

## Poly[( $\mu_4$ -2,5-dimethoxybenzene-1,4-dicarboxylato)manganese(II)] and its zinc(II) analogue: three-dimensional coordination polymers containing unusually coordinated metal centres

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Received 3 September 2010

Accepted 12 November 2010

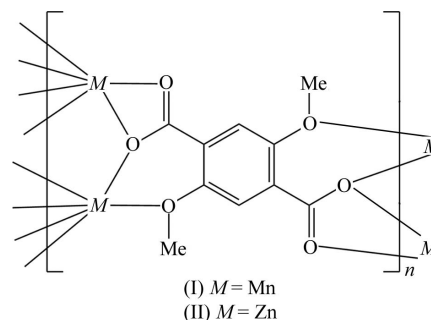
Online 8 December 2010

The title compounds,  $[\text{Mn}(\text{C}_{10}\text{H}_8\text{O}_6)]_n$  and  $[\text{Zn}(\text{C}_{10}\text{H}_8\text{O}_6)]_n$ , are isomorphous coordination polymers prepared from 2,5-dimethoxyterephthalic acid ( $\text{H}_2\text{dmt}$ ) and the respective metal(II) salts. Both complexes form three-dimensional metal–organic frameworks with each  $M^{\text{II}}$  centre bridged by four 2,5-dimethoxyterephthalate ( $\text{dmt}^{2-}$ ) anions, resulting in the same type of network topology. The asymmetric unit consists of one  $M^{\text{II}}$  cation on a twofold axis and one half of a  $\text{dmt}^{2-}$  anion (located on a centre of inversion). In the crystal structure, the  $M^{\text{II}}$  centres are coordinated in a rather unusual way, as there is a distorted tetrahedral inner coordination sphere formed by four carboxylate O atoms of four different  $\text{dmt}^{2-}$  anions, and an additional outer coordination sphere formed by two methoxy and two carboxylate O atoms, with each of the O atoms belonging to one of the four different  $\text{dmt}^{2-}$  anions forming the inner coordination sphere. Consideration of both coordination spheres results in a super-dodecahedral coordination geometry for the  $M^{\text{II}}$  centres. Besides the numerous  $M^{\text{II}} \cdots \text{O}$  interactions, both structures are further stabilized by weak  $\text{C}—\text{H} \cdots \text{O}$  contacts.

### Comment

Metal–organic coordination polymers (MOCPs) are crystalline frameworks composed of metal ions or clusters of metal ions called secondary building units (SBUs) and organic molecules called linkers, to form one-, two- or three-dimensional structures possessing cavities (Li *et al.*, 1999). In specific cases, knowledge of the SBU and linker geometries, in conjunction with their interaction principles, allows the prediction of network topologies and thus supports rational framework design. It is known that specific reaction conditions

such as temperature, solvent and moisture can influence SBU formation (Hausdorf *et al.*, 2008). Nevertheless, generation of SBUs subject to linker properties has only rarely been investigated (Choi *et al.*, 2009).

