

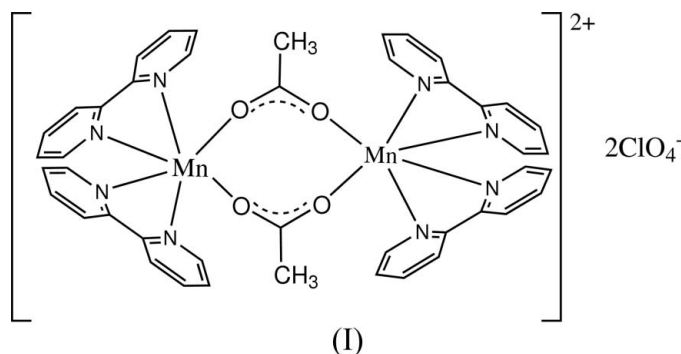
Xue-Li Niu,^{a,b} Jian-Min Dou,^{a*}
Chang-Wen Hu,^b Da-Cheng Li^a
and Da-Qi Wang^a^aSchool of Chemistry and Chemical Engineering,
Liaocheng University, Liaocheng 252059,
People's Republic of China, and ^bThe Institute
for Chemical Physics and the Department of
Chemistry, Beijing Institute of Technology,
Beijing 100081, People's Republic of China

Correspondence e-mail: jmdou@lctu.edu.cn

Key indicators

Single-crystal X-ray study
 $T = 298\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.008\text{ \AA}$
 R factor = 0.052
 wR factor = 0.143
Data-to-parameter ratio = 12.9For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Di- μ -acetato- $\kappa^4\text{O}:\text{O}'$ -bis[bis(2,2'-bipyridine- $\kappa^2\text{N},\text{N}'$)-
manganese(II)] bis(perchlorate)In the binuclear title manganese(II) complex, $[\text{Mn}_2(\text{C}_2\text{H}_3\text{O}_2)_2(\text{C}_{10}\text{H}_8\text{N}_2)_4](\text{ClO}_4)_2$, the Mn atoms are six-coordinate in a distorted octahedral coordination geometry. The two Mn atoms are bridged by two acetate groups to form a dimeric cation. The complex forms chains through π - π stacking interactions.

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 at aggregates containing two or four Mn atoms (Arulsamy *et al.*, 1994). Owing to their relevance to the catalytic center of the photosystem, binuclear manganese complexes have become the subject of intensive research. Binuclear manganese complexes that have been synthesized include those 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), and isophthalate bridges (Tan *et al.*, 1997), but examples with two acetate groups bridging a binuclear manganese complex are limited to two, namely $[\text{Mn}^{\text{II}}(\text{tpa})(\mu\text{-O}_2\text{CCH}_3)]_2(\text{TCNQ})_2 \cdot 2\text{CH}_3\text{CN}$ [tpa is tris(2-pyridylmethyl)amine and TCNQ is tetracyanoquinodimethane; Oshio *et al.*, 1993] and $[\text{Mn}(\text{bipa})(\mu\text{-OAc})_2](\text{ClO}_4)_2$ [bipa is bis(picoly)(*N*-methylimidazol-2-yl)amine; Triller *et al.*, 2002]. We now report the binuclear manganese(II) complex (I), containing 2,2'-bipyridine ligands $[\text{Mn}_2(\mu\text{-OAc}^-)_2(\text{bipy})_4](\text{ClO}_4)_2$ (OAc is CH_3COOH and bipy is 2,2'-bipyridine).The molecular structure of (I) is shown in Fig. 1. The manganese complex is a centrosymmetric binuclear cation with an $\text{Mn}\cdots\text{Mn}$ separation of $4.5574(15)\text{ \AA}$. The two Mn^{II} atoms are bridged by two OAc^- ligands. The coordination polyhedron around Mn is a distorted octahedron, whose

