

## Di- $\mu$ -acetato-bis[bis(4-aminobenzoato)(2,2'-bipyridyl)manganese(II)]

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In the title compound,  $[\text{Mn}_2(\text{C}_7\text{H}_6\text{NO}_2)_2(\text{C}_2\text{H}_3\text{O}_2)_2(\text{C}_{10}\text{H}_8\text{N}_2)_2]$ , the two  $\text{Mn}^{\text{II}}$  atoms are each coordinated by one 2,2'-bipyridyl molecule, one 4-aminobenzoate ion and two acetate ions. The two Mn atoms exhibit different coordination environments: one is coordinated by two N and four O atoms, while the other is coordinated by two N and three O atoms. The two Mn atoms are bridged by two acetate ions in a *syn-anti* mode, with an  $\text{Mn}\cdots\text{Mn}$  distance of 4.081 (1) Å.

### Comment

As a bifunctional organic ligand, 4-aminobenzoic acid (4-abzH) has been extensively reported in coordination chemistry because of the richness of its coordination modes.

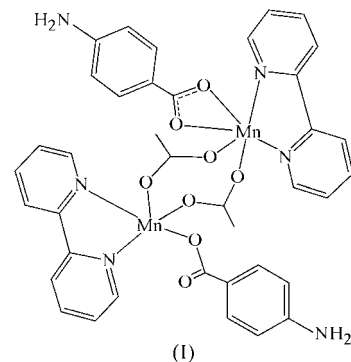
(i) 4-abzH can act as a carboxylic acid synthon and also as a good monodentate ligand through the amine group (Fur & Masse, 1996; Chen & Chen, 2002).

(ii) Deprotonated 4-abzH can act as a monodentate ligand through a carboxylate O atom (Sundberg *et al.*, 1998; Chandrasekhar *et al.*, 1988; Amiraslanov *et al.*, 1979), and as a chelating and/or bridging ligand through its amine and/or carboxylate groups (Zheng *et al.*, 2001; Rzaezynska & Belskii, 1994; Hauptmann *et al.*, 2000).

(iii) 4-abzH may be protonated to form organic cation templating agents (Wang *et al.*, 2002).

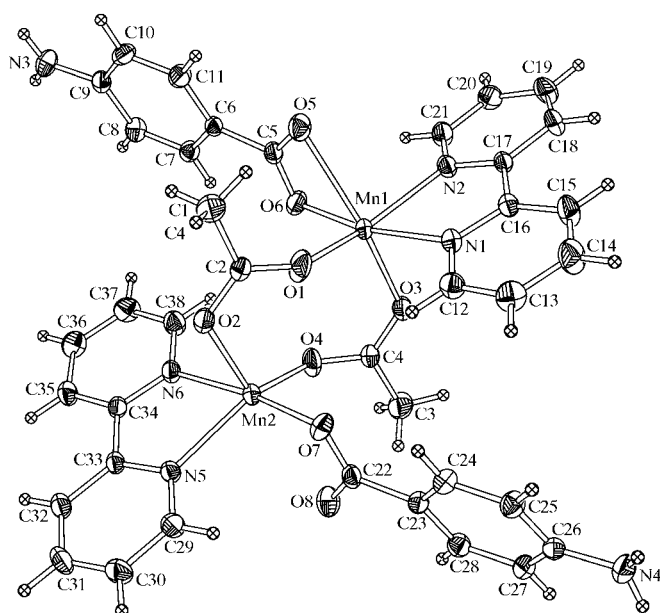
Although some complexes containing mixed 4-aminobenzoate and other N-atom donor ligands have been synthesized and characterized, complexes containing mixed 4-aminobenzoate and 2,2'-bipyridyl (2,2'-bipy) ligands have rarely been reported. To the best of our knowledge, there are only three reports of structures with 4-aminobenzoate/2,2'-bipyridyl ligands, *viz.*  $[\text{Cu}(4\text{-abz})_2(2,2'\text{-bipy})]\cdot 0.5\text{H}_2\text{O}$  (Naldini *et al.*, 1984),  $[\text{Cu}(4\text{-abz})(2,2'\text{-bipy})(4\text{-abzH})_2(\text{NO}_3)_2\cdot 1.5\text{H}_2\text{O}$  and  $\{[\text{Cu}(4\text{-abz})(2,2'\text{-bipy})(4,4'\text{-bipy})_{0.5}](\text{ClO}_4)\cdot 0.5\text{H}_2\text{O}\}_n$  (Hu *et al.*, 2003). We report here the synthesis and characterization of the title complex, (I), in which the amine group of the 4-aminobenzoate moiety is uncoordinated.

