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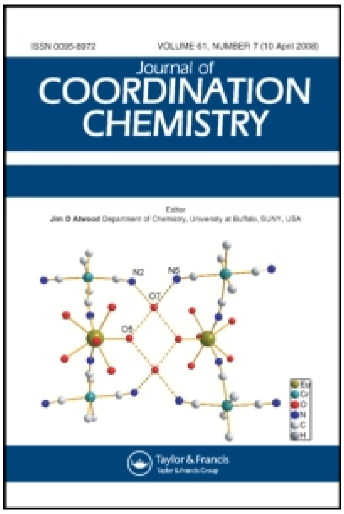

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Syntheses and crystal structures of two supramolecular isomers of manganese(II) with 3,5-bis(isonicotinamido)benzoate

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Syntheses and crystal structures of two supramolecular isomers of manganese(II) with 3,5-bis(isonicotinamido)benzoate

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Two new supramolecular isomeric complexes $[Mn(BBA)_2(H_2O)_2]_n \cdot 4nH_2O$ (**1**) and $[Mn(BBA)_2(H_2O)_2] \cdot 4H_2O$ (**2**) were obtained by hydrothermal reactions of $MnCl_2 \cdot 4H_2O$ with 3,5-bis(isonicotinamido)benzoic acid (HBBA) under different ratio of NaOH/HBBA. Complex **1** is a 1-D zigzag chain in which the Mn(II) is six-coordinate with distorted octahedral geometry. The 1-D chains are further connected by hydrogen bonds to give a 3-D supramolecular framework. Complex **2** is a monomeric molecular complex, assembled through intermolecular hydrogen bonds into a 3-D supramolecular network. Reaction conditions have remarkable influence on the structures of the complexes. The thermal and non-linear optical properties of the complexes were studied.

Keywords: Manganese(II) complex; 3,5-Bis(isonicotinamido)benzoic acid; Hydrothermal reaction; Supramolecular isomerism

1. Introduction

Supramolecular isomerism was proposed for crystalline solids with the same chemical compositions but two or more superstructures for the same building blocks [1]. Design and synthesis of new extended supramolecular frameworks by covalent and weak intra/intermolecular interactions have brought forth architectures with intriguing structural motifs [2–7]. However, control of formation of supramolecular complexes is still a challenge. Our strategy in this approach is using a new organic ligand 3,5-bis(isonicotinamido)benzoic acid (HBBA), prepared according to the procedure reported by Burchell *et al.* [8], containing carboxylate and pyridine. Amide possesses two types of hydrogen bonding sites, –NH as an electron acceptor and –C=O as an electron donor [9–11]. Such multifunctional moieties tend to form hydrogen bonds

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among themselves and interact with guest molecules [12]. Therefore, HBBA, with both carboxylate and amido-pyridine groups, is a multifunctional ligand used in this study to react with $MnCl_2 \cdot 4H_2O$ under different ratio of NaOH/HBBA; we report herein the syntheses, X-ray crystal structures and properties of $[Mn(BBA)_2(H_2O)_2]_n \cdot 4nH_2O$ (**1**) and $[Mn(BBA)_2(H_2O)_2] \cdot 4H_2O$ (**2**), which are supramolecular isomers.

2. Experimental

2.1. *Materials and methods*

All commercially available chemicals are of reagent grade and used as received. Elemental analyses were performed on a Perkin–Elmer 240C elemental analyzer. IR spectra were recorded on a Bruker Vector22 FT-IR spectrophotometer using KBr discs. Thermogravimetric analyses were performed on a simultaneous SDT 2960 thermal analyzer under nitrogen with a heating rate of 10°C min^{-1}. The second-order nonlinear optical (NLO) intensity was estimated by measuring a powder sample of 80–150 µm diameter in the form of a pellet relative to urea. A pulsed Q-switched Nd:YAG laser at a wavelength of 1064 nm was used to generate a SHG signal from powder samples. The backscattered SHG light was collected by a spherical concave mirror and passed through a filter that transmits only 532 nm radiation.