Received 20 September 2005

Accepted 24 October 2005

Online 10 November 2005

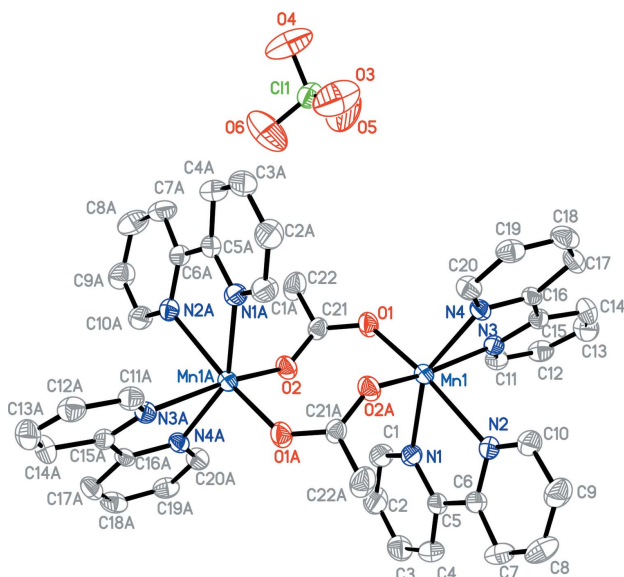


Figure 1
The title complex, with the atomic numbering scheme and displacement ellipsoids drawn at the 30% probability level. H atoms have been omitted for clarity. [Symmetry code: (A) $1 - x, 2 - y, 1 - z$.]

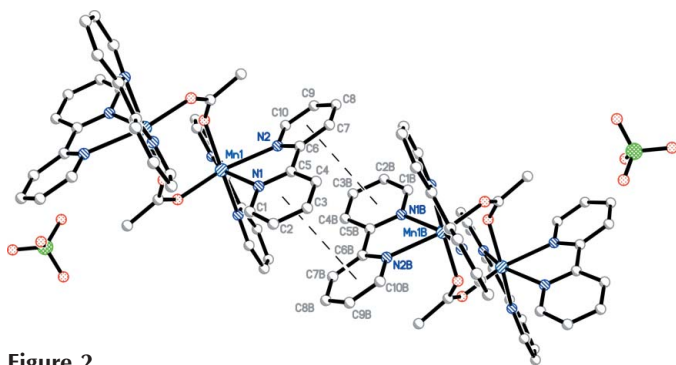


Figure 2
The π - π stacking of the title complex. H atoms have been omitted for clarity.

equatorial plane is formed by one O atom (O1) and three N atoms (N1, N2 and N4); the axial positions are occupied by one N atom (N3) and one O atom (O2ⁱ); selected bond lengths and angles are shown in Table 1.

The complex cations are assembled into a one-dimensional chain by π - π stacking interactions, as shown in Fig. 2. Both pyridyl rings of the relevant bipy ligand take part in the π - π stacking. The distance between the ring centroids is 4.110 Å, and the perpendicular distance of the two ring planes is 3.849 Å. The slip angle, between the ring normal and the line joining the centroids, is 20.6°. The centroid-centroid distance in the title complex is much shorter than that of the reported stacking of naphthalene groups, *viz.* 4.6 Å (Onoue *et al.*, 1997) and 4.83 Å (Ortholand *et al.*, 1989), indicating a strong π - π stacking interaction.

Experimental

Mn(OAc)₂·4H₂O (0.815 mmol) was dissolved in a mixed solvent (3 ml pyridine, 12 ml acetic acid, 20 ml ethanol), and fresh N(CH₂CH₂CH₂CH₂)₄MnO₄ (0.315 mmol) was added slowly with

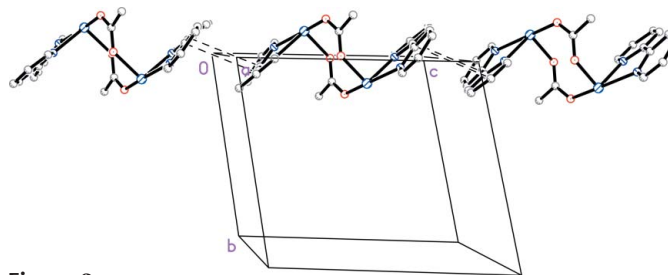


Figure 3
The one-dimensional chain of the title complex, viewed approximately along the *a* axis. H atoms, the bipy molecules that do not take part in the π - π stacking, and the perchlorate anions have been omitted for clarity.

continuous stirring. NaClO₄ (0.565 mmol) was then added. After 1 h, solid bipy (2.0 mmol) was added, and the reaction solution was stirred for 12 h. The final mixture was filtered, and the filtrate was layered with diethyl ether. After two weeks, yellow crystals of (I) were obtained; m.p. >573 K. Analysis calculated for C₄₄H₃₈Mn₂N₈O₁₂: C 50.26, H 3.64, N 10.66%; found: C 50.19, H 3.69, N 10.73%. Selected FT-IR (KBr, cm⁻¹): ν 3438 (*m*), 3107 (*m*), 2999 (*m*), 1603 (*s*), 1414 (*s*), 1337 (*m*), 1172 (*m*), 1018 (*m*), 938 (*w*), 770 (*m*), 737 (*m*), 649 (*m*), 510 (*w*).