Compound (I) consists of a dimeric unit,  $[\text{Mn}_2(\text{MeCOO})_2(4\text{-abz})_2(2,2'\text{-bipy})_2]$  (Fig. 1). The coordination geometry

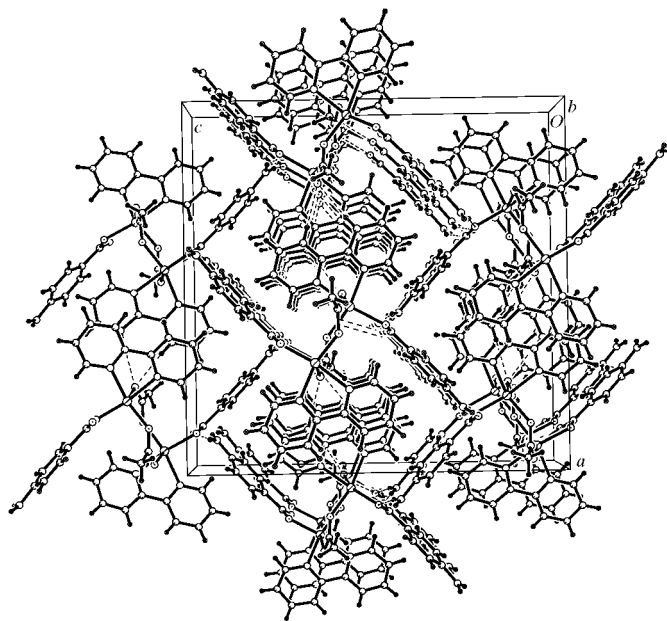


around atom Mn1 is distorted octahedral, the six coordination sites being occupied by two N atoms from a 2,2'-bipy molecule and four O atoms from one 4-aminobenzoate and two acetate ligands. The Mn–N distances are 2.242 (3) and 2.296 (3) Å, and the Mn–O distances range from 2.087 (3) to 2.454 (3) Å (Table 1). Atom Mn2 is coordinated by two N atoms from a 2,2'-bipy ligand and three O atoms from one 4-aminobenzoate and two acetate ions, forming a highly distorted square pyramid. The apical position of the pyramid is occupied by atom O2, with an Mn–O distance of 2.146 (2) Å, while the equatorial plane is defined by atoms N5, N6, O4 and O7, with Mn–N distances of 2.253 (3) and 2.298 (3) Å, and Mn–O distances of 2.069 (2) and 2.155 (2) Å. In the Mn1 coordination environment, the 4-aminobenzoate molecule exhibits a bidentate coordination mode, while in the Mn2 coordination environment, the 4-aminobenzoate molecule exhibits a monodentate coordination mode, the  $\text{Mn2}\cdots\text{O8}$  distance being 2.655 (3) Å.

Atoms N3 and N4 of the 4-aminobenzoate ligands are uncoordinated but link the molecules *via* hydrogen bonds



**Figure 1**  
The molecular structure of (I), showing displacement ellipsoids at the 30% probability level.



**Figure 2**  
The crystal structure of (I). Broken lines indicate hydrogen bonds.

(Table 2). A C—H··· $\pi$  interaction is also present (Table 2). Thus, the binuclear complexes are bound together through N—H···O hydrogen bonds and C—H··· $\pi$  interactions into a three-dimensional network (Fig. 2). There are no  $\pi$ — $\pi$  stacking interactions.