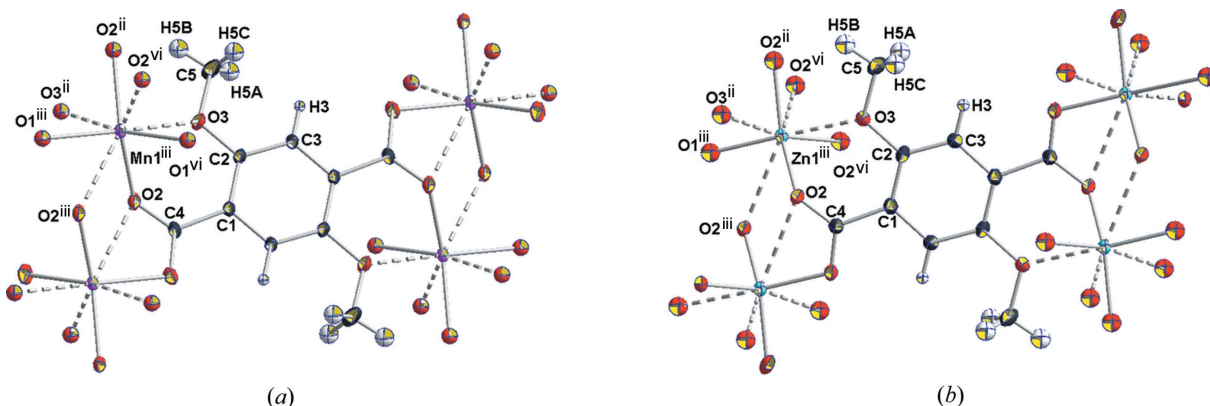


While the reaction of 2,5-dihydroxyterephthalic acid and  $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  [carried out under conditions (Tranchemontagne *et al.*, 2008) comparable with those used here] leads to MOF-74-type networks (Rosi *et al.*, 2005), the reaction of 2,5-di-*n*-propoxyterephthalic acid and  $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  gives rise to IRMOF-type structures (Eddaoudi *et al.*, 2002). However, three-dimensional coordination polymers containing the  $\text{dmt}^{2-}$  anion as a linker with  $\text{Zn}^{\text{II}}$  or  $\text{Mn}^{\text{II}}$  as metal ions for the SBU have not been reported so far. This prompted us to use the  $\text{dmt}^{2-}$  anion as a rigid dicarboxylate with small weakly coordinating substituents for our investigations of the formation of appropriate new types of MOCPs.

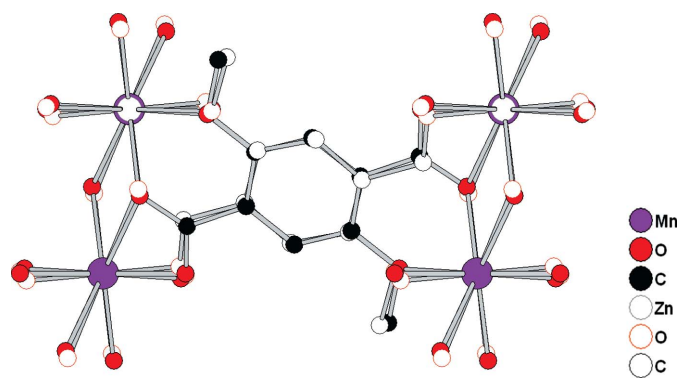
The title compounds,  $[\text{Mn}(\text{dmt})]_n$  (I), and  $[\text{Zn}(\text{dmt})]_n$  (II), crystallize in the monoclinic space group  $C2/c$ , with asymmetric units containing one  $M^{\text{II}}$  cation ( $M = \text{Mn}$  or  $\text{Zn}$ ) and one half of a  $\text{dmt}^{2-}$  anion (Fig. 1). Indeed, the two compounds are isomorphous, which is shown in the molecular overlay plot in Fig. 2. Besides a slight difference in the monoclinic angle  $\beta$ , the unit-cell dimensions do not differ significantly from each other.

As shown in Fig. 1, each of the  $M^{\text{II}}$  cations adopts a distorted  $M^{\text{II}}\text{O}_4$  tetrahedral geometry, coordinated by four O atoms from four different  $\text{dmt}^{2-}$  anions. The  $\text{Mn1—O1}$  and  $\text{Mn1—O2}$  bond lengths of 2.1391 (6) and 2.0761 (5) Å, respectively, in (I) are in accordance with those reported for related manganese(II) terephthalates [ $\text{Mn—O} = 2.100$  (4)–2.188 (3) Å; Xu *et al.*, 2010; Luo *et al.*, 2008]. The corresponding  $\text{O—Mn—O}$  angles range from 93.73 (2) to 141.52 (3)°, thus deviating considerably from the ideal value of 109.4° for a tetrahedral coordination sphere. The  $\text{Zn—O}$  bond lengths in (II) range from 2.0023 (13) Å for  $\text{Zn1—O1}$  to 1.9547 (13) Å for  $\text{Zn1—O2}$  and do not vary significantly from literature values for related zinc(II) terephthalate-based MOCPs [ $\text{Zn—O} = 1.935$  (2)–2.104 (5) Å; Higuchi *et al.*, 2009; Wang *et al.*, 2008]. However, the distortion of the  $\text{O—Zn—O}$  angles from ideal tetrahedral geometry in (II), ranging from 99.51 (5) to 137.03 (8)°, is smaller than in (I). These structural differences between (I) and (II) may be caused by the different ionic radii of the  $\text{Mn}^{\text{II}}$  and  $\text{Zn}^{\text{II}}$  cations (0.91 and 0.83 Å, respectively; Riedel, 2004).

