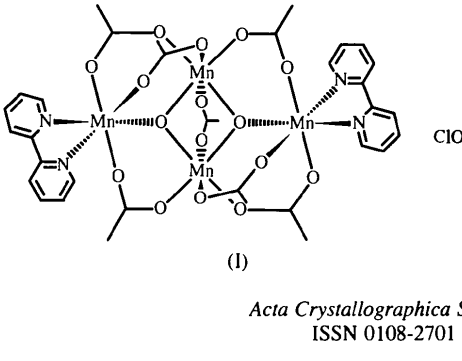
Abstract

The anhydrous form of a known tetramanganese cluster, which was previously isolated in its trihydrate form, has been prepared from a different starting material. The new complex, bis(μ_3-oxo)-1:2:4κ^3*O*;2:3:4κ^3*O*-heptakis(μ-acetato)-1:2κ^4*O*:*O*′;1:4κ^2*O*:*O*′;2:3κ^2*O*:*O*′;2:4κ^2-*O*:*O*′;3:4κ^4*O*:*O*′-bis(2,2′-bipyridine)-1κ^2*N*,*N*′;3κ^2*N*,*N*′-tetramanganese perchlorate, [$Mn_4(O)_2(C_2H_3O_2)_7$-$(C_{10}H_8N_2)_2$]ClO_4, crystallizes in the monoclinic space group *C*2/*c*, in a higher symmetry compared to the previous form. A crystallographic twofold axis passes through the centre of the molecule. The fundamental structure of the complex clearly resembles that of the form already reported.

Comment

Vincent *et al.* (1989) previously reported a variety of tetramanganese clusters as synthetic models for the O_2-evolving centre in Photosystem II. They prepared a tetramanganese(III) complex, [$Mn_4(\mu_3$-$O)_2(\mu$-$O_2CMe)_7(bpy)_2$]$ClO_4.3H_2O$ (bpy = 2,2′-bipyridine), from the reaction of [$Mn_3(\mu_3$-$O)(\mu$-$O_2CMe)_6$-(pyridine)$_3$]ClO_4 with bpy. We report here the anhydrous form of this complex, (I). In the preparation of the title complex, [$Mn_3(\mu_3$-$O)(\mu$-$O_2CMe)_6(OH_2)_3$]-$MeCO_2$ was employed in place of the starting trimer having pyridines in the terminal sites. Although Vincent *et al.* (1989) paid attention to the use of pyridine in the syntheses of such complexes, this result suggests that the presence of pyridine is not essential for the formation of the complex. Their trihydrate form crystallizes in the triclinic space group $P\bar{1}$ and the tetramanganese



(I)

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unit possesses no imposed symmetry, whereas the tetramanganese compound reported here crystallizes in the monoclinic space group *C*2/*c* and the complex cation has a crystallographic twofold axis passing through its centre and the C(3)—C(4) bond. No doubt the crystallizability of each form merely depends on the solution conditions in the synthesis.

An *ORTEP* view (Johnson, 1965) of the complex cation is shown in Fig. 1. The ClO_4^- ion, which is located at a position close to an inversion centre, was treated as disordered. The two triangular planes defined by atoms Mn(1), Mn(1^i), Mn(2) and Mn(1), Mn(1^i), Mn(2^i) [symmetry code: (i) $1-x, y, \frac{1}{2}-z$] are canted at an angle of 138.43 (7)°, which compares with the value of 135.4° observed for the trihydrate form (Vincent *et al.*, 1989). The μ_3-oxide atom [O(1)] is displaced out of the Mn(1), Mn(1^i), Mn(2) plane by 0.312 (7) Å in the direction of the C(3)—C(4) bond. The corresponding shifts of the two independent μ_3-oxide atoms in the trihydrate form were observed to be 0.351 and 0.318 Å. The detailed geometric parameters of the two tetramanganese cations are thus not equal, but the fundamental structural difference between them is almost insignificant.

