

# Crystal structure of bis( $\mu$ -4-nitrobenzoato- $\kappa^2$ O:O')-bis[bis(4-methylpyridine- $\kappa$ N)(4-nitrobenzoato- $\kappa^2$ O,O')manganese(II)]

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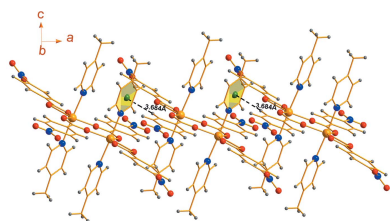
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**Keywords:** crystal structure; manganese 4-nitrobenzoate; Mn<sup>II</sup> tetracarboxylate dimer; asymmetric carboxylate bridge.**CCDC reference:** 1508004**Supporting information:** this article has supporting information at journals.iucr.org/e

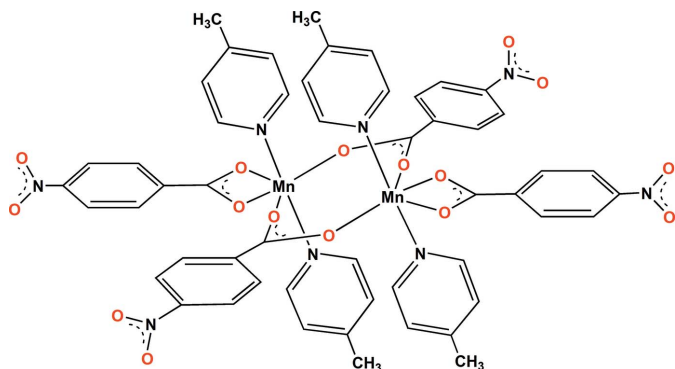
The title compound, [Mn<sub>2</sub>(C<sub>7</sub>H<sub>4</sub>NO<sub>4</sub>)<sub>4</sub>(C<sub>6</sub>H<sub>7</sub>N)<sub>4</sub>] or [Mn<sub>2</sub>( $\mu$ -NBz)<sub>2</sub>( $\kappa^2$ -NBz)<sub>2</sub>(4-Mepy)<sub>4</sub>], where NBz is 4-nitrobenzoate and 4-Mepy is 4-methylpyridine, is a centrosymmetric dinuclear complex in which the Mn<sup>II</sup> atoms are bridged by two NBz ligands with Mn...Mn = 4.1324 (4) Å. The Mn<sup>II</sup> atom in this dimeric species is present in a distorted octahedral environment with the four coordinating O atoms forming the equatorial plane and the two pyridyl N atoms occupying the axial sites. An important structural feature of the dimeric complex is that each of the bridging carboxylate ligands binds to the metal ions in an asymmetric fashion involving bent and linear Mn—O—C units. The crystal packing is consolidated by C—H...O and C—H... $\pi$  interactions.

## 1. Chemical context

Polynuclear manganese complexes with carboxylate ligation have received great attention due to their potential applications in catalysis (Arafa *et al.*, 2014), magnetism (Miyasaka *et al.*, 2004) and their antitumor activity (Dey *et al.*, 2015) as well as in other areas. The occurrence of Mn in a number of oxidation states (II–IV) under normal conditions and also the ability of carboxylate ligands to display a variety of coordination modes are the main reasons why Mn–carboxylates have received a lot of attention in the recent past. It has been reported that an Mn-based binuclear complex of composition [Mn<sub>2</sub>(bbppnol)( $\mu$ -O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub>] [bbppnol = *N,N'*-bis(2-hydroxybenzyl)*N,N'*-bis(2-methylpyridyl)-2-ol-1,3-propanediamine] with two bridging acetato ligands is active as a catalyst in the epoxidation of cyclohexene and cyclooctene (Castaman *et al.*, 2009). A series of dimeric complexes with the general formula [Mn<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)L] {where L = 2,2'-[2-hydroxy-5-(pivalamidomethyl)-1,3-phenylene]bis(1*H*-benzo[*d*]imidazole-4-carboxylic acid), 2,2'-(5-benzyl-2-hydroxy-1,3-phenylene)bis(1*H*-benzo[*d*]imidazole-4-carboxylic acid) *etc.*} have been explored as catalysts for the water-oxidation reaction with a view to generating O<sub>2</sub> and H<sub>2</sub> (Arafa *et al.*, 2014). Microwave-assisted alcohol oxidation with *tert*-butylhydroperoxide (TBHP) has been carried out (Sutradhar *et al.*, 2014) using a Schiff base-containing Mn dimer. Manganese complexes are also recognized for their magnetic behaviour since coordination compounds of this metal often display large ground-state spin (*S*) values and the polynuclear manganese cluster [Mn<sub>12</sub>O<sub>12</sub>(CH<sub>3</sub>COO)<sub>16</sub>(H<sub>2</sub>O)<sub>4</sub>]-2CH<sub>3</sub>-COOH-4H<sub>2</sub>O is considered to be the first single molecule magnet (SMM) (Uhrecký *et al.*, 2013; Sessoli *et al.*, 1993). Complexes of manganese are also considered to be important



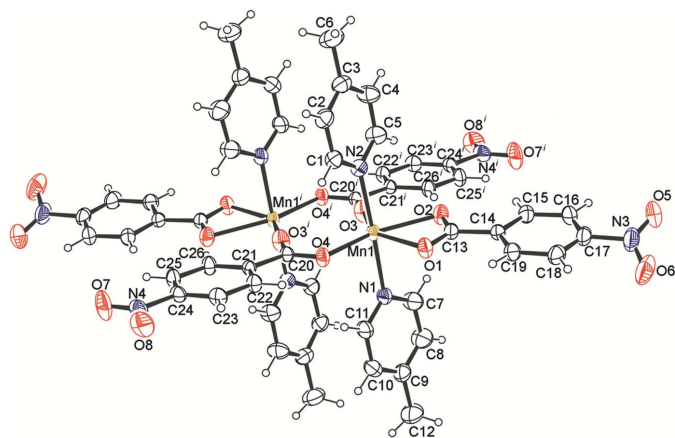
in view of the occurrence of an  $Mn_4Ca$  unit in the active site of Photosystem II that catalyses the water-splitting reaction to evolve oxygen in nature (Nocera, 2012).