Crystal data

[Mn₂(C₂H₃O₂)₂(C₁₀H₈N₂)₄](ClO₄)₂
M_r = 1051.60
 Triclinic, *P* $\bar{1}$
a = 10.436 (3) Å
b = 10.542 (3) Å
c = 11.756 (4) Å
 α = 78.135 (4)°
 β = 73.553 (4)°
 γ = 67.874 (4)°
V = 1141.8 (6) Å³

Z = 1
D_x = 1.529 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 1539 reflections
 θ = 2.5–21.7°
 μ = 0.74 mm⁻¹
T = 298 (2) K
 Block, yellow
 0.39 × 0.31 × 0.25 mm

Data collection

Siemens SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.761, *T_{max}* = 0.836
 6048 measured reflections

3968 independent reflections
 2533 reflections with *I* > 2 σ (*I*)
R_{int} = 0.026
 θ_{max} = 25.0°
h = -12 → 10
k = -12 → 12
l = -13 → 13

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.052
 wR (*F*²) = 0.143
S = 1.00
 3968 reflections
 308 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0676P)^2 + 0.3213P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.40 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{min} = -0.35 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Mn1—O1	2.097 (3)	Mn1—N1	2.268 (3)
Mn1—O2 ⁱ	2.100 (3)	Mn1—N3	2.275 (3)
Mn1—N4	2.244 (3)	Mn1—N2	2.377 (3)
O1—Mn1—O2 ⁱ	98.15 (11)	N4—Mn1—N3	72.14 (12)
O1—Mn1—N4	105.13 (12)	N1—Mn1—N3	92.79 (12)
O2 ⁱ —Mn1—N4	91.28 (12)	O2 ⁱ —Mn1—N2	88.49 (11)
O1—Mn1—N1	97.43 (12)	N4—Mn1—N2	85.77 (12)
O2 ⁱ —Mn1—N1	101.48 (12)	N1—Mn1—N2	70.20 (12)
O1—Mn1—N3	88.47 (11)	N3—Mn1—N2	88.21 (11)
O2 ⁱ —Mn1—N3	163.29 (12)		

Symmetry code: (i) $-x + 1, -y + 2, -z + 1$.

The H atoms were positioned geometrically and refined as riding [C–H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aromatic H atoms, and C–H = 0.96 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms].

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

This work was supported by the Natural Science Funding Council of China (NSFC, Nos. 20331010, 20271007 and 90406002) and the Specialized Research Fund for the Doctoral Program of Higher Education (SRFDP, No. 20030007014).

References

Arulsamy, N., Glerap, J., Hazell, A., Hodgson, D. J., McKenzie, C. J. & Toftlund, H. (1994). *Inorg. Chem.* **33**, 3023–3025.
Goodwin, J. C., Price, D. J. & Heath, S. L. (2004). *Dalton Trans.* pp. 2833–2835.

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.
Onoue, N. C. K. K., Osawa, Y., Nakahama, S., Ohashi, Y. & Yamaguchi, K. (1997). *Bull. Chem. Soc. Jpn.*, **70**, 1961–1968.
Ortholand, J. Y., Slawin, A. M. Z., Spencer, N., Stoddart, J. F. & Williams, D. J. (1989). *Angew. Chem. Int. Ed.* **28**, 1394–1399.
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. (1997a). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
Sheldrick, G. M. (1997b). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
Siemens (1996). *SMART* and *SAINTE*. 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.
Triller, M. U., Hsieh, W. Y., Pecoraro, V. L., Rompel, A. & Krebs, B. (2002). *Inorg. Chem.* **41**, 5544–5554.
Wieghardt, K., Bossek, U., Ventur, D. & Weiss, J. (1985). *J. Chem. Soc. Chem. Commun.* pp. 347–349.