2.2. *Synthesis of compounds*

2.2.1. $[Mn(BBA)_2(H_2O)_2]_n \cdot 4nH_2O$ (1). A mixture containing $MnCl_2 \cdot 4H_2O$ (19.8 mg, 0.1 mmol), HBBA (36.5 mg, 0.1 mmol), NaOH (4.0 mg, 0.1 mmol), and 10 mL H_2O was sealed in a 16 mL Teflon-lined stainless steel container and heated at 100°C for 3 days. After cooling to room temperature within 12 h, block brown crystals of **1** suitable for X-ray diffraction were obtained in 59% yield. Anal. Calcd for $C_{38}H_{38}MnN_8O_{14}$: C, 51.53; H, 4.32; N, 12.65. Found: C, 52.03%; H, 4.61%; N, 12.51%. Main IR (KBr, cm^{-1}): 3448 (s), 1655 (s), 1617 (m), 1561 (s), 1499 (w), 1387 (s), 1291 (m), 755 (w), 670 (w).

2.2.2. $[Mn(BBA)_2(H_2O)_2] \cdot 4H_2O$ (2). This compound was prepared by the same method as for **1** except that the amount of NaOH used in **2** was 2.0 mg (0.05 mmol), and colorless crystals of **2** suitable for structural analysis were isolated. Yield 65%. Anal. Calcd for $C_{38}H_{38}MnN_8O_{14}$: C, 51.53; H, 4.32; N, 12.65. Found: C, 52.07%; H, 4.48%; N, 12.66%. Main IR (KBr, cm^{-1}): 3449 (s), 1670 (s), 1618 (m), 1559 (vs), 1499 (w), 1389 (s), 1295 (m), 756 (w), 669 (w).

2.3. *X-ray structure determination*

The crystallographic data of **1** and **2** were collected on a Rigaku RAXIS-RAPID imaging plate diffractometer at −73°C with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71075$ Å). The structures were solved by direct methods using SIR92 [13] and

Table 1. Crystal data and structure refinement for **1** and **2**.

Complexes	**1**	**2**
Empirical formula	$MnO_{14}N_8C_{38}H_{38}$	$MnO_{14}N_8C_{38}H_{38}$
Formula weight	885.70	885.70
Crystal system	Monoclinic	Orthorhombic
Space group	*C*2/c	$P2_12_12$
Unit cell dimension (Å, °)		
a	17.478(7)	14.539(3)
b	10.811(6)	25.159(5)
c	21.685(7)	5.2664(9)
α	90.00	90.00
β	103.985(14)	90.00
γ	90.00	90.00
Volume (Å^3)	3976.0(29)	1926.3(6)
D_{Calcd} (g cm^{-3})	1.479	1.527
Z	4	2
Absorption coefficient (mm^{-1})	0.412	0.425
F(000)	1836	918
Data/restraints/parameters	4531/15/294	4407/15/295
$R_1{}^a/wR_2{}^b$	0.0617/0.1240	0.0601/0.1124
R_1/wR_2 (all data)	0.1069/0.1414	0.1026/0.1262
Goodness-of-fit on F^2	1.033	1.021
Largest difference peak and hole (e Å^{-3})	0.34 and −0.48	0.26 and −0.36

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^bwR_2 = |\Sigma w(|F_o|^2 - |F_c|^2)|/\Sigma|w(F_o)^2|^{1/2}$.

expanded using Fourier techniques [14]. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2. The hydrogens were generated geometrically. All calculations were carried out on an SGI workstation using the teXsan crystallographic software package of Molecular Structure Corporation [15]. Details of the crystal parameters, data collection, and refinement for **1** and **2** are summarized in table 1. Selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *Description of the crystal structures of 1 and 2*

X-ray structural analysis revealed that **1** is a 1-D zigzag chain coordination polymer. As shown in figure 1(a), each Mn(II) is coordinated by two nitrogens from two different BBA^- ligands and two oxygens of water with Mn–N, Mn–O bond distances of 2.265(2) and 2.248(2) Å, respectively (table 2). Two additional positions are occupied by two oxygens from two BBA^- ligands with O–Mn–O bond angle of 176.05(11)° and Mn–O bond distances of 2.115(2) Å. Therefore, the six-coordinate Mn(II) has a slightly distorted octahedral coordination geometry with a N_2O_4 donor set. Each BBA^- ligand uses its carboxylate and one of the two pyridinyl groups to connect two metal centers, while another pyridinyl group is not coordinated. Two Mn(II) and two BBA^- ligands form a M_2L_2 macrocyclic ring with Mn $\cdots$ Mn distance of 12.1995(34) Å. Such M_2L_2 macrocyclic rings are further connected by Mn–N and Mn–O coordination to give an infinite 1-D zigzag chain (figure 1b). In the crystal packing diagram of **1**, the 1-D chains pack *via* O–H $\cdots$ N, N–H $\cdots$ O, and O–H $\cdots$ O hydrogen bonds (figure 2) with D $\cdots$ A