Keeping in mind earlier results published from our laboratory (Chakrabarty *et al.*, 2007) on the synthesis and catalytic properties of cobalt(III)-oxide pseudo-cubane units of the type  $[Co_4O_4(\mu-O_2CR)_4L_4]$ , where  $R$  is an alkyl or aryl group and  $L$  is a monodentate pyridyl ligand, and also due to their relevance as catalysts for the water-oxidation reaction (McCool *et al.*, 2011), we explored whether analogous manganese complexes could also be synthesized. These efforts have led to the synthesis of the title complex, among others. Herein we report the synthesis, crystal structure and some salient properties of the dimeric manganese(II) compound  $[Mn_2(\mu-NBz)_2(\kappa^2-NBz)_2(4-Mepy)_4]$ , **I**, which belongs to a structure type constituted of only a limited number of complexes (*vide infra*).

## 2. Structural commentary

Fig. 1 shows the molecular structure of the dimeric complex. The two Mn atoms are related by an inversion centre and are bridged by the carboxylate anions of two NBz ligands in a *syn*-



**Figure 1**  
An ORTEP-style view of the molecular structure of  $[Mn_2(\mu-NBz)_2(\kappa^2-NBz)_2(4-Mepy)_4]$  **I** with displacement ellipsoids drawn at the 50% probability level.

**Table 1**  
Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Mn1—O3	2.1122 (10)	O1—C13	1.2460 (17)
Mn1—O4	2.1328 (9)	O3—C20 <sup>i</sup>	1.2358 (15)
Mn1—N2	2.2621 (12)	O4—C20	1.2523 (16)
Mn1—O2	2.2672 (11)	O7—N4	1.230 (3)
Mn1—N1	2.2746 (13)	N4—O8	1.198 (3)
Mn1—O1	2.3285 (11)	N3—O6	1.204 (2)
O2—C13	1.2495 (17)	N3—O5	1.212 (2)
O3—Mn1—O4	120.82 (4)	O3—Mn1—O1	144.94 (4)
O3—Mn1—N2	89.91 (5)	O4—Mn1—O1	94.05 (4)
O4—Mn1—N2	89.04 (4)	N2—Mn1—O1	94.59 (4)
O3—Mn1—O2	88.38 (4)	O2—Mn1—O1	56.95 (4)
O4—Mn1—O2	150.77 (4)	N1—Mn1—O1	88.02 (5)
N2—Mn1—O2	89.75 (5)	C13—O2—Mn1	91.41 (8)
O3—Mn1—N1	88.27 (5)	C13—O1—Mn1	88.68 (8)
O4—Mn1—N1	90.22 (4)	C20 <sup>i</sup> —O3—Mn1	178.20 (10)
N2—Mn1—N1	177.33 (4)	C20—O4—Mn1	116.68 (8)
O2—Mn1—N1	92.15 (4)		

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

*syn* fashion. Each  $Mn^{II}$  atom is further coordinated by a carboxylato ligand in chelating mode. The four oxygen atoms – two from a pair of bridging NBz ligands and two from a chelating NBz ligand – are nearly coplanar with each of the central Mn atoms, forming an equatorial plane; the axial positions for both are occupied by two 4-methylpyridine ligands completing the distorted octahedral geometry around each  $Mn^{II}$  atom. The bridging Mn—O(carboxyl) bond lengths ( $\sim 2.1$   $\text{\AA}$ ) are found to be shorter than the Mn—O(carboxyl) distances ( $\sim 2.3$   $\text{\AA}$ ) in the chelating ligands (Table 1). For the chelating NBz anions, the longer Mn—O distances can be attributed to the steric crowding imposed by the neighbouring bridging bis-monodentate NBz anions.

The Mn $\cdots$ Mn distance of 4.1324 (4)  $\text{\AA}$  in **I** precludes any direct bonding interaction between the  $Mn^{II}$  atoms and is comparable to the corresponding distances in the structurally related  $Co^{II}$  complexes  $[[Co(dpe)(NO_2BDC)]\cdot 0.5(dpe)]_n\cdot nH_2O$  (4.181  $\text{\AA}$ ; Luo *et al.* 2003),  $[Co_2(4,4'-bipy)_2(O_2CC_6H_5)_4]_n$  (4.060  $\text{\AA}$ ; Zhang *et al.* 2007) and  $Co_2(\mu-4-nbz)_2(\kappa^2-4-nbz)_2(4-CNpy)_4$  (4.226  $\text{\AA}$ ; Chakravorty & Das, 2016). However, it is considerably shorter than in its most closely related analogue  $[Mn_2(\mu-OBz)_2(\kappa^2-OBz)_2(py)_4]$  in which the Mn $\cdots$ Mn separation is 4.531  $\text{\AA}$  (Ran *et al.*, 2006).

The highly distorted nature of the  $MnO_4N_2$  octahedron in the title species, which is probably due to the steric crowding of both the bridging and chelating NBz ligands surrounding the  $Mn^{II}$  atom, is manifested by the O—Mn—O and O—Mn—N angles. While the former are in the range 56.95 (4)–150.77 (4) $^\circ$ , the latter are in the range 88.02 (5)–94.59 (5) $^\circ$ .

