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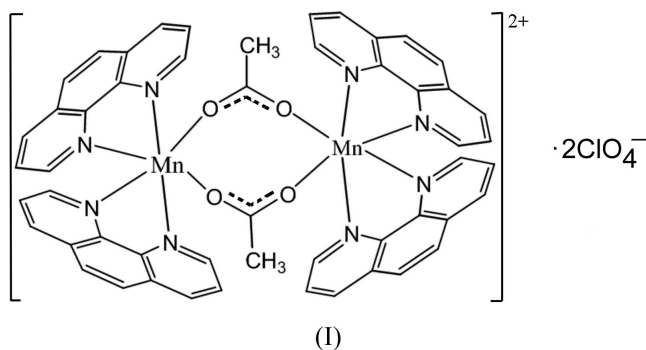
Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.005$ Å
 R factor = 0.044
 wR factor = 0.132
Data-to-parameter ratio = 12.9For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.A binuclear manganese(II) complex: di- μ -
acetato- $\kappa^4\text{O}:\text{O}'$ -bis[bis(1,10-phenanthroline-
 $\kappa^2\text{N},\text{N}'$)manganese(II)] bis(perchlorate)

The title binuclear manganese(II) complex, $[\text{Mn}_2(\text{C}_2\text{H}_3\text{O}_2)_2(\text{C}_{12}\text{H}_8\text{N}_2)_4](\text{ClO}_4)_2$, has been synthesized by the reaction of manganese(II) acetate and tetra-*n*-butylammonium manganate(VII) with 1,10-phenanthroline in a mixed solvent of acetic acid, ethanol and pyridine. In the centrosymmetric cation, the two Mn^{II} atoms are linked to each other by the four O atoms of two acetate ions. Each Mn^{II} atom adopts a six-coordinate geometry and the six coordinating atoms form a distorted octahedron.

Comment

The photosystem II oxygen-evolving complex (PSII OEC) found in the chloroplast thylakoid membranes of higher plants and algae catalyzes the splitting of water. The process is generally believed to occur on four or two manganese aggregates (Arulsamy *et al.*, 1994). Owing to their relevance to the catalytic centre of the photosystem, binuclear manganese complexes have become the subjects of intensive research. Some binuclear manganese complexes have been synthesized, including some with two O-atom bridges (Tan *et al.*, 1996; Goodwin *et al.*, 2004), O-atom and OAc^- (CH_3COO^-) mixed bridges (Arulsamy *et al.*, 1994; Oberhausen *et al.*, 1993; Sheats *et al.*, 1987; Wieghardt *et al.*, 1985), isophthalate bridges (Tan *et al.*, 1997) and two OAc^- bridges (Oshio *et al.*, 1993; Ishida *et al.*, 2001; Iriller *et al.*, 2002). We report here the title binuclear manganese(II) complex $[\text{Mn}_2(\mu\text{-OAc}^-)_2(\text{phen})_4](\text{ClO}_4)_2$ (phen = 1,10-phenanthroline), (I).



The molecular structure and a packing diagram of (I) are shown in Figs. 1 and 2, respectively. The manganese complex is a centrosymmetric cation with an $\text{Mn}\cdots\text{Mn}$ separation of 4.588 (2) Å. The two Mn^{II} atoms are bridged by two OAc^- ligands. Four N atoms of two phen ligands and two O atoms from two OAc^- anions coordinate each Mn^{II} atom to form a distorted octahedron. Atoms N1, N2, O1 and N4 form the equatorial plane, the N2–Mn1–N1, N1–Mn1–O1, O1–

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Mn1–N4 and N4–Mn1–N2 bond angles being 72.62 (9), 162.44 (9), 102.61 (8) and 163.76 (9)°, respectively. Atoms N3 and O2 lie in the axial positions with an N3–Mn1–O2 angle of 166.39 (8)°.

Experimental

Mn(OAc[−])₂·4H₂O (0.815 mmol) was dissolved in a mixed solvent (3 ml pyridine, 12 ml acetic acid, 20 ml EtOH); fresh [(C₄H₉)₄N][MnO₄] (0.315 mmol) was added slowly with continuous stirring and then NaClO₄ (0.565 mmol) was added. After 1 h, solid phen (2.0 mmol) was added to the reaction solution with continuous stirring. The final mixture was filtered, and the filtrate was layered with diethyl ether. After three weeks, a red pole-shaped crystal of (I) was obtained (m.p. >573 K). Analysis calculated for C₅₂H₃₈Cl₂Mn₂N₈O₁₂: C 54.37, H 3.31, N 9.76%; found: C 54.23, H 3.25, N 9.71%. Selected FT-IR (KBr, cm^{−1}): ν 3072 (m), 3000 (s), 1625 (m), 1567 (s), 1516 (s), 1494 (m), 1094 (s), 865 (w), 848 (s), 770 (w), 728 (s).