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

1			
Mn(1)–O(3)	2.248(2)	Mn(1)–O(6)#1	2.115(2)
Mn(1)–O(3)#1	2.248(2)	Mn(1)–N(11)#2	2.265(2)
Mn(1)–O(6)	2.115(2)	Mn(1)–N(11)#3	2.265(2)
O(3)–Mn(1)–O(3)#1	100.48(13)	O(6)#1–Mn(1)–N(11)#3	91.22(8)
O(3)–Mn(1)–O(6)	88.12(8)	O(6)–Mn(1)–N(11)#3	91.69(9)
O(3)–Mn(1)–O(6)#1	89.36(8)	O(6)–Mn(1)–N(11)#2	91.22(8)
O(3)–Mn(1)–N(11)#2	87.35(9)	O(3)#1–Mn(1)–N(11)#3	87.35(9)
O(3)–Mn(1)–N(11)#3	172.16(9)	O(3)#1–Mn(1)–O(6)	89.36(8)
O(3)#1–Mn(1)–O(6)#1	88.12(8)	O(3)–Mn(1)–N(11)#2	172.16(9)
O(6)#1–Mn(1)–O(6)#1	176.05(11)	O(6)#1–Mn(1)–N(11)#2	91.69(9)
2			
Mn(1)–O(10)	2.100(3)	Mn(1)–O(51)#4	2.235(3)
Mn(1)–O(10)#4	2.100(3)	Mn(1)–O(52)	2.250(2)
Mn(1)–O(51)	2.235(3)	Mn(1)–O(52)#4	2.250(2)
O(10)–Mn(1)–O(10)#4	98.89(16)	O(10)#4–Mn(1)–O(51)#4	93.06(11)
O(10)–Mn(1)–O(51)#4	146.60(9)	O(10)#4–Mn(1)–O(52)	88.17(9)
O(10)–Mn(1)–O(52)	110.57(10)	O(10)#4–Mn(1)–O(52)#4	110.57(10)
O(10)–Mn(1)–O(52)#4	88.17(9)	O(51)–Mn(1)–O(51)#4	93.84(14)
O(10)#4–Mn(1)–O(51)	146.60(9)	O(51)–Mn(1)–O(52)	58.44(8)
O(51)#4–Mn(1)–O(52)#4	151.56(14)	O(51)–Mn(1)–O(52)#4	100.82(10)
O(51)#4–Mn(1)–O(52)	100.82(10)		

Symmetry transformations used to generate equivalent atoms: #1: $-x+1$, y, $-z+1/2$; #2: $-x+1$,$-y$, $-z+1$; #3: x, $-y$, $z+1/2$; #4: $-x+1$, $-y$, z.

distances in the range of 2.675(4)–3.153(5) Å and the D–H–A angles ranging from 152° to 176(3)° to generate a 3-D structure.

When the ratio of NaOH/HBBA is changed from 1 : 1 used in preparation of **1** to 1 : 2 for synthesis of **2**, a new structure was isolated. Compound **2** is a mononuclear molecular complex with chiral space group $P2_12_12$, and absolute structure Flack parameter of 0.00(3), rather than a 1-D coordination polymer as observed for **1**. As illustrated in figure 3(a), each Mn(II) is six-coordinate by two oxygens from two waters and four carboxylate oxygens from two different BBA^- ligands. The coordination mode of the carboxylate group is bidentate-chelating with average $Mn–O_{(carboxyl)}$ distance of 2.2425 Å, slightly longer than that in **1**. The $Mn–O_{H_2O}$ bond length is 2.100(3) Å, slightly shorter than that in **1** [2.248(2) Å]. Thus, the coordination geometry of Mn(II) in **2** is seriously distorted octahedral since coordination angles around Mn(II) range from 58.44(8)° to 110.57(10)° (table 2).