The unusual values for the  $\text{O—M}^{\text{II}}—\text{O}$  bond angles mentioned above can be explained by the existence of a



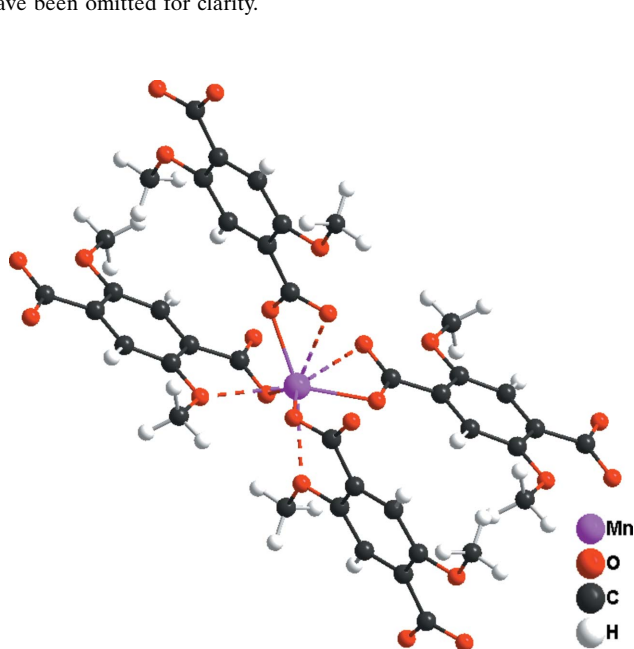
**Figure 1**  
The asymmetric units of (a) (I) and (b) (II), showing the atom-labelling schemes. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (ii)  $-x + 2, y, -z + \frac{1}{2}$ ; (iii)  $-x + 2, -y, -z + 1$ ; (vi)  $x, -y, z + \frac{1}{2}$ ]



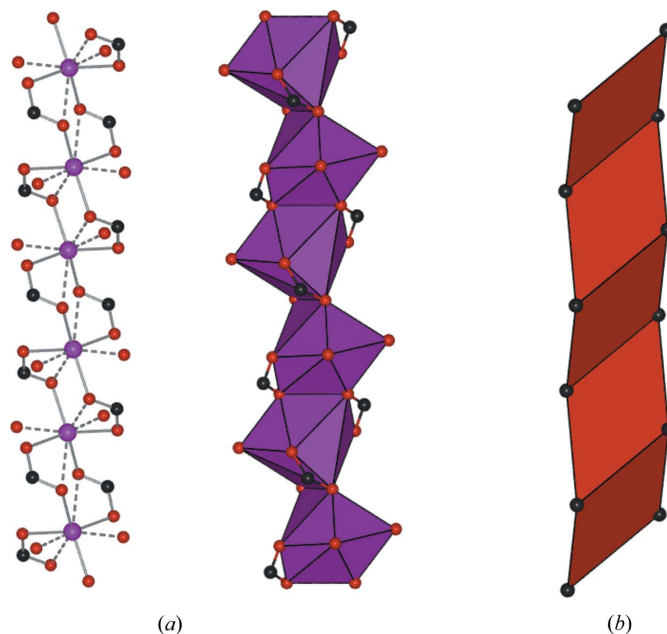
**Figure 2**  
A molecular overlay of the asymmetric units of (I) and (II), showing only minor differences in the atom positions. The atoms of (I) are shown as shaded balls and those of (II) as white balls with shaded borders. H atoms have been omitted for clarity.

