

|            |             |          |             |
|------------|-------------|----------|-------------|
| Cp1—Fe—Cp2 | 178.6       | O1—C3—C2 | 119.4 (2)   |
| Cp1—Fe—Cp3 | 174.4       | O1—C3—C4 | 119.3 (2)   |
| C11—C1—C2  | 110.81 (12) | C2—C3—C4 | 121.30 (14) |
| C3—C2—C5   | 109.11 (12) | O2—C5—C6 | 121.7 (2)   |
| C3—C2—C1   | 110.38 (13) | O2—C5—C2 | 119.7 (2)   |
| C5—C2—C1   | 109.99 (13) | C6—C5—C2 | 118.58 (13) |

Data collection and cell refinement: *Enraf-Nonius CAD-4/PC Software* (Enraf-Nonius, 1992). Data reduction, structure solution and refinement, and preparation of material for publication: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Molecule (I) crystallized in the triclinic system; space group  $P\bar{1}$  was assumed and confirmed by the successful refinement. It became obvious during the analysis of the data that the unsubstituted C<sub>5</sub>H<sub>5</sub> ring was disordered over two sites. This was allowed for in the *SHELXL* (Sheldrick, 1994) refinement with the minor site constrained to be a regular pentagon with C—C 1.40 Å. The site occupancies refined to 0.781 (8) and 0.219 (8), respectively, for the major and minor sites, which are rotated by some 36° from an eclipsed conformation. The C atoms of the ring with 0.219 occupancy were allowed isotropic motion; all other non-H atoms were refined anisotropically. H atoms were positioned geometrically (C—H 0.95 Å) and included as riding atoms in the structure-factor calculations. Fig. 1 was prepared using *ORTEPII* (Johnson, 1976). Examination of the structures with *PLATON* (Spek, 1992) showed that there were no solvent-accessible voids in the crystal lattice.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1202). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## [Mn(salphen)(EtOH)<sub>2</sub>](BPh<sub>4</sub>) [salphenH<sub>2</sub> = *N,N'*-bis(salicylidene)-1,2-diaminobenzene], a Further Example of a Photosynthetic Model Compound Forming Dimers Linked by Hydrogen and $\pi$ Bonds

C. A. MCAULIFFE, A. NABHAN, R. G. PRITCHARD  
AND M. WATKINSON

*Department of Chemistry, University of Manchester  
Institute of Science and Technology, PO Box 88,  
Manchester M60 1QD, England*

M. BERMEJO AND A. SOUSA

*Departamento de Química Inorganica, Universidad de  
Santiago, 15706 Santiago de Compostela, Spain*

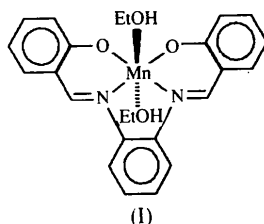
(Received 8 March 1994; accepted 28 March 1994)

## Abstract

The title molecule, bis(ethanol-*O*){2,2'-[*o*-phenylenebis(nitrilomethylidyne)diphenolato]-*N,N',O,O'*}manganese(III) tetraphenylborate, [Mn(C<sub>20</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>)(C<sub>2</sub>H<sub>6</sub>O)<sub>2</sub>](C<sub>24</sub>H<sub>20</sub>B), comprises a planar tetradentate Schiff base tightly bound to Mn<sup>III</sup> via Mn—N bonds of 1.97 (1) and 1.99 (2) Å, and two Mn—O bonds of 1.85 (1) Å, with capping ethanol groups at the longer Mn—O distances of 2.27 (1) and 2.28 (1) Å completing a distorted octahedral arrangement. Pairs of molecules are linked across inversion centres by hydrogen bonds from the ethanol to the phenoxy O atoms [O···O 2.90 (2) Å], which are augmented by  $\pi$ -bonds between overlapping phenyl rings, resulting in an Mn···Mn separation of 4.995 (6) cf. 5.21 (1) Å for the salpn analogue [salpn = *N,N'*-bis(salicylidene)-1,3-diaminopropane] [Ashmawy, Beagley, McAuliffe, Parish & Pritchard (1990). *J. Chem. Soc. Chem. Commun.* pp. 936–937].