In the title compound, the carboxyl  $-COO$  and  $-NOO$  planes of the chelating NBz anion deviate slightly from the phenyl ring plane, forming dihedral angles of 2.6 (3) and 23.6 (4) $^\circ$ , respectively. According to Kaduk (2000) and Kaduk & Golab (1999), completely planar phenyl carboxylates are associated with low conformational energy and any deviation from planarity leads to an increase in the energy of the system. However, this destabilization can be compensated for by efficient crystal packing in the solid state.

**Table 2**  
 Hydrogen-bond geometry (Å, °).

 C<sub>g</sub> is the centroid of the N2/C1–C5 ring.

<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>
C1–H1···O4	0.93	2.61	3.172 (2)	119
C2–H2···O1 <sup>ii</sup>	0.93	2.65	3.278 (2)	125
C11–H10···O4	0.93	2.55	3.161 (2)	124
C22–H25···C <sub>g</sub> <sup>ii</sup>	0.93	2.80	3.6844 (16)	160

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

### 3. Supramolecular features

The crystal structure of **I** features several intramolecular as well as intermolecular C–H···O interactions wherein the O atoms from –NO<sub>2</sub> and –CO<sub>2</sub> groups of the NBz ligand act as hydrogen acceptors (Table 2 and Fig. 2). While the *D*···*A* separations for these weak contacts are in the range of 3.161 (2) to 3.369 (2) Å, the <C–H···O angles are generally lower than 130°, except in one case where a hydrogen bond with a greater *D*···*A* separation of 3.369 (2) Å forms has an angle of 172°. In addition, intermolecular C–H···π interactions involving the pyridyl ring π system of the 4-Mepy ligand link the complex molecules into chains along the *a* axis (Fig. 3). Although each of the above non-covalent contacts is individually weak, the presence of many of these supramolecular contacts clearly result in extra stability of the species in the solid state. Indeed, the involvement of the –NO<sub>2</sub> and –CH<sub>3</sub> groups at the 4-positions of the phenyl ring of the NBz ligand and the pyridyl ring of the 4-Mepy ligand may explain why the isolation of complexes analogous to **I** has not been possible for some combinations of carboxylato and pyridyl ligands.

### 4. Database survey

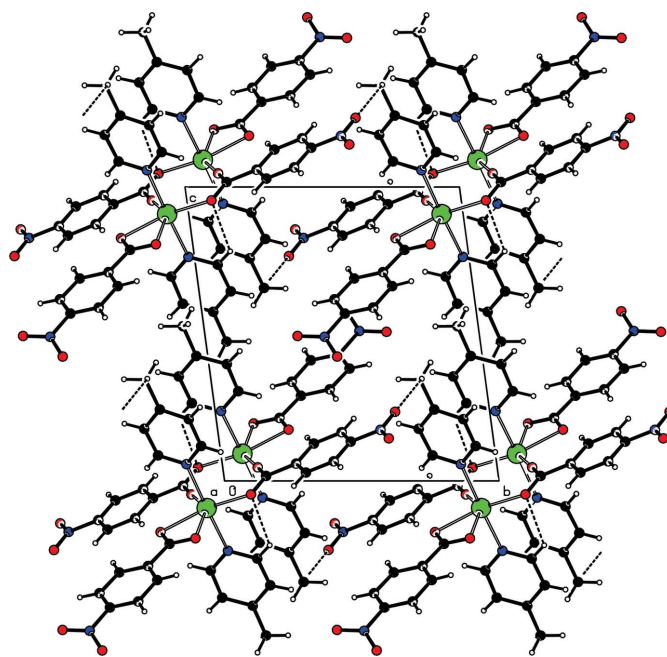
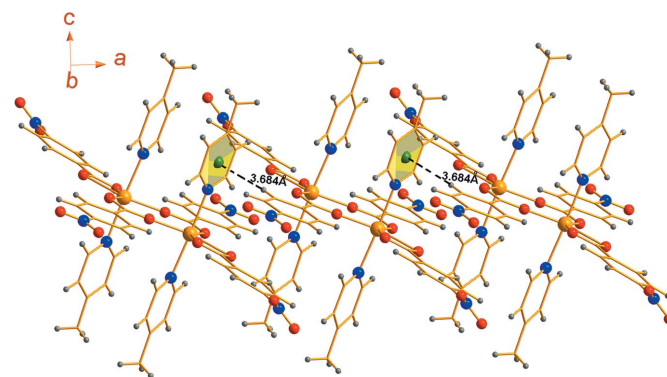
A survey of the Cambridge Structural Database (Groom *et al.* 2016) shows that only a few dinuclear Mn complexes with both bridging and chelating carboxylate linkages are known. We have tabulated some of the available data for complexes of the type [Mn<sub>2</sub>(μ-O<sub>2</sub>CR)<sub>2</sub>(κ<sup>2</sup>-O<sub>2</sub>CR)<sub>2</sub>L<sub>4</sub>] in Table 3 in order to compare some of the important geometric parameters. For all complexes, the Mn–O bonds involving the chelating carboxylato ligands are longer than the corresponding Mn–O bonds in the bridging carboxylato ligands. Of particular note

**Table 3**

 Comparison of geometrical parameters (Å, °) for [Mn<sub>2</sub>(μ-NBz)<sub>2</sub>(κ<sup>2</sup>-NBz)<sub>2</sub>(4-Mepy)<sub>4</sub>] **I** and structurally related Mn<sup>II</sup>-carboxylate complexes.