In (I), atoms Mn1 and Mn2 are bridged by the two acetate ions in a *syn-anti* fashion, and the Mn—O<sub>syn</sub> bond distances are longer than the Mn—O<sub>anti</sub> distances (Table 3). This configuration is in contrast to the reverse relationship observed in another two *syn-anti* diacetate-bridged complexes, [Mn<sub>2</sub>( $\mu$ -MeCOO)<sub>2</sub>(tpa)<sub>2</sub>](TCNQ)<sub>2</sub>·2CH<sub>3</sub>CN, (II) [tpa is tris(2-pyridylmethyl)amine and TCNQ is tetracyanoquinodimethane; Oshio *et al.*, 1993], and [Mn<sub>2</sub>( $\mu$ -MeCOO)<sub>2</sub>(bpia)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, (III) [bpia is bis(picoly)(*N*-methylimidazol-2-yl)amine; Triller *et al.*, 2002]. This difference may be attributed to the different coordination geometry around the Mn atoms and the influence of the co-existing ligands. The Mn1···Mn2 distance of 4.081 (1) Å in (I) is comparable to those in (II) and (III), but is considerably shorter than those in the other *syn-anti* dicarboxylate-bridged complexes [Mn<sub>2</sub>( $\mu$ -EtCOO)<sub>2</sub>(2,2'-bipy)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub>, (IV) [4.653 (3) Å; Zhang & Janiak, 2001], and [Mn<sub>2</sub>( $\mu$ -PhCOO)<sub>2</sub>(2,2'-bipy)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub>, (V) [4.509 (1) Å; Albela *et al.*, 1998]. The longer Mn···Mn distances in (IV) and (V) may be attributed to the fact that the Mn—O—C angles of the EtCOO and PhCOO bridges are larger than those of the MeCOO bridge.

## Experimental

An ethanol solution (8 ml) of 2,2'-bipyridyl (1.2 mmol) and 4-aminobenzoic acid (1.6 mmol) was added slowly to an aqueous solution (10 ml) of Mn(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>·4H<sub>2</sub>O (1 mmol) with continuous stirring. After half an hour, the reaction mixture was allowed to stand at room temperature undisturbed for two weeks, resulting in yellow

crystals (yield 61%). Analysis calculated for C<sub>38</sub>H<sub>34</sub>Mn<sub>2</sub>N<sub>6</sub>O<sub>8</sub>: C 56.17, H 4.22, N 10.34%; found: C 56.01, H 4.31, N 10.37%. IR (KBr, cm<sup>-1</sup>): 3421 (s), 3325 (s), 3221 (s), 1639 (s), 1574 (s), 1443 (s), 1383 (s), 1306 (m), 1173 (m), 1016 (m), 854 (m), 791 (s), 773 (s), 627 (m).

### Crystal data

[Mn<sub>2</sub>(C<sub>7</sub>H<sub>6</sub>NO<sub>2</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>·  
(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>]  
*M<sub>r</sub>* = 812.59  
Orthorhombic, *Pca*2<sub>1</sub>  
*a* = 20.8346 (7) Å  
*b* = 8.0289 (3) Å  
*c* = 21.3189 (8) Å  
*V* = 3566.2 (2) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.513 Mg m<sup>-3</sup>

Mo *K*α radiation  
Cell parameters from 7843  
reflections  
 $\theta$  = 3.0–27.5°  
 $\mu$  = 0.77 mm<sup>-1</sup>  
*T* = 293 (2) K  
Prism, yellow  
0.44 × 0.40 × 0.16 mm

### Data collection

Siemens SMART CCD  
diffractometer  
 $\omega$  scans  
Absorption correction: multi-scan  
(*SADABS*; Sheldrick, 1996)  
*T<sub>min</sub>* = 0.759, *T<sub>max</sub>* = 0.884  
26 202 measured reflections

7506 independent reflections  
7084 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.027  
 $\theta_{\max}$  = 27.5°  
*h* = −26 → 26  
*k* = −10 → 10  
*l* = −22 → 27

### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.040  
*wR* (*F*<sup>2</sup>) = 0.101  
*S* = 1.07  
7506 reflections  
487 parameters  
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0547P)^2 + 1.202P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
( $\Delta/\sigma$ )<sub>max</sub> = 0.001  
 $\Delta\rho_{\max} = 0.97 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.26 \text{ e \AA}^{-3}$   
Absolute structure: Flack (1983),  
3306 Friedel pairs  
Flack parameter = 0.446 (15)

**Table 1**

Selected geometric parameters (Å, °).