There are N–H ⋯ O, N–H ⋯ N, O–H ⋯ N, and O–H ⋯ O hydrogen bonding interactions with D ⋯ A separations in the 2.675(4)–3.212(5) Å region and the D–H–A angles ranging from 129° to 170(5)° [16]. Such different hydrogen bonding interactions extend the mononuclear compound into a 3-D supramolecular network (figure 3b). The reaction conditions have remarkable influence on the structure of the complexes.

3.2. *Infrared spectra*

In the IR spectrum of **1**, characteristic carboxylate bands of $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ are at 1617 and 1387 cm^{-1}, respectively. Separation between ν_{as} and ν_s of 230 cm^{-1}

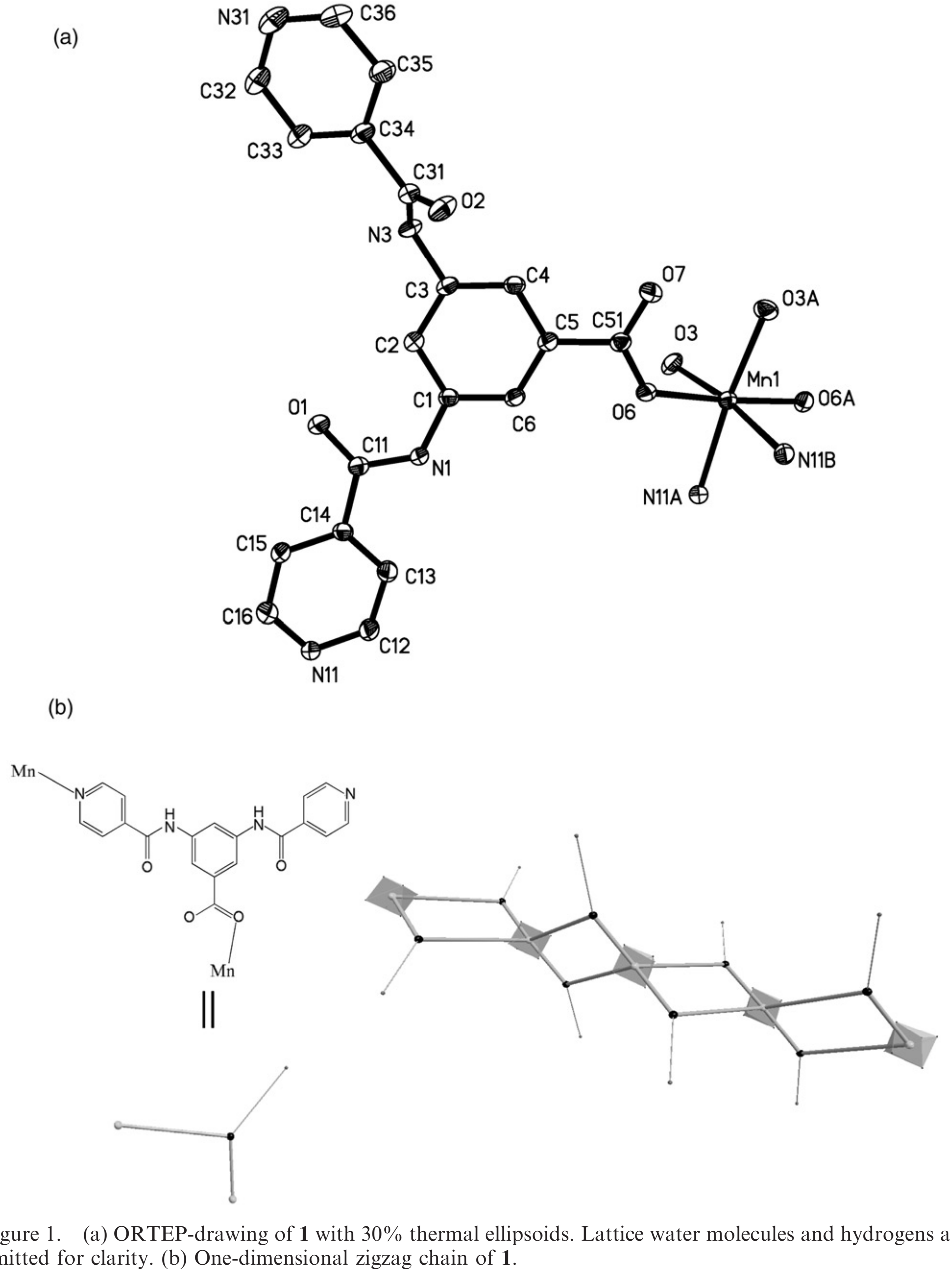

Figure 1. (a) ORTEP-drawing of **1** with 30% thermal ellipsoids. Lattice water molecules and hydrogens are omitted for clarity. (b) One-dimensional zigzag chain of **1**.

indicates that the carboxylate coordinates monodentate with Mn(II) [17], consistent with the crystal structure. For **2**, the strong vibrations at 1559 and $1389\,\mathrm{cm^{-1}}$ are assigned to $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ of BBA^-, and the splitting of $170\,\mathrm{cm^{-1}}$ indicates chelating carboxylate, also coincident with crystallographic structural analysis.