Compound	Mn···Mn	Mn–O–C	M–O (chelate)	M–O (bridge)
[Mn <sub>2</sub> (μ-NBz) <sub>2</sub> (κ <sup>2</sup> -NBz) <sub>2</sub> (4-Mepy) <sub>4</sub> ] <sup>a</sup>	4.1324 (4)	178.20 (1), 116.68 (8)	2.267 (1), 2.329 (1)	2.112 (1), 2.132 (1)
[Mn <sub>2</sub> (μ-tolf) <sub>2</sub> (κ <sup>2</sup> -tolf) <sub>2</sub> (bipyam) <sub>2</sub> ] <sup>b</sup>	4.548	150.37 (2), 139.28 (2)	2.215 (2), 2.363 (2)	2.087 (2), 2.102 (2)
[Mn <sub>2</sub> (μ-OAc) <sub>2</sub> (κ <sup>2</sup> -OAc) <sub>2</sub> (L1) <sub>2</sub> ] <sup>c</sup>	4.160	151.50 (3), 127.72 (3)	2.280 (3), 2.294 (3)	2.142 (5), 2.280 (4)
[Mn <sub>2</sub> (μ-OBz) <sub>2</sub> (κ <sup>2</sup> -OBz) <sub>2</sub> (py) <sub>4</sub> ] <sup>d</sup>	4.531	149.32 (1), 133.39 (1)	2.305 (1), 2.232 (1)	2.109 (1), 2.094 (1)
[Mn <sub>2</sub> (μ-DFBz) <sub>2</sub> (κ <sup>2</sup> -DFBz) <sub>2</sub> (THF) <sub>2</sub> ] <sup>e</sup>	4.299	155.76 (3), 131.40 (3)	2.194 (3), 2.226 (3)	2.061 (4), 2.040 (3)

Notes: (a) present work (HNBz is 4-nitrobenzoic acid and 4-Mepy is 4-methylpyridine); (b) Zampakou *et al.* (2014) (Htolf is tolfenamic acid and bipyam is 2,2'-bipyridylamine); (c) Mukherjee *et al.* (2004) (HOAc is acetic acid and L1 is 1,8-bis(4-pyridylethynyl)anthracene); (d) Ran *et al.* (2006) (HOBz is benzoic acid); (e) Sivanesan *et al.* (2014) (HDFBz is 2,6-di(4-fluorophenyl)benzoic acid).


**Figure 2**  
 Packing diagram showing C–H···O interactions (dashed lines) in the crystal structure of **I**.

**Figure 3**  
 Intermolecular C–H···π interactions observed between phenyl-ring H atoms of NBz and phenyl ring π-systems of 4-Mepy in the crystal structure of **I**.

among the listed parameters is the near linearity of one of the the <Mn–O–C angles [178.20 (1)° and 116.68 (8)°] observed in the crystal structure of **I**. For its most closely related known

**Table 4**  
Experimental details.

Crystal data	
Chemical formula	[Mn <sub>2</sub> (C <sub>7</sub> H <sub>4</sub> NO <sub>4</sub> ) <sub>4</sub> (C <sub>6</sub> H <sub>7</sub> N) <sub>4</sub> ]
<i>M<sub>r</sub></i>	1146.83
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.8337 (3), 12.4240 (4), 12.9995 (4)
$\alpha$ , $\beta$ , $\gamma$ (°)	94.357 (1), 99.607 (1), 107.270 (1)
<i>V</i> (Å <sup>3</sup> )	1331.28 (7)
<i>Z</i>	1
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.55
Crystal size (mm)	0.28 × 0.24 × 0.18
Data collection	
Diffractometer	Bruker SMART APEXII CCD
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 2012)
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	31721, 7705, 6595
<i>R</i> <sub>int</sub>	0.022
(sin $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.704
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.036, 0.110, 1.03
No. of reflections	7705
No. of parameters	354
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.33, -0.25

Computer programs: *APEX2* (Bruker, 2012), *SAINT* (Bruker, 2012), *SHELXT2013* (Sheldrick, 2015a), *SHELXL2013* (Sheldrick, 2015b), *ORTEP-3 for Windows* (Farrugia, 2012), *WinGX* (Farrugia, 2012), *PLATON* (Spek, 2009), *DIAMOND* (Brandenburg, 2006) and *pubCIF* (Westrip, 2010).

species, [Mn<sub>2</sub>( $\mu$ -OBz)<sub>2</sub>( $\kappa^2$ -OBz)<sub>2</sub>(py)<sub>4</sub>] (Ran *et al.* 2006), the corresponding angles are 149.32 (1) and 133.39 (1)°, respectively. The more pronounced asymmetry of bonding in the bridging carboxylato groups in **I** may be ascribed to steric factors and also to differences in molecular packing effects resulting from the presence of substituents on the aromatic rings of both types of ligand.

## 5. Synthesis and crystallization

A mixture of MnSO<sub>4</sub>·H<sub>2</sub>O (0.845 g, 5 mmol), NaNBz (1.89 g, 10 mmol) and 4-Mepy (1 ml, 10 mmol) was stirred mechanically in water (20 ml) at room temperature for 4 h. The yellow precipitate that appeared was washed thoroughly with water and then with methanol before being dried in a vacuum desiccator over fused CaCl<sub>2</sub>. Yield: 2.58 g (85% based on Mn). Light-yellow transparent crystals of **I** suitable for X-ray analysis were obtained in 2–3 days from a solution prepared by mixing 2 ml of a methanolic solution of NaNBz (1 mmol) with a solution (2 ml) of MnSO<sub>4</sub>·H<sub>2</sub>O (0.5 mmol) containing 4-Mepy (1 mmol) in methanol/water (1:1 *v/v*). Analysis calculated for C<sub>48</sub>H<sub>36</sub>N<sub>8</sub>O<sub>16</sub>Mn<sub>2</sub>: C, 52.84%; H, 3.30%; N, 10.27%; found: C, 52.04%; H, 3.02%; N, 9.8%;  $\mu_{\text{eff}}$  (295 K)/Mn = 5.36 BM.