Crystal data

[Mn ₂ (C ₂ H ₃ O ₂) ₂ (C ₁₂ H ₈ N ₂) ₄](ClO ₄) ₂	<i>D</i> _x = 1.506 Mg m ^{−3}
<i>M</i> _r = 1147.68	Mo Kα radiation
Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Cell parameters from 5713 reflections
<i>a</i> = 9.5474 (12) Å	<i>θ</i> = 2.6–27.6°
<i>b</i> = 14.1858 (18) Å	<i>μ</i> = 0.68 mm ^{−1}
<i>c</i> = 18.802 (2) Å	<i>T</i> = 293 (2) K
<i>β</i> = 96.224 (2)°	Pole, red
<i>V</i> = 2531.5 (5) Å ³	0.45 × 0.38 × 0.31 mm
<i>Z</i> = 2	

Data collection

Siemens SMART CCD area-detector diffractometer	4444 independent reflections
<i>φ</i> and <i>ω</i> scans	3681 reflections with <i>I</i> > 2σ(<i>I</i>)
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	<i>R</i> _{int} = 0.031
<i>T</i> _{min} = 0.751, <i>T</i> _{max} = 0.818	<i>θ</i> _{max} = 25.0°
12909 measured reflections	<i>h</i> = −10 → 11
	<i>k</i> = −16 → 13
	<i>l</i> = −22 → 22

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0794P)^2 + 1.191P]$
$R[F^2 > 2\sigma(F^2)] = 0.044$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.132$	(Δ/σ) _{max} < 0.001
<i>S</i> = 1.01	$\Delta\rho_{max} = 0.64 \text{ e } \text{Å}^{-3}$
4444 reflections	$\Delta\rho_{min} = -0.33 \text{ e } \text{Å}^{-3}$
344 parameters	
H-atom parameters constrained	

The H atoms on the ligands were positioned geometrically and refined as riding [C–H = 0.93 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C) for aromatic H atoms, and C–H = 0.97 Å and *U*_{iso}(H) = 1.5*U*_{eq}(C) for methyl H atoms].

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1997); software used to prepare material for publication: SHELXTL.

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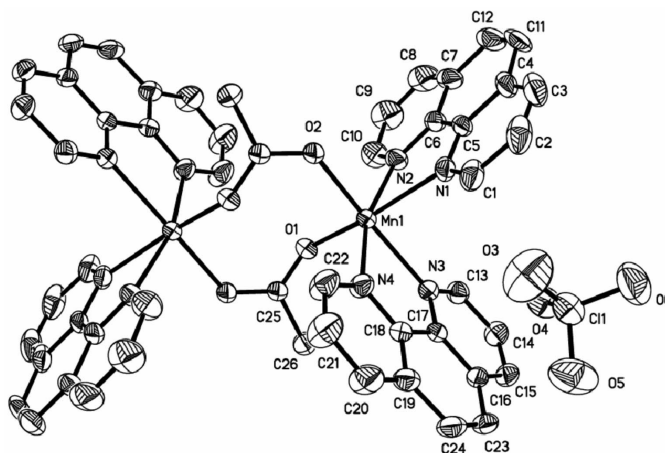


Figure 1

The title complex, with the atomic numbering scheme and displacement ellipsoids at the 30% probability level. H atoms have been omitted for clarity. Unlabelled atoms are related to labelled atoms by the symmetry operator (1 − *x*, −*y*, −*z*).

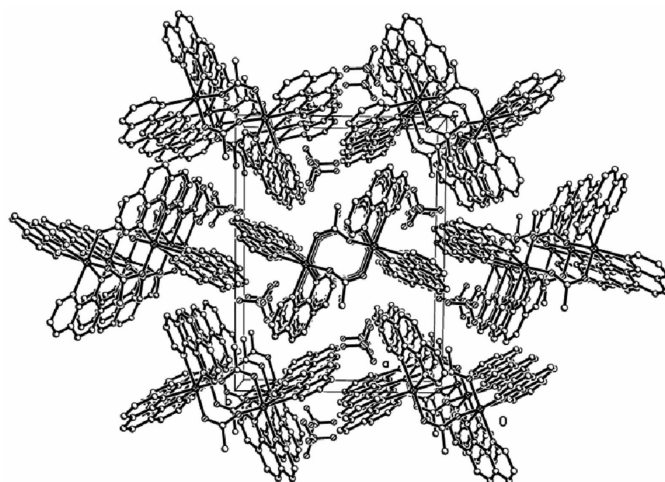


Figure 2

The packing of the title complex viewed along the *a* axis. H atoms have been omitted.

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References

- Arulsamy, N., Glerap, J., Hazell, A., Hodgson, D. J., McKenzie, C. J. & Toftlund, H. (1994). *Inorg. Chem.* **33**, 3023–3025.
- Bruker (1997). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
- Goodwin, J. C., Price, D. J. & Heath, S. L. (2004). *Dalton Trans.* pp. 2833–2835.
- Iriller, M. U., Hsieh, W. Y., Pecoraro, V. L., Rompel, A. & Krebs, B. (2002). *Inorg. Chem.* **41**, 5544–5554.
- Ishida, T., Mitsubori, S. I., Nogami, T., Takeda, N., Ishikawa, M. & Iwamura, H. (2001). *Inorg. Chem.* **40**, 7059–7064.
- Oberhausen, K. J., O'Brien, R. J., Richardson, J. F., Buchanan, R. M., Costa, R., Latour, J. M., Tsai, H. L. & Hendrickson, D. N. (1993). *Inorg. Chem.* **32**, 4561–4565.
- Oshio, H., Ino, E., Mogi, I. & Ito, T. (1993). *Inorg. Chem.* **32**, 5697–5703.
- Sheats, J. E., Czernuszewicz, R. S., Dismukes, G. C., Rheingold, A. L., Petrouleas, V., Stubbe, J., Armstrong, W. H., Beer, R. H. & Lippard, S. J. (1987). *J. Am. Chem. Soc.* **109**, 1435–1444.

- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
- Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Tan, X. S., Sun, J., Xiang, D. F. & Tang, W. X. (1997). *Inorg. Chim. Acta*, **255**, 157–161.
- Tan, X. S., Tang, W. X. & Sun, J. (1996). *Polyhedron*, **16**, 2671–2675.
- Wieghardt, K., Bossek, U., Ventur, D. & Weiss, J. (1985). *J. Chem. Soc. Chem. Commun.* pp. 347–349.