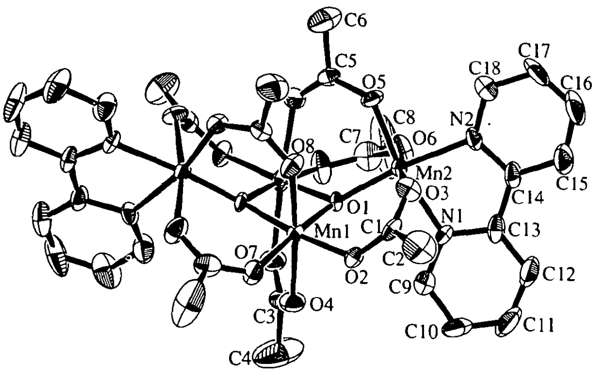

Fig. 1. View of the $[Mn^{III}_4(\mu_3\text{-}O)_2(\mu\text{-}O_2CMe)_7(bpy)_2]^+$ cation showing 50% displacement ellipsoids. H atoms have been omitted for clarity.

Experimental

$[Mn_3(\mu_3\text{-}O)(\mu\text{-}O_2CMe)_6(OH_2)_3]MeCO_2$ (0.268 g, 1 mmol), prepared according to the literature method of Bush & Frinkbeiner (1968), and 2,2′-bipyridine (0.156 g, 1 mmol) were dissolved in ethanol (20 ml). The solution was stirred at room temperature for 3 h, after which time it was filtered to remove any insoluble material. To the filtrate was added a small amount of 60% $HClO_4$ (0.2 g). On standing the solution at room temperature in air for a week, the title compound gradually formed as dark-red plates (yield 31%). Analysis: calculated for $C_{34}H_{37}ClMn_4N_4O_{20}$ C 37.92, H 3.46, N 5.20%; found C 36.31, H 3.51, N 4.61%. IR spectrum (KBr): 3530 (*s*, br), 1600 (*s*), 1450 (*m*), 1400 (*s*), 1340 (*w*), 1280 (*w*), 1140 (*m*), 1120 (*s*), 1090 (*s*, sh), 770 (*m*), 730 (*s*), 670 (*s*, sh), 600 cm^{-1} (*s*).

Crystal data

$[Mn_4(O)_2(C_2H_3O_2)_7\text{-}(C_{10}H_8N_2)_2]ClO_4$
$M_r = 1076.89$
Monoclinic
*C*2/*c*
$a = 27.638\ (2)$ Å
$b = 11.938\ (3)$ Å
$c = 16.433\ (2)$ Å
$\beta = 120.208\ (6)°$
$V = 4686\ (1)$ Å^3
$Z = 4$
$D_x = 1.5264$ Mg m^{-3}

Mo *Kα* radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 27.56–29.78°$
$\mu = 1.187$ mm^{-1}
$T = 296$ K
Plate
0.50 × 0.30 × 0.10 mm
Dark red

Data collection

Rigaku AFC-5*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{min} = 0.802$, $T_{max} = 1.000$
5785 measured reflections
5670 independent reflections

2680 observed reflections $[I > 3\sigma(I)]$
$R_{int} = 0.0407$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 35$
$k = 0 \rightarrow 15$
$l = -21 \rightarrow 18$
3 standard reflections monitored every 150 reflections
intensity decay: 3.0%