The method developed by us to prepare **I** is simpler than the reported procedure for preparing the related species [Mn<sub>2</sub>( $\mu$ -OBz)<sub>2</sub>( $\kappa^2$ -OBz)<sub>2</sub>(py)<sub>4</sub>] (Ran *et al.* 2006) and the present

method can be easily extended to obtain other analogous manganese(II) complexes.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. Hydrogen atoms were positioned geometrically (aromatic C–H = 0.93 Å, methyl C–H = 0.96 Å) and were included in the refinement in the riding-model approximation, with *U*<sub>iso</sub>(H) set at 1.2–1.5*U*<sub>eq</sub>(C).

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## supporting information

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## Crystal structure of bis( $\mu$ -4-nitrobenzoato- $\kappa^2$ O:O')bis[bis(4-methylpyridine- $\kappa$ N)(4-nitrobenzoato- $\kappa^2$ O,O')manganese(II)]

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### Computing details

Data collection: *SMART* (Bruker, 2012); cell refinement: *SMART* (Bruker, 2012); data reduction: *SAINTE* (Bruker, 2012); program(s) used to solve structure: *SHELXT2013* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012), *PLATON* (Spek, 2009) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *pubCIF* (Westrip, 2010).

### Bis( $\mu$ -4-nitrobenzoato- $\kappa^2$ O:O')bis[bis(4-methylpyridine- $\kappa$ N)(4-nitrobenzoato- $\kappa^2$ O,O')manganese(II)]

#### Crystal data

$[\text{Mn}_2(\text{C}_7\text{H}_4\text{NO}_4)_4(\text{C}_6\text{H}_7\text{N})_4]$

$M_r = 1146.83$

Triclinic,  $P\bar{1}$

$a = 8.8337$  (3) Å

$b = 12.4240$  (4) Å

$c = 12.9995$  (4) Å

$\alpha = 94.357$  (1)°

$\beta = 99.607$  (1)°

$\gamma = 107.270$  (1)°

$V = 1331.28$  (7) Å<sup>3</sup>

$Z = 1$

$F(000) = 590$

$D_x = 1.430$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 31721 reflections

$\theta = 2.5\text{--}30.0^\circ$

$\mu = 0.55$  mm<sup>-1</sup>

$T = 293$  K

Prism, yellow

$0.28 \times 0.24 \times 0.18$  mm

#### Data collection

Bruker SMART APEXII CCD

diffractometer

Radiation source: Sealed X-ray Tube

phi and  $\omega$  scans

Absorption correction: multi-scan

(SADABS; Bruker, 2012)

7705 independent reflections

6595 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.022$

$\theta_{\text{max}} = 30.0^\circ$ ,  $\theta_{\text{min}} = 2.5^\circ$

$h = -12 \rightarrow 12$

$k = -15 \rightarrow 17$

$l = -18 \rightarrow 18$

31721 measured reflections

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.110$

$S = 1.03$

7705 reflections

354 parameters

0 restraints

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0619P)^2 + 0.2308P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$

$\Delta\rho_{\text{max}} = 0.33$  e Å<sup>-3</sup>

$\Delta\rho_{\text{min}} = -0.25$  e Å<sup>-3</sup>

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Mn1	0.88391 (2)	0.07843 (2)	0.09236 (2)	0.03854 (7)
N1	1.00416 (16)	0.02174 (10)	0.23777 (10)	0.0501 (3)
N2	0.77004 (14)	0.13048 (10)	-0.05684 (9)	0.0468 (2)
C1	0.62898 (18)	0.06804 (13)	-0.11848 (12)	0.0520 (3)
H1	0.5724	-0.0002	-0.0982	0.062*
C2	0.5640 (2)	0.09997 (16)	-0.21003 (13)	0.0605 (4)
H2	0.4657	0.0536	-0.2502	0.073*
C4	0.7884 (2)	0.26701 (18)	-0.17717 (16)	0.0701 (5)
H4	0.8456	0.3367	-0.1947	0.084*
C5	0.8460 (2)	0.22967 (16)	-0.08665 (15)	0.0629 (4)
H5	0.9425	0.2755	-0.0440	0.075*
C3	0.6444 (2)	0.20080 (17)	-0.24265 (13)	0.0617 (4)
C11	0.9461 (3)	-0.08110 (14)	0.26426 (14)	0.0697 (5)
H10	0.8573	-0.1330	0.2190	0.084*
C7	1.1308 (2)	0.09397 (17)	0.30492 (16)	0.0734 (5)
H6	1.1740	0.1670	0.2885	0.088*
C9	1.1406 (3)	-0.04168 (18)	0.42468 (14)	0.0672 (4)
C8	1.2006 (3)	0.0656 (2)	0.39734 (17)	0.0845 (6)
H7	1.2888	0.1191	0.4416	0.101*
C10	1.0100 (3)	-0.11549 (16)	0.35530 (16)	0.0805 (6)
H9	0.9644	-0.1890	0.3698	0.097*
O2	0.94565 (14)	0.25815 (9)	0.17435 (9)	0.0561 (3)
O1	0.72129 (14)	0.13417 (9)	0.19520 (9)	0.0562 (3)
C13	0.82251 (17)	0.23111 (11)	0.21416 (10)	0.0435 (3)
C14	0.79795 (17)	0.32023 (11)	0.28965 (10)	0.0432 (3)
C6	0.5793 (4)	0.2384 (3)	-0.34382 (18)	0.0925 (7)
H13A	0.6391	0.3164	-0.3456	0.139*
H13B	0.4672	0.2312	-0.3475	0.139*
H13C	0.5901	0.1917	-0.4027	0.139*
C15	0.9106 (2)	0.42822 (13)	0.31145 (12)	0.0552 (3)
H18	0.9995	0.4456	0.2790	0.066*
C19	0.6653 (2)	0.29372 (14)	0.33749 (12)	0.0529 (3)
H14	0.5888	0.2218	0.3207	0.063*
C17	0.7585 (3)	0.47953 (16)	0.43073 (12)	0.0646 (4)
C16	0.8904 (3)	0.51050 (14)	0.38215 (14)	0.0668 (5)
H17	0.9631	0.5839	0.3963	0.080*
C18	0.6454 (2)	0.37356 (17)	0.41029 (14)	0.0639 (4)
H15	0.5581	0.3557	0.4442	0.077*
O3	1.11026 (12)	0.12734 (10)	0.04622 (11)	0.0629 (3)