second coordination sphere formed by weak interactions between the  $M^{II}$  cations and the O atoms of the methoxy and carboxylate groups (Fig. 1). This leads to a distorted  $[M^{II}O_4(O)_2(OMe)_2]$  super dodecahedron (Fig. 3), where the methoxy O atoms are located in positions *trans* to each other, while the two bidentate and two monodentate carboxylates coordinate in positions *cis* to each other (Fig. 4).

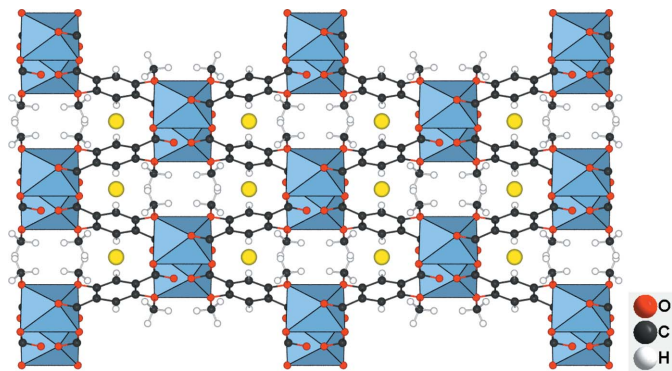
The bond lengths for  $M-OMe$  [ $Mn1-O3^{iii} = 2.5596(6) \text{ \AA}$  and  $Zn1-O3^{iii} = 2.6224(17) \text{ \AA}$ ; symmetry code: (iii)  $-x + 2, -y, -z + 1$ ] and  $M-O2'$  [ $Mn1-O2^{iv} = 2.7570(6) \text{ \AA}$  and  $Zn1-O2^{iv} = 2.8772(16) \text{ \AA}$ ; symmetry code: (iv)  $-x + 2, y, -z + \frac{1}{2}$ ] reveal that these bonds are much weaker than the  $M-O$  bonds of the inner coordination sphere. Similar coordination modes have already been reported for  $Cd^{II}$



**Figure 3**  
The super-dodecahedral coordination spheres of  $MnO_4(O)_2(OMe)_2$ , showing the coordination modes of the anions. The  $M^{II}-O$  bonds of the second coordination spheres are shown as dashed lines. The atom coordinates from (I) were exemplarily used to create the diagram.

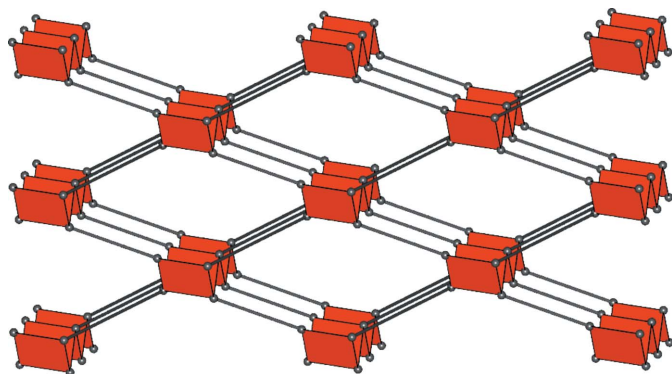


**Figure 4**  
(a) The one-dimensional chains of  $[Mn-(\mu-CO_2)_2-Mn]_n$ . The  $M^{II}-O$  bonds of the second coordination spheres are shown as dashed lines. (b) The inorganic  $M^{II}O_8$  SBUs are chains of edge-sharing dodecahedra, in which the C atoms can be connected to form a zigzag ladder. The atom coordinates from (I) were exemplarily used to create the diagram.