Refinement

Refinement on *F*
$R = 0.0752$
$wR = 0.0660$
$S = 3.33$
2680 reflections
274 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{max} = 0.062$
$\Delta\rho_{max} = 1.26$ e Å^{-3}
$\Delta\rho_{min} = -0.71$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}/U_{iso}
Mn(1)	0.54071 (8)	0.2369 (2)	0.2213 (1)	0.0343 (5)
Mn(2)	0.41112 (7)	0.3267 (2)	0.0612 (1)	0.0326 (5)
Cl(1)†	0.2136 (4)	0.6747 (9)	−0.0097 (7)	0.1837
O(1)	0.4620 (3)	0.2485 (6)	0.1659 (4)	0.032 (2)
O(2)	0.5400 (3)	0.2399 (7)	0.1033 (5)	0.042 (3)
O(3)	0.4739 (3)	0.3685 (6)	0.0237 (5)	0.045 (3)
O(4)	0.5282 (4)	0.0572 (7)	0.2206 (6)	0.051 (3)
O(5)	0.4167 (3)	0.4669 (6)	0.1221 (5)	0.044 (3)
O(6)	0.3418 (3)	0.2757 (7)	0.0757 (5)	0.056 (3)
O(7)	0.6192 (3)	0.2056 (7)	0.2770 (5)	0.052 (3)
O(8)	0.5605 (3)	0.4170 (7)	0.2317 (5)	0.051 (3)
O(9)†	0.2547 (9)	0.760 (2)	0.041 (1)	0.1657
O(10)†	0.240 (1)	0.567 (1)	0.014 (2)	0.3484
O(11)†	0.189 (1)	0.694 (3)	−0.1094 (7)	0.5592
O(12)†	0.1709 (9)	0.678 (3)	0.016 (2)	0.4193
N(1)	0.3952 (4)	0.1949 (8)	−0.0319 (6)	0.040 (3)
N(2)	0.3542 (4)	0.3966 (8)	−0.0673 (6)	0.040 (3)
C(1)	0.5156 (5)	0.313 (1)	0.0389 (7)	0.035 (4)
C(2)	0.5390 (5)	0.330 (1)	−0.0225 (8)	0.069 (5)
C(3)	1/2	0.012 (2)	1/4	0.053 (7)
C(4)	1/2	−0.114 (2)	1/4	0.13 (1)
C(5)	0.4264 (5)	0.486 (1)	0.2074 (8)	0.037 (4)

C(6)	0.4208 (6)	0.605 (1)	0.2264 (9)	0.075 (6)
C(7)	0.3405 (5)	0.228 (1)	0.1429 (9)	0.051 (5)
C(8)	0.2846 (6)	0.195 (2)	0.1263 (10)	0.134 (8)
C(9)	0.4200 (6)	0.095 (1)	−0.0081 (8)	0.062 (5)
C(10)	0.4122 (6)	0.013 (1)	−0.075 (1)	0.082 (6)
C(11)	0.3815 (6)	0.036 (1)	−0.165 (1)	0.085 (6)
C(12)	0.3554 (6)	0.144 (1)	−0.1921 (8)	0.068 (5)
C(13)	0.3626 (5)	0.221 (1)	−0.1240 (8)	0.046 (4)
C(14)	0.3391 (5)	0.333 (1)	−0.1449 (7)	0.043 (4)
C(15)	0.3040 (6)	0.376 (1)	−0.2297 (8)	0.066 (5)
C(16)	0.2844 (7)	0.481 (2)	−0.2411 (9)	0.081 (6)
C(17)	0.2987 (6)	0.545 (1)	−0.167 (1)	0.075 (6)
C(18)	0.3331 (6)	0.501 (1)	−0.0810 (9)	0.062 (5)

† Occupancy factor of 0.5; refined isotropically.