O4	0.72018 (12)	-0.08983 (8)	0.04584 (8)	0.0502 (2)
C20	0.75917 (14)	-0.15375 (10)	-0.01671 (9)	0.0371 (2)
C12	1.2107 (4)	-0.0756 (3)	0.52625 (19)	0.0975 (8)
H20A	1.3259	-0.0563	0.5335	0.146*
H20B	1.1647	-0.1561	0.5256	0.146*
H20C	1.1861	-0.0360	0.5843	0.146*
O7	0.6629 (3)	0.5287 (2)	0.57701 (14)	0.1149 (7)
N4	0.7411 (3)	0.56459 (19)	0.50990 (14)	0.0906 (6)
O8	0.8087 (4)	0.66309 (18)	0.50708 (18)	0.1545 (11)
C21	0.63841 (13)	-0.26916 (9)	-0.05861 (9)	0.0351 (2)
C22	0.48941 (15)	-0.30059 (11)	-0.02844 (11)	0.0436 (3)
H25	0.4642	-0.2502	0.0173	0.052*
C26	0.67611 (16)	-0.34382 (11)	-0.12700 (11)	0.0464 (3)
H26	0.7759	-0.3226	-0.1472	0.056*
C24	0.41926 (16)	-0.47908 (11)	-0.13350 (11)	0.0450 (3)
C23	0.37778 (16)	-0.40726 (12)	-0.06645 (12)	0.0488 (3)
H29	0.2776	-0.4292	-0.0468	0.059*
C25	0.56483 (18)	-0.45045 (12)	-0.16547 (12)	0.0519 (3)
H27	0.5885	-0.5011	-0.2118	0.062*
N3	0.30228 (18)	-0.59308 (11)	-0.17352 (12)	0.0619 (4)
O6	0.17528 (17)	-0.61927 (12)	-0.14453 (14)	0.0885 (5)
O5	0.3380 (2)	-0.65513 (12)	-0.23506 (16)	0.1027 (6)

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Mn1	0.03514 (10)	0.03326 (10)	0.04133 (11)	0.00359 (7)	0.00826 (7)	-0.00303 (7)
N1	0.0530 (6)	0.0418 (6)	0.0483 (6)	0.0099 (5)	0.0026 (5)	-0.0001 (5)
N2	0.0387 (5)	0.0488 (6)	0.0485 (6)	0.0070 (5)	0.0100 (4)	0.0052 (5)
C1	0.0444 (7)	0.0508 (8)	0.0530 (7)	0.0058 (6)	0.0067 (6)	0.0035 (6)
C2	0.0559 (9)	0.0651 (10)	0.0518 (8)	0.0134 (7)	0.0004 (6)	0.0009 (7)
C4	0.0625 (10)	0.0703 (11)	0.0750 (11)	0.0090 (8)	0.0192 (8)	0.0299 (9)
C5	0.0465 (8)	0.0635 (10)	0.0671 (10)	0.0002 (7)	0.0075 (7)	0.0163 (8)
C3	0.0668 (10)	0.0764 (11)	0.0482 (8)	0.0293 (9)	0.0148 (7)	0.0126 (7)
C11	0.0932 (13)	0.0409 (7)	0.0563 (9)	0.0073 (8)	-0.0085 (9)	0.0009 (6)
C7	0.0692 (11)	0.0588 (10)	0.0678 (10)	-0.0029 (8)	-0.0121 (8)	0.0113 (8)
C9	0.0855 (12)	0.0702 (11)	0.0515 (8)	0.0401 (9)	0.0027 (8)	0.0043 (7)
C8	0.0787 (13)	0.0807 (13)	0.0687 (11)	0.0079 (10)	-0.0214 (10)	0.0055 (10)
C10	0.1193 (18)	0.0469 (9)	0.0643 (10)	0.0218 (10)	-0.0049 (11)	0.0090 (8)
O2	0.0551 (6)	0.0512 (6)	0.0608 (6)	0.0120 (5)	0.0226 (5)	-0.0055 (5)
O1	0.0568 (6)	0.0422 (5)	0.0649 (6)	0.0086 (4)	0.0177 (5)	-0.0055 (4)
C13	0.0488 (7)	0.0408 (6)	0.0414 (6)	0.0162 (5)	0.0085 (5)	0.0004 (5)
C14	0.0519 (7)	0.0416 (6)	0.0390 (6)	0.0203 (5)	0.0080 (5)	0.0033 (5)
C6	0.1128 (19)	0.1115 (19)	0.0593 (11)	0.0439 (15)	0.0106 (11)	0.0272 (12)
C15	0.0659 (9)	0.0451 (7)	0.0507 (7)	0.0128 (7)	0.0126 (7)	-0.0009 (6)
C19	0.0585 (8)	0.0535 (8)	0.0534 (7)	0.0251 (7)	0.0162 (6)	0.0064 (6)
C17	0.0943 (13)	0.0664 (10)	0.0448 (7)	0.0498 (10)	0.0064 (8)	-0.0035 (7)
C16	0.0943 (13)	0.0436 (8)	0.0567 (9)	0.0219 (8)	0.0038 (9)	-0.0056 (6)