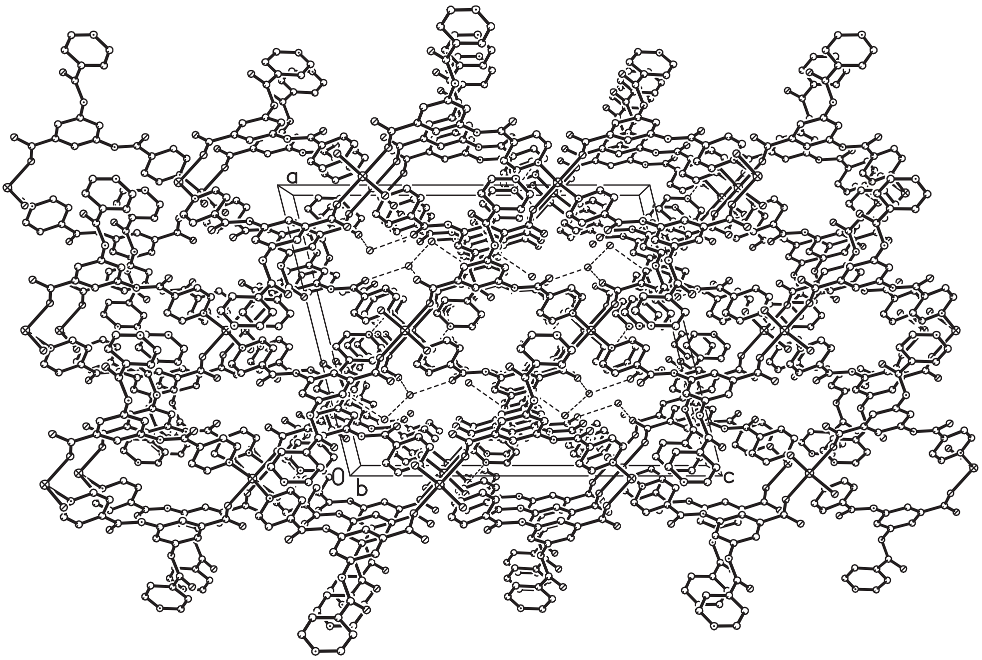

Figure 2. Unit cell and hydrogen bonds of **1**.

3.3. *Thermogravimetric analysis and non-linear optical property*

Thermal gravimetric analyses (TGA) verify the thermal stability of the complexes (Supplemental material). Complex **1** lost 14.43% weight from room temperature to 190°C (Anal. Calcd 12.20%) due to loss of coordinated and free water, and the residue decomposed at 320°C. For **2**, a weight loss of 13.46% was observed from room temperature to 155°C, corresponding to the release of coordinated and uncoordinated water molecules (Anal. Calcd 12.20%); the residue after loss of water was stable to 360°C.

Only non-centrosymmetric structures may have second-order non-linear optical (NLO) effect. Complex **2** crystalyzed in a chiral space group of $P2_12_12$ and may have NLO response. Therefore, a quasi-Kurtz second-harmonic-generation (SHG) measurement was performed to evaluate its application as a second-order NLO material [18]. The preliminary experimental results revealed that **2** exhibits modest powder SHG intensity with a response 0.5 times that for urea, which means that this complex may be used as a potential optical material.