### Comment

The title compound (I) exhibits the type of combined hydrogen- and  $\pi$ -bonded coupling as seen in several pseudo-octahedral manganese–Schiff base



complexes with capping ethanol or water ligands, *e.g.* [Mn(salpn)(EtOH)<sub>2</sub>][Mn(salpn)(H<sub>2</sub>O)(EtOH)](BPh<sub>4</sub>)<sub>2</sub> (Ashmawy, Beagley, McAuliffe, Parish & Pritchard, 1990) and [Mn(salpnCl)(H<sub>2</sub>O)<sub>2</sub>]ClO<sub>4</sub> (McAuliffe, Pritchard, Garcia-Deibe, Sousa & Bermejo, 1992) where salpnCl = *N,N'*-bis(5'-chlorosalicylidene)-1,3-diaminopropane. This implies that the dimeric clusters have an inherent stability and merits their consideration as 'secondary building units' in photolytic reactions. In particular, in aqueous solutions the molecules are configured so that they can easily associate to form bis- $\mu$ -bridged water dimers [LMnH<sub>2</sub>O]<sub>2</sub>, the first step in water photolysis (Ashmawy, McAuliffe, Parish & Tames, 1985).

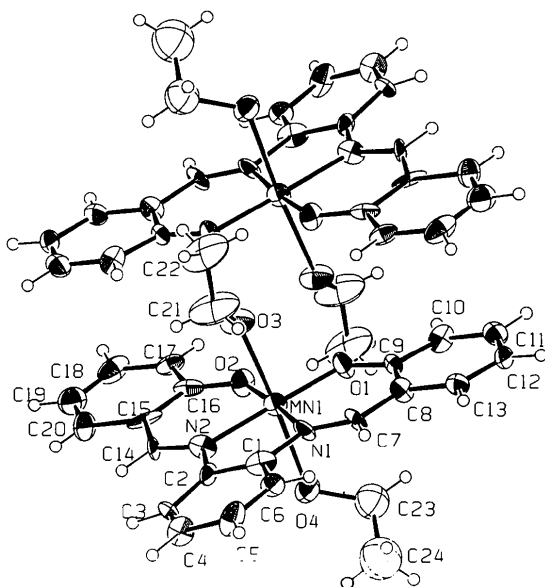


Fig. 1. A centrosymmetric hydrogen- and  $\pi$ -bonded dimer, including atomic numbering scheme, drawn using ORTEP II (Johnson, 1976).

### Experimental

[Mn(salphen)H<sub>2</sub>O]ClO<sub>4</sub> was prepared by a modification of the method of Oki & Hodgson (1990) (analysis: found, C 49.2, H 4.0, N 5.4, Mn 10.9%; calculated, C 49.2, H

3.3, N 5.7, Mn 11.3%). After several unsuccessful attempts at recrystallization, BPh<sub>4</sub><sup>-</sup> was substituted for the ClO<sub>4</sub><sup>-</sup> counterion by mixing equimolar amounts of NaBPh<sub>4</sub> and the complex in ethanol and allowing the solution to evaporate slowly to give dark needles.

### Crystal data

[Mn(C<sub>20</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>)-  
(C<sub>2</sub>H<sub>6</sub>O)<sub>2</sub>](C<sub>24</sub>H<sub>20</sub>B)  
*M<sub>r</sub>* = 780.67  
Monoclinic  
*P*2<sub>1</sub>/*n*  
*a* = 11.967 (9) Å  
*b* = 18.125 (9) Å  
*c* = 19.502 (7) Å  
 $\beta$  = 106.62 (3)°  
*V* = 4053 (7) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.28 Mg m<sup>-3</sup>