C18	0.0770 (11)	0.0768 (11)	0.0540 (8)	0.0444 (10)	0.0213 (8)	0.0061 (8)
O3	0.0379 (5)	0.0517 (6)	0.0875 (8)	-0.0050 (4)	0.0227 (5)	-0.0058 (5)
O4	0.0497 (5)	0.0379 (5)	0.0530 (5)	0.0022 (4)	0.0110 (4)	-0.0086 (4)
C20	0.0335 (5)	0.0327 (5)	0.0383 (5)	0.0035 (4)	0.0020 (4)	0.0020 (4)
C12	0.123 (2)	0.1125 (19)	0.0656 (12)	0.0615 (17)	-0.0041 (13)	0.0184 (12)
O7	0.1355 (16)	0.1494 (18)	0.0750 (10)	0.0728 (14)	0.0291 (10)	-0.0241 (11)
N4	0.1326 (17)	0.0931 (14)	0.0602 (9)	0.0709 (13)	0.0042 (10)	-0.0155 (9)
O8	0.302 (4)	0.0794 (12)	0.1036 (15)	0.0949 (18)	0.0474 (18)	-0.0120 (10)
C21	0.0308 (5)	0.0315 (5)	0.0377 (5)	0.0042 (4)	0.0042 (4)	0.0016 (4)
C22	0.0354 (5)	0.0406 (6)	0.0504 (7)	0.0056 (5)	0.0109 (5)	0.0000 (5)
C26	0.0397 (6)	0.0387 (6)	0.0547 (7)	0.0031 (5)	0.0150 (5)	-0.0045 (5)
C24	0.0412 (6)	0.0326 (5)	0.0486 (6)	-0.0010 (5)	-0.0018 (5)	0.0048 (5)
C23	0.0336 (6)	0.0460 (7)	0.0588 (8)	0.0003 (5)	0.0096 (5)	0.0070 (6)
C25	0.0540 (8)	0.0366 (6)	0.0567 (8)	0.0053 (5)	0.0114 (6)	-0.0079 (5)
N3	0.0581 (8)	0.0389 (6)	0.0681 (8)	-0.0058 (5)	-0.0046 (6)	0.0061 (6)
O6	0.0597 (7)	0.0637 (8)	0.1117 (12)	-0.0219 (6)	0.0109 (7)	0.0083 (8)
O5	0.1001 (12)	0.0485 (7)	0.1288 (14)	-0.0105 (7)	0.0213 (10)	-0.0325 (8)

*Geometric parameters (Å, °)*

Mn1—O3	2.1122 (10)	C6—H13A	0.9600
Mn1—O4	2.1328 (9)	C6—H13B	0.9600
Mn1—N2	2.2621 (12)	C6—H13C	0.9600
Mn1—O2	2.2672 (11)	C15—C16	1.394 (2)
Mn1—N1	2.2746 (13)	C15—H18	0.9300
Mn1—O1	2.3285 (11)	C19—C18	1.388 (2)
Mn1—C13	2.6155 (13)	C19—H14	0.9300
Mn1—Mn1 <sup>i</sup>	4.1324 (4)	C17—C18	1.371 (3)
N1—C11	1.323 (2)	C17—C16	1.385 (3)
N1—C7	1.333 (2)	C17—N4	1.478 (2)
N2—C5	1.337 (2)	C16—H17	0.9300
N2—C1	1.3398 (18)	C18—H15	0.9300
C1—C2	1.372 (2)	O3—C20 <sup>i</sup>	1.2358 (15)
C1—H1	0.9300	O4—C20	1.2523 (16)
C2—C3	1.381 (3)	C20—O3 <sup>i</sup>	1.2358 (15)
C2—H2	0.9300	C20—C21	1.5065 (15)
C4—C5	1.372 (3)	C12—H20A	0.9600
C4—C3	1.389 (3)	C12—H20B	0.9600
C4—H4	0.9300	C12—H20C	0.9600
C5—H5	0.9300	O7—N4	1.230 (3)
C3—C6	1.510 (3)	N4—O8	1.198 (3)
C11—C10	1.378 (3)	C21—C26	1.3852 (17)
C11—H10	0.9300	C21—C22	1.3889 (16)
C7—C8	1.377 (3)	C22—C23	1.3909 (18)
C7—H6	0.9300	C22—H25	0.9300
C9—C10	1.373 (3)	C26—C25	1.3905 (17)
C9—C8	1.378 (3)	C26—H26	0.9300
C9—C12	1.507 (3)	C24—C23	1.369 (2)