|           |             |           |             |
|-----------|-------------|-----------|-------------|
| Mn1—O1    | 2.087 (3)   | Mn2—O4    | 2.069 (2)   |
| Mn1—O3    | 2.122 (2)   | Mn2—O2    | 2.146 (2)   |
| Mn1—O6    | 2.189 (2)   | Mn2—O7    | 2.155 (2)   |
| Mn1—N2    | 2.242 (3)   | Mn2—N5    | 2.253 (3)   |
| Mn1—N1    | 2.296 (3)   | Mn2—N6    | 2.298 (3)   |
| Mn1—O5    | 2.454 (3)   |           |             |
| O1—Mn1—O3 | 108.04 (11) | N2—Mn1—O5 | 85.72 (9)   |
| O1—Mn1—O6 | 101.75 (11) | N1—Mn1—O5 | 118.45 (8)  |
| O3—Mn1—O6 | 95.20 (9)   | O4—Mn2—O2 | 118.58 (11) |
| O1—Mn1—N2 | 150.39 (12) | O4—Mn2—O7 | 103.32 (9)  |
| O3—Mn1—N2 | 91.24 (9)   | O2—Mn2—O7 | 92.39 (9)   |
| O6—Mn1—N2 | 98.51 (9)   | O4—Mn2—N5 | 137.28 (10) |
| O1—Mn1—N1 | 86.74 (11)  | O2—Mn2—N5 | 95.02 (9)   |
| O3—Mn1—N1 | 88.14 (9)   | O7—Mn2—N5 | 100.56 (10) |
| O6—Mn1—N1 | 169.36 (9)  | O4—Mn2—N6 | 84.84 (9)   |
| N2—Mn1—N1 | 71.27 (10)  | O2—Mn2—N6 | 85.81 (9)   |
| O1—Mn1—O5 | 87.80 (10)  | O7—Mn2—N6 | 171.44 (9)  |
| O3—Mn1—O5 | 150.28 (9)  | N5—Mn2—N6 | 71.31 (10)  |
| O6—Mn1—O5 | 56.26 (8)   |           |             |

**Table 2**

Hydrogen-bonding geometry (Å, °).

*C<sub>g</sub>* is the centroid of the C23—C28 ring of the 4-aminobenzoate ligand.

| <i>D</i> —H··· <i>A</i>                  | <i>D</i> —H | H··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> —H··· <i>A</i> |
|--|-------------|---------------|-----------------------|-------------------------|
| N3—H3A···O8 <sup>i</sup>                 | 0.86        | 2.27          | 3.074 (4)             | 155                     |
| N4—H4B···O6 <sup>ii</sup>                | 0.86        | 2.29          | 3.087 (4)             | 155                     |
| C36—H36A···C <sub>g</sub> <sup>iii</sup> | 0.93        | 2.79          | 3.66                  | 156                     |

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

**Table 3**

Comparison of the bond lengths (Å) and angles (°) in the *syn-anti* RCOO-bridged dimanganese moiety of (I) with corresponding values in the related compounds (II)–(V).

|       | R  | Mn...Mn   | Mn–O <sub>syn</sub> | Mn–O <sub>anti</sub> | Mn–O–C <sub>syn</sub> | Mn–O–C <sub>anti</sub> |
|-------|----|-----------|---------------------|----------------------|-----------------------|------------------------|
| (I)   | Me | 4.081 (1) | 2.146 (2)           | 2.087 (3)            | 114.1 (2)             | 146.9 (3)              |
|       |    |           | 2.122 (2)           | 2.069 (2)            | 122.6 (2)             | 139.0 (2)              |
| (II)  | Me | 4.145 (1) | 2.060 (3)           | 2.160 (3)            | 133.5 (2)             | 127.8 (3)              |
| (III) | Me | 4.128 (1) | 2.087 (2)           | 2.128 (2)            | 128.5 (2)             | 131.3 (2)              |
| (IV)  | Et | 4.653 (3) | 2.119 (3)           | 2.107 (4)            | 127.5 (3)             | 150.6 (2)              |
| (V)   | Ph | 4.509 (1) | 2.117 (4)           | 2.139 (4)            | 126.4 (3)             | 151.9 (4)              |

Notes: for (I), the first and second lines are for the O1–C2–O2 and O3–C4–O4 bridges, respectively.

All H atoms were positioned geometrically and treated as riding, with N–H distances of 0.86 Å and C–H distances of 0.93–0.96 Å, and with  $U_{\text{iso}}(\text{H})$  values of  $1.2U_{\text{eq}}(\text{C},\text{N})$  or  $1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$ . The maximum residual density is located 1.76 Å from atom H1A and the minimum density is 0.72 Å from atom Mn1. The H atoms of the two methyl groups were not well defined.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1994); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Siemens, 1994); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1213). Services for accessing these data are described at the back of the journal.

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