Mo *K* $\alpha$  radiation

$\lambda$  = 0.71069 Å

Cell parameters from 24 reflections

$\theta$  = 12.64–18.43°

$\mu$  = 0.3565 mm<sup>-1</sup>

*T* = 296 K

Tablet

0.30 × 0.25 × 0.10 mm

Black

### Data collection

AFC-6S diffractometer  
 $\omega/2\theta$  scans  
Absorption correction:  
refined from  $\Delta F$   
*T<sub>min</sub>* = 0.82, *T<sub>max</sub>* = 1.00  
6269 measured reflections  
5891 independent reflections  
1423 observed reflections  
[*I* > 2.5 $\sigma$ (*I*)]  
*R<sub>int</sub>* = 0.0704

$\theta_{\max}$  = 25.0°

*h* = 0 → 12

*k* = 0 → 19

*l* = -19 → 19

3 standard reflections

monitored every 150

reflections

intensity variation:

-1.50%

### Refinement

Refinement on *F*  
*R* = 0.070  
*wR* = 0.067  
*S* = 1.512  
1423 reflections  
332 parameters  
H-atom parameters not refined  
Weighting scheme based  
on measured *e.s.d.*'s  
( $\Delta/\sigma$ )<sub>max</sub> = 0.0279

$\Delta\rho_{\max}$  = 0.39 e Å<sup>-3</sup>

$\Delta\rho_{\min}$  = -0.32 e Å<sup>-3</sup>

Extinction correction:

Zachariasen (1963) type

2 Gaussian isotropic

Extinction coefficient:

0.50229 × 10<sup>-7</sup>

Atomic scattering factors

from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \cdot a_i \cdot a_j$$

|       | <i>x</i>   | <i>y</i>    | <i>z</i>    | <i>U<sub>eq</sub></i> |
|-------|------------|-------------|-------------|-----------------------|
| Mn(1) | 0.9394 (3) | 0.1270 (2)  | 0.9548 (1)  | 0.046 (1)             |
| O(1)  | 0.9928 (9) | 0.0579 (6)  | 0.9022 (6)  | 0.054 (7)             |
| O(2)  | 0.8312 (9) | 0.0602 (6)  | 0.9686 (5)  | 0.054 (7)             |
| O(3)  | 1.068 (1)  | 0.0875 (7)  | 1.0577 (7)  | 0.075 (8)             |
| O(4)  | 0.8066 (9) | 0.1729 (7)  | 0.8559 (6)  | 0.065 (7)             |
| N(1)  | 1.050 (1)  | 0.2033 (8)  | 0.9436 (8)  | 0.043 (8)             |
| N(2)  | 0.886 (1)  | 0.2043 (8)  | 1.0112 (8)  | 0.047 (9)             |
| C(1)  | 1.037 (2)  | 0.2703 (10) | 0.9806 (8)  | 0.05 (1)              |
| C(2)  | 0.946 (2)  | 0.271 (1)   | 1.0131 (9)  | 0.05 (1)              |
| C(3)  | 0.932 (2)  | 0.340 (1)   | 1.0438 (9)  | 0.05 (1)              |
| C(4)  | 1.005 (2)  | 0.3989 (10) | 1.0445 (9)  | 0.05 (1)              |
| C(5)  | 1.096 (2)  | 0.396 (1)   | 1.0140 (10) | 0.07 (1)              |
| C(6)  | 1.110 (2)  | 0.332 (1)   | 0.9809 (9)  | 0.05 (1)              |