Supplementary material

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC-707338 (**1**) and 707339 (**2**). Copies of the data can be obtained free of

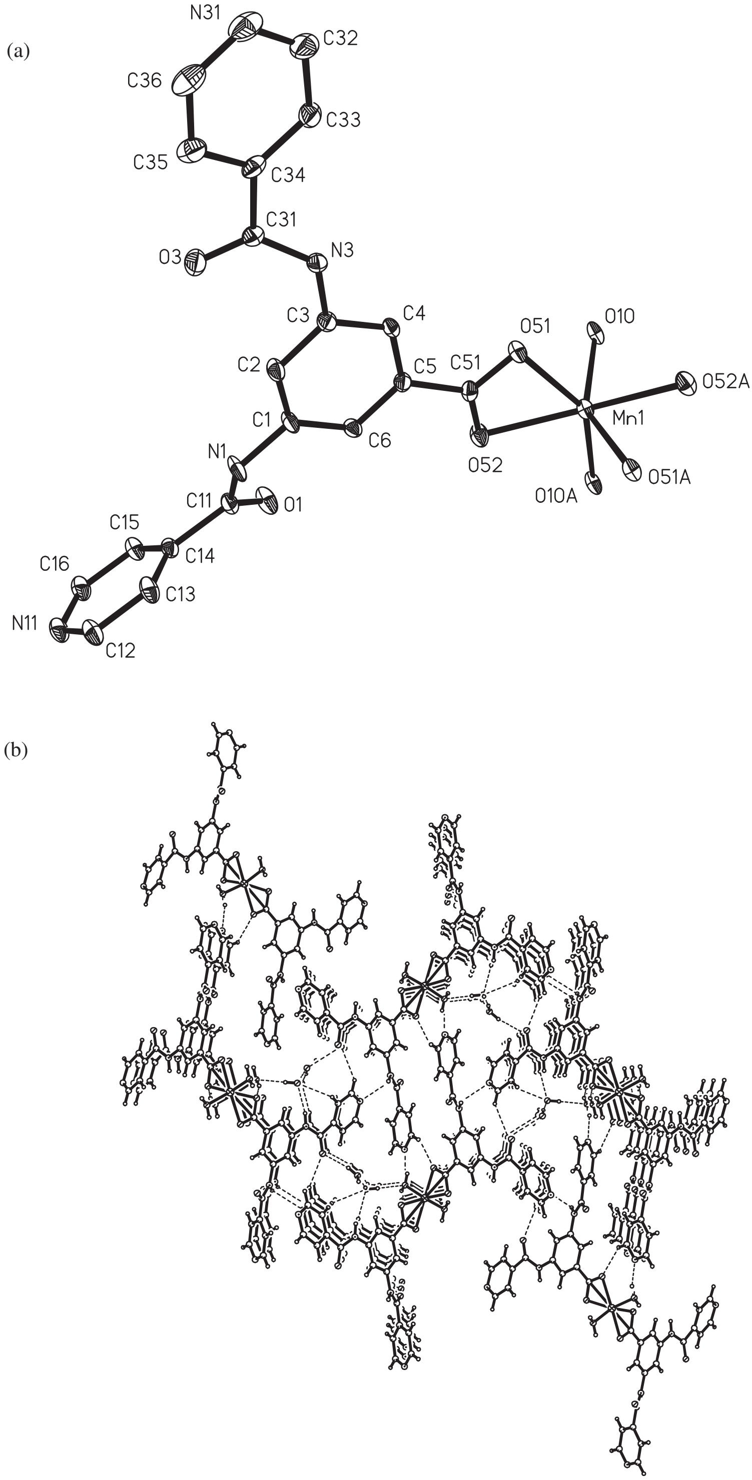

Figure 3. (a) ORTEP-drawing of **2** with 30% thermal ellipsoids. Lattice water molecules and hydrogens are omitted for clarity. (b) View of the packing structure of **2** formed by hydrogen bonds.

charge, Union Road, on application to CCDC, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336-033; Email: deposit@ccdc.cam.ac.uk).

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