Table 2. *Selected geometric parameters (Å, °)*

Mn(1)···Mn(1^{i})	2.844 (4)	Mn(1)—O(8)	2.204 (8)
Mn(1)···Mn(2^{i})	3.303 (3)	Mn(2)—O(1)	1.838 (6)
Mn(1)···Mn(2)	3.379 (2)	Mn(2)—O(3)	2.17 (1)
Mn(1)—O(1)	1.893 (7)	Mn(2)—O(5)	1.916 (8)
Mn(1)—O(1^{i})	1.898 (8)	Mn(2)—O(6)	2.13 (1)
Mn(1)—O(2)	1.930 (9)	Mn(2)—N(1)	2.081 (10)
Mn(1)—O(4)	2.172 (8)	Mn(2)—N(2)	2.070 (8)
Mn(1)—O(7)	1.919 (8)		
O(1)—Mn(1)—O(1^{i})	82.1 (2)	O(1)—Mn(2)—O(6)	93.3 (3)
O(1)—Mn(1)—O(2)	95.0 (3)	O(1)—Mn(2)—N(1)	94.8 (3)
O(1)—Mn(1)—O(4)	85.9 (3)	O(1)—Mn(2)—N(2)	172.2 (4)
O(1)—Mn(1)—O(7)	173.0 (3)	O(3)—Mn(2)—O(5)	94.7 (4)
O(1)—Mn(1)—O(8)	98.4 (3)	O(3)—Mn(2)—O(6)	170.9 (3)
O(1^{i})—Mn(1)—O(2)	174.1 (3)	O(3)—Mn(2)—N(1)	82.5 (4)
O(1^{i})—Mn(1)—O(4)	89.6 (4)	O(3)—Mn(2)—N(2)	85.6 (4)
O(1^{i})—Mn(1)—O(7)	98.0 (3)	O(5)—Mn(2)—O(6)	91.8 (4)
O(1^{i})—Mn(1)—O(8)	89.0 (3)	O(5)—Mn(2)—N(1)	167.4 (3)
O(2)—Mn(1)—O(4)	95.3 (4)	O(5)—Mn(2)—N(2)	90.1 (3)
O(2)—Mn(1)—O(7)	85.5 (4)	O(6)—Mn(2)—N(1)	89.8 (4)
O(2)—Mn(1)—O(8)	86.3 (3)	O(6)—Mn(2)—N(2)	88.0 (4)
O(4)—Mn(1)—O(7)	87.1 (3)	N(1)—Mn(2)—N(2)	77.5 (4)
O(4)—Mn(1)—O(8)	175.3 (3)	Mn(1)—O(1)—Mn(1^{i})	97.2 (2)
O(7)—Mn(1)—O(8)	88.6 (3)	Mn(1)—O(1)—Mn(2)	129.8 (5)
O(1)—Mn(2)—O(3)	92.2 (3)	Mn(1^{i})—O(1)—Mn(2)	124.3 (4)
O(1)—Mn(2)—O(5)	97.6 (3)		

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

Data collection and cell refinement used *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1994*a*). The metal-atom positions were determined by direct methods (*SAPI90*; Fan, 1990). The remaining non-H atoms were located using the *DIRDIF* program (Parthasarathi, Beurskens & Bruins Slot, 1992) and refined anisotropically by full-matrix least squares, except for the atoms of the disordered ClO_4^- ion which were refined isotropically under a rigid-group constraint (Cl—O = 1.44 Å). The isotropic displacement parameter of each atom was independently shifted [the e.s.d.'s of these were not reported by *TEXSAN* (Molecular Structure Corporation, 1994*b*), so they are not presented]. In the final difference Fourier map, the largest peak (1.26 e Å^{-3}) was located 0.53 Å from the Cl atom, which is reflected by the relatively large reliability factors. All H atoms were located in their calculated positions (C—H = 0.95 Å) and not refined. Best-planes calculations were performed with the *BP70* program developed by Ito (1982). All other calculations were performed using *TEXSAN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1198). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Two Different Crystal Forms of *cis*-Diamminebis(pyrazole)platinum(II) Dinitrate

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Abstract

The crystal structures of *cis*-diamminebis(pyrazole)platinum(II) dinitrate, *cis*-$[Pt(NH_3)_2(C_3H_4N_2)_2](NO_3)_2$, (1), and *cis*-diamminebis(pyrazole)platinum(II) dinitrate pyrazole solvate, *cis*-$[Pt(NH_3)_2(C_3H_4N_2)_2](NO_3)_2.C_3H_4N_2$, (2), have been determined by X-ray diffraction. Interestingly, compound (1) crystallizes in the centrosymmetric space group $P2_1/n$, while compound (2) somehow crystallizes in the non-centrosymmetric space group $P2_1$. In both (1) and (2), the two coordinated pyrazole planes are twisted with respect to the Pt coordination planes at angles of between 46.0 (9) and 60.5 (4)°. The free pyrazole molecule contained as a crystal solvent in compound (2) forms a strong hydrogen bond [2.82 (1) Å] with one of the two coordinated pyrazole ligands. In each crystal, the packing is electrostatically stabilized through hydrogen bonds formed

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