|        |             |             |             |           |
|--------|-------------|-------------|-------------|-----------|
| C(7)   | 1.121 (2)   | 0.195 (1)   | 0.9071 (9)  | 0.05 (1)  |
| C(8)   | 1.138 (1)   | 0.133 (1)   | 0.8675 (9)  | 0.05 (1)  |
| C(9)   | 1.069 (1)   | 0.066 (1)   | 0.8663 (8)  | 0.04 (1)  |
| C(10)  | 1.084 (1)   | 0.009 (1)   | 0.8228 (9)  | 0.05 (1)  |
| C(11)  | 1.166 (2)   | 0.012 (1)   | 0.7846 (9)  | 0.06 (1)  |
| C(12)  | 1.233 (2)   | 0.075 (1)   | 0.7859 (9)  | 0.06 (1)  |
| C(13)  | 1.216 (2)   | 0.132 (1)   | 0.8269 (9)  | 0.05 (1)  |
| C(14)  | 0.807 (2)   | 0.195 (1)   | 1.0450 (9)  | 0.06 (1)  |
| C(15)  | 0.748 (2)   | 0.128 (1)   | 1.0475 (10) | 0.06 (1)  |
| C(16)  | 0.761 (2)   | 0.063 (1)   | 1.0097 (10) | 0.05 (1)  |
| C(17)  | 0.692 (2)   | 0.0055 (10) | 1.0188 (9)  | 0.05 (1)  |
| C(18)  | 0.621 (2)   | 0.010 (1)   | 1.063 (1)   | 0.07 (1)  |
| C(19)  | 0.608 (2)   | 0.072 (2)   | 1.097 (1)   | 0.08 (1)  |
| C(20)  | 0.672 (2)   | 0.134 (1)   | 1.0934 (10) | 0.07 (1)  |
| C(21)  | 1.146 (2)   | 0.118 (2)   | 1.110 (2)   | 0.14 (2)  |
| C(22)  | 1.235 (2)   | 0.084 (1)   | 1.161 (1)   | 0.15 (2)  |
| C(23)  | 0.814 (3)   | 0.158 (2)   | 0.781 (2)   | 0.11 (1)  |
| C(24)  | 0.817 (3)   | 0.238 (1)   | 0.755 (3)   | 0.16 (2)  |
| C(25)  | 0.832 (6)   | 0.213 (6)   | 0.806 (3)   | 0.08 (1)  |
| C(26)  | 0.792 (5)   | 0.190 (5)   | 0.727 (3)   | 0.08 (1)  |
| C(101) | 0.0103 (10) | 0.1821 (6)  | 0.4835 (4)  | 0.05 (2)  |
| C(102) | 0.0958 (8)  | 0.1416 (5)  | 0.5328 (6)  | 0.07 (2)  |
| C(103) | 0.1089 (8)  | 0.1490 (5)  | 0.6059 (6)  | 0.08 (2)  |
| C(104) | 0.0365 (10) | 0.1968 (6)  | 0.6297 (4)  | 0.06 (2)  |
| C(105) | -0.0490 (8) | 0.2372 (5)  | 0.5804 (6)  | 0.06 (2)  |
| C(106) | -0.0621 (8) | 0.2299 (5)  | 0.5073 (5)  | 0.07 (2)  |
| C(107) | 0.0845 (9)  | 0.1079 (7)  | 0.3822 (5)  | 0.055 (5) |
| C(108) | 0.192 (1)   | 0.1378 (5)  | 0.3822 (5)  | 0.074 (6) |
| C(109) | 0.2772 (8)  | 0.0929 (7)  | 0.3678 (5)  | 0.069 (6) |
| C(110) | 0.2551 (9)  | 0.0181 (7)  | 0.3534 (5)  | 0.081 (6) |
| C(111) | 0.148 (1)   | -0.0118 (5) | 0.3534 (5)  | 0.098 (7) |
| C(112) | 0.0624 (8)  | 0.0331 (7)  | 0.3677 (5)  | 0.077 (6) |
| C(113) | -0.1516 (7) | 0.1308 (6)  | 0.3683 (6)  | 0.048 (5) |
| C(114) | -0.1737 (9) | 0.0690 (6)  | 0.4049 (4)  | 0.066 (6) |
| C(115) | -0.284 (1)  | 0.0365 (5)  | 0.3851 (6)  | 0.074 (6) |
| C(116) | -0.3722 (8) | 0.0660 (6)  | 0.3286 (6)  | 0.068 (6) |
| C(117) | -0.3501 (9) | 0.1278 (6)  | 0.2920 (4)  | 0.070 (6) |
| C(118) | -0.240 (1)  | 0.1603 (5)  | 0.3118 (5)  | 0.064 (6) |
| C(119) | -0.0037 (8) | 0.2432 (5)  | 0.3510 (6)  | 0.046 (5) |
| C(120) | 0.0279 (8)  | 0.3114 (7)  | 0.3839 (4)  | 0.051 (5) |
| C(121) | 0.0403 (8)  | 0.3725 (5)  | 0.3431 (6)  | 0.077 (6) |
| C(122) | 0.0210 (9)  | 0.3653 (5)  | 0.2694 (6)  | 0.076 (6) |
| C(123) | -0.0106 (9) | 0.2971 (7)  | 0.2365 (4)  | 0.080 (6) |
| C(124) | -0.0229 (8) | 0.2360 (5)  | 0.2773 (6)  | 0.075 (6) |
| B(101) | -0.013 (2)  | 0.166 (1)   | 0.3945 (10) | 0.042 (6) |

