Three Mn(II) complexes based on 6-(3-pyridyl)isophthalic acid ligand: structure modulation, stability and magnetic properties

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ABSTRACT

Based on the 6-(3-pyridyl)isophthalic acid (H_2pip) ligand, three new complexes $[\text{Mn}(\text{Hpip})_2(\text{bipy})_2(\text{H}_2\text{O})_2]$ (**1**), $\{[\text{Mn}(\text{pip})(\text{bibp})]\cdot\text{DMA}\}_n$ (**2**) and $[\text{Mn}(\text{pip})]_n$ (**3**), have been obtained under hydrothermal conditions and characterized by single-crystal X-ray diffraction. Compound **1** reveals a 0D mononuclear structure, and isolated molecules are further linked by hydrogen-bonds into a 3D supramolecular structure. In **2**, the binuclear $\text{Mn}_2(\text{COO})_4\text{N}_4$ secondary building units (SBUs) are linked by neighboring ligands to result in a 2D layer structure. Inside of the structure of **3**, one-dimensional (1D) chains are formed by the coordination of carboxylate groups and Mn^{2+} , which are further connected by the ligands generating a 3D network. Notably, complex **3** reveals high thermal and aqueous stability, suggested by TGA and PXRD data. Moreover, the magnetic measurements indicate polymers **2** and **3** are both exhibit antiferromagnetic behavior.

Keywords

Coordination polymer; Synthesis; Crystal structure; Stability; Magnetic property

1 Introduction

During the past few decades, the rational design and construction of coordination polymers (CPs) have been widely studied not only due to their fascinating structures and topologies but also the potential applications such as magnetism, gas storage, separation, catalysis, luminescence, ion exchange and so on [1-10]. However, it is still a big challenge to synthesize CPs more predictably and controllably at present, since the self-assembly of frameworks and final structures of polymers could be affected by too many factors, such as solvents, temperatures, pH value of the solution, ligand structures and so on [11-19]. As CPs are commonly obtained through the assembly of various organic ligands and inorganic secondary building units (SBUs, generally metal ions or metal-containing units), the exploitation of proper kinds of ligands is of great importance [20-22]. Among numerous kinds of organic ligands, carboxylate ligands with N-donors has been of specially interest in recent years. Their strong affinities with transitional metal ions and diverse coordination modes make them good candidates to construct CPs with various dimensional structures and interesting properties [23-26]. Our previous work showed that 6-(3-pyridyl)isophthalic acid (H_2pip), as a ligand