C8—H7	0.9300	C24—C25	1.372 (2)
C10—H9	0.9300	C24—N3	1.4779 (16)
O2—C13	1.2495 (17)	C23—H29	0.9300
O1—C13	1.2460 (17)	C25—H27	0.9300
C13—C14	1.5115 (18)	N3—O6	1.204 (2)
C14—C19	1.383 (2)	N3—O5	1.212 (2)
C14—C15	1.388 (2)		
O3—Mn1—O4	120.82 (4)	O1—C13—O2	122.88 (12)
O3—Mn1—N2	89.91 (5)	O1—C13—C14	119.14 (12)
O4—Mn1—N2	89.04 (4)	O2—C13—C14	117.98 (12)
O3—Mn1—O2	88.38 (4)	O1—C13—Mn1	62.88 (7)
O4—Mn1—O2	150.77 (4)	O2—C13—Mn1	60.06 (7)
N2—Mn1—O2	89.75 (5)	C14—C13—Mn1	176.03 (10)
O3—Mn1—N1	88.27 (5)	C19—C14—C15	120.42 (13)
O4—Mn1—N1	90.22 (4)	C19—C14—C13	120.16 (13)
N2—Mn1—N1	177.33 (4)	C15—C14—C13	119.42 (13)
O2—Mn1—N1	92.15 (4)	C3—C6—H13A	109.5
O3—Mn1—O1	144.94 (4)	C3—C6—H13B	109.5
O4—Mn1—O1	94.05 (4)	H13A—C6—H13B	109.5
N2—Mn1—O1	94.59 (4)	C3—C6—H13C	109.5
O2—Mn1—O1	56.95 (4)	H13A—C6—H13C	109.5
N1—Mn1—O1	88.02 (5)	H13B—C6—H13C	109.5
O3—Mn1—C13	116.67 (4)	C14—C15—C16	119.86 (16)
O4—Mn1—C13	122.47 (4)	C14—C15—H18	120.1
N2—Mn1—C13	93.26 (4)	C16—C15—H18	120.1
O2—Mn1—C13	28.53 (4)	C14—C19—C18	120.55 (16)
N1—Mn1—C13	89.30 (4)	C14—C19—H14	119.7
O1—Mn1—C13	28.44 (4)	C18—C19—H14	119.7
O3—Mn1—Mn1 <sup>i</sup>	44.99 (3)	C18—C17—C16	123.28 (14)
O4—Mn1—Mn1 <sup>i</sup>	75.87 (3)	C18—C17—N4	118.56 (19)
N2—Mn1—Mn1 <sup>i</sup>	87.25 (3)	C16—C17—N4	118.15 (19)
O2—Mn1—Mn1 <sup>i</sup>	133.23 (3)	C17—C16—C15	117.91 (16)
N1—Mn1—Mn1 <sup>i</sup>	90.09 (3)	C17—C16—H17	121.0
O1—Mn1—Mn1 <sup>i</sup>	169.73 (3)	C15—C16—H17	121.0
C13—Mn1—Mn1 <sup>i</sup>	161.66 (3)	C17—C18—C19	117.93 (17)
C11—N1—C7	116.50 (15)	C17—C18—H15	121.0
C11—N1—Mn1	122.21 (11)	C19—C18—H15	121.0
C7—N1—Mn1	121.12 (11)	C20 <sup>i</sup> —O3—Mn1	178.20 (10)
C5—N2—C1	116.88 (14)	C20—O4—Mn1	116.68 (8)
C5—N2—Mn1	118.98 (10)	O3 <sup>i</sup> —C20—O4	123.88 (11)
C1—N2—Mn1	124.14 (10)	O3 <sup>i</sup> —C20—C21	118.52 (11)
N2—C1—C2	123.16 (15)	O4—C20—C21	117.61 (10)
N2—C1—H1	118.4	C9—C12—H20A	109.5
C2—C1—H1	118.4	C9—C12—H20B	109.5
C1—C2—C3	120.12 (15)	H20A—C12—H20B	109.5
C1—C2—H2	119.9	C9—C12—H20C	109.5
C3—C2—H2	119.9	H20A—C12—H20C	109.5

C5—C4—C3	119.99 (16)	H20B—C12—H20C	109.5
C5—C4—H4	120.0	O8—N4—O7	124.4 (2)
C3—C4—H4	120.0	O8—N4—C17	118.2 (2)
N2—C5—C4	123.14 (16)	O7—N4—C17	117.4 (2)
N2—C5—H5	118.4	C26—C21—C22	120.08 (11)
C4—C5—H5	118.4	C26—C21—C20	120.01 (10)
C2—C3—C4	116.67 (15)	C22—C21—C20	119.91 (11)
C2—C3—C6	122.02 (18)	C21—C22—C23	120.16 (12)
C4—C3—C6	121.31 (19)	C21—C22—H25	119.9
N1—C11—C10	123.56 (17)	C23—C22—H25	119.9
N1—C11—H10	118.2	C21—C26—C25	120.02 (12)
C10—C11—H10	118.2	C21—C26—H26	120.0
N1—C7—C8	123.10 (17)	C25—C26—H26	120.0
N1—C7—H6	118.5	C23—C24—C25	123.12 (11)
C8—C7—H6	118.5	C23—C24—N3	118.70 (13)
C10—C9—C8	116.18 (16)	C25—C24—N3	118.17 (14)
C10—C9—C12	121.6 (2)	C24—C23—C22	118.22 (12)
C8—C9—C12	122.2 (2)	C24—C23—H29	120.9
C7—C8—C9	120.40 (18)	C22—C23—H29	120.9
C7—C8—H7	119.8	C24—C25—C26	118.39 (13)
C9—C8—H7	119.8	C24—C25—H27	120.8
C9—C10—C11	120.27 (18)	C26—C25—H27	120.8
C9—C10—H9	119.9	O6—N3—O5	123.18 (15)
C11—C10—H9	119.9	O6—N3—C24	118.46 (16)
C13—O2—Mn1	91.41 (8)	O5—N3—C24	118.36 (15)
C13—O1—Mn1	88.68 (8)		

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

#### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

C<sub>g</sub> is the centroid of the N2/C1—C5 ring.

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
C1—H1 $\cdots$ O4	0.93	2.61	3.172 (2)	119
C2—H2 $\cdots$ O1 <sup>ii</sup>	0.93	2.65	3.278 (2)	125
C11—H10 $\cdots$ O4	0.93	2.55	3.161 (2)	124
C22—H25 $\cdots$ C <sub>g</sub> <sup>ii</sup>	0.93	2.80	3.6844 (16)	160

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