**Figure 5**

A view of the network of (I) and (II) along the  $c$  axis with shaded  $M^{\text{II}}\text{O}_4(\text{O})_2(\text{OMe})_2$  super dodecahedra. The large balls show the accessible pores. The atom coordinates from (I) were used as the example to create the diagram.



**Figure 6**

The topology of the network, reduced to a simple SBU-and-linker geometry model. The  $M^{\text{II}}\text{O}_4(\text{OMe})_2$  SBUs are reduced to rods of shaded quadrangles and the  $\text{dmt}^{2-}$  linkers are represented by thin grey rods.

complexes (Li *et al.*, 2008). The  $M^{\text{II}}\text{O}_8$  super dodecahedra are edge-sharing, giving a one-dimensional chain along the  $c$  axis (Fig. 4). Two adjacent one-dimensional chains are interconnected by  $\text{dmt}^{2-}$  anions to obtain a three-dimensional coordination network, with shortest  $\text{Mn1}^{\text{I}} \cdots \text{Mn1}^{\text{V}}$  and  $\text{Zn1}^{\text{I}} \cdots \text{Zn1}^{\text{V}}$  distances [symmetry code: (v)  $-x + 2, -y - 1, -z$ ] between the one-dimensional chains of 8.0793 (3) and 8.0552 (2) Å, respectively. Apart from these  $M^{\text{II}}-\text{O}$  interactions, there are weak intermolecular  $\text{C}-\text{H} \cdots \text{O}$  hydrogen-bonding interactions in both networks, involving  $\text{C3}-\text{H3} \cdots \text{O1}^{\text{i}}$  and  $\text{C5}-\text{H5B} \cdots \text{O2}^{\text{ii}}$  for both (I) and (II), contributing to the stabilization of the crystal structures (symmetry codes are given in Tables 1 and 2).

One-dimensional rhombic channels of  $9.1 \times 13.1$  Å in cross-section (measured between atoms in opposite corners) are located along the  $c$  axis in the networks of (I) and (II). The methoxy groups point inside these channels and subdivide them into two smaller pores, shown as balls in the network structure (Fig. 5). Taking the van der Waals radii into account, their diameter is reduced to about 1.2 Å, which is much too small for the uptake of any solvent molecules or nitrogen. A better understanding of the network structures of (I) and (II) can be achieved by a topological investigation, reducing

complex network structures to simple SBU-and-linker networks (Rosi *et al.*, 2005) (Fig. 6). To derive the nets of (I) and (II), the SBUs were reduced to rods of shaded quadrangles linked by sharing opposite edges, which leads to a ladder-like conformation of the one-dimensional SBU chains. The linkers are represented by rungs to form a 4-connected net with parallel rungs, analogous to the Al net in  $\text{SrAl}_2$ . This is called a network with  $\text{sra}^{12}$  topology, also found in metal-organic frameworks such as MIL-47 (Barthelet *et al.*, 2002), MIL-53 (Loiseau *et al.*, 2004) and MOF-71 (Rosi *et al.*, 2005).

The main reason for the generation of the more or less unusual isomorphous structures of (I) and (II) may be the formation of metal centres with high coordination numbers. The reaction of  $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  with a rigid dicarboxylic acid in dimethylformamide usually leads to an IRMOF-type framework (Eddaoudi *et al.*, 2002) containing a four-coordinated Zn metal centre. Performing these reactions with 2,5-dihydroxyterephthalic acid instead leads to MOF-74-type frameworks, caused by the linker molecule facilitating the formation of a much more stable five-coordinated metal species. The frameworks of (I) and (II) discussed here exhibit eight-coordinated metal centres, which seems to be the most stable coordination geometry under these conditions.