Table 2. Selected geometric parameters (Å, °)

|                 |           |                 |           |
|-----------------|-----------|-----------------|-----------|
| Mn(1)—O(1)      | 1.85 (1)  | O(1)—C(9)       | 1.31 (2)  |
| Mn(1)—O(2)      | 1.85 (1)  | O(2)—C(16)      | 1.32 (3)  |
| Mn(1)—O(3)      | 2.27 (1)  | N(1)—C(1)       | 1.44 (2)  |
| Mn(1)—O(4)      | 2.28 (1)  | N(1)—C(7)       | 1.27 (3)  |
| Mn(1)—N(1)      | 1.97 (1)  | N(2)—C(2)       | 1.40 (3)  |
| Mn(1)—N(2)      | 1.99 (2)  | N(2)—C(14)      | 1.32 (3)  |
| O(1)—Mn(1)—O(2) | 90.2 (5)  | O(2)—Mn(1)—O(3) | 89.5 (5)  |
| O(1)—Mn(1)—O(3) | 91.2 (5)  | O(2)—Mn(1)—O(4) | 90.8 (4)  |
| O(1)—Mn(1)—O(4) | 92.6 (4)  | O(2)—Mn(1)—N(1) | 176.0 (6) |
| O(1)—Mn(1)—N(1) | 93.8 (6)  | O(2)—Mn(1)—N(2) | 91.9 (6)  |
| O(1)—Mn(1)—N(2) | 177.8 (6) |                 |           |

The tetraphenylborate C atoms were constrained to be regular hexagons (C—C 1.40 Å) with isotropic vibrational parameters. Disorder in one of the capping ethanol molecules was represented by two semi-populated ethyl chains [C(23),C(24) and C(25),C(26)]. H atoms were placed in calculated positions except for those attached to O3 and O4, which were ignored.

Data collection and cell refinement: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *ORTEPII* (Johnson 1976). Software used to prepare material for publication: *TEXSAN FINISH*. Literature survey: *CSSR* (1984).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: LI1115). 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.* (1994). **C50**, 1678–1681

## ( $\eta^6$ -Fluorene)( $\eta^6$ -1-isopropyl-4-methylbenzene)ruthenium(II) Bis(tetrafluoroborate), [Ru(C<sub>10</sub>H<sub>14</sub>)(C<sub>13</sub>H<sub>10</sub>)](BF<sub>4</sub>)<sub>2</sub>

SANDHYA SURAVAJALA, FRANCISCO CERVANTES-LEE  
AND LEIGH CHRISTOPHER PORTER\*

*Department of Chemistry, The University of Texas,  
El Paso, Texas 79968, USA*

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## Abstract

The Ru<sup>II</sup> atom is located symmetrically between the two arene rings forming a sandwich-type complex. There are two BF<sub>4</sub><sup>-</sup> counterions per molecule and the cations pack as canted stacks in the lattice. Many of the structural features of the coordinated fluorene ligand resemble those observed in the X-ray crystal structure of free fluorene. The arene ligands adopt an eclipsed conformation and are separated at a distance of 3.450 Å.