## Experimental

All chemicals and solvents were commercially available and used without further purification. 2,5-Dimethoxyterephthalic acid was synthesized according to the procedure published by Passaniti *et al.* (2002). For the synthesis of  $[\text{Mn}(\text{dmt})]_n$ , (I),  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (105 mg, 0.53 mmol) and 2,5-dimethoxyterephthalic acid (40 mg, 0.18 mmol) were dissolved in dimethylformamide (40 ml) and heated in a sealed tube for 24 h at 373 K. Yellow crystals of (I) precipitated after 24 h (yield 72%). For the synthesis of  $[\text{Zn}(\text{dmt})]_n$ , (II), the same procedure was used as for (I), using  $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (140 mg, 0.53 mmol) instead of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ . Colourless crystals of (II) precipitated after 18 h (yield 79%).

## Compound (I)

### Crystal data

$[\text{Mn}(\text{C}_{10}\text{H}_8\text{O}_6)]$	$V = 1043.66$ (7) Å <sup>3</sup>
$M_r = 279.10$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 16.7686$ (6) Å	$\mu = 1.28$ mm <sup>-1</sup>
$b = 8.4646$ (3) Å	$T = 153$ K
$c = 7.4464$ (3) Å	$0.52 \times 0.35 \times 0.33$ mm
$\beta = 99.093$ (1)°	

### Data collection

Bruker Kappa APEXII CCD area-detector diffractometer	11427 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2007)	2156 independent reflections
$T_{\text{min}} = 0.633$ , $T_{\text{max}} = 0.747$	2084 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.019$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.019$	79 parameters
$wR(F^2) = 0.052$	H-atom parameters constrained
$S = 1.09$	$\Delta\rho_{\text{max}} = 0.42$ e Å <sup>-3</sup>
2156 reflections	$\Delta\rho_{\text{min}} = -0.34$ e Å <sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C3-H3\cdots O1^i$	0.95	2.37	2.7209 (8)	101
$C5-H5B\cdots O2^{ii}$	0.98	2.47	3.0654 (11)	119

 Symmetry codes: (i)  $-x + \frac{3}{2}, -y + \frac{1}{2}, -z + 1$ ; (ii)  $-x + 2, y, -z + \frac{3}{2}$ .

**Table 2**

Hydrogen-bond geometry (Å, °) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C3-H3\cdots O1^i$	0.95	2.36	2.713 (2)	101
$C5-H5B\cdots O2^{ii}$	0.98	2.47	3.071 (3)	120

 Symmetry codes: (i)  $-x + \frac{3}{2}, -y + \frac{1}{2}, -z + 1$ ; (ii)  $-x + 2, y, -z + \frac{3}{2}$ .

## Compound (II)

### Crystal data

$[Zn(C_{10}H_8O_6)]$	$V = 1039.25 (7) \text{ \AA}^3$
$M_r = 289.53$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 16.5936 (6) \text{ \AA}$	$\mu = 2.38 \text{ mm}^{-1}$
$b = 8.4438 (3) \text{ \AA}$	$T = 153 \text{ K}$
$c = 7.4838 (3) \text{ \AA}$	$0.21 \times 0.15 \times 0.13 \text{ mm}$
$\beta = 97.649 (2)^\circ$	

### Data collection

Bruker Kappa APEXII CCD area-detector diffractometer	6781 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2007)	1005 independent reflections
$T_{\min} = 0.695, T_{\max} = 0.746$	898 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.032$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.022$	79 parameters
$wR(F^2) = 0.049$	H-atom parameters constrained
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.31 \text{ e \AA}^{-3}$
1005 reflections	$\Delta\rho_{\text{min}} = -0.28 \text{ e \AA}^{-3}$

For both compounds, H atoms were positioned geometrically and allowed to ride on their respective parent atoms, with  $C-H = 0.98 \text{ \AA}$  and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for methyl, and  $C-H = 0.95 \text{ \AA}$  and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for aryl H atoms.

For both compounds, data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008) and *PLATON*.

The authors thank the German Research Foundation within the priority programme 'Porous Metal-Organic Frameworks' (SPP 1362, MOFs).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3245). Services for accessing these data are described at the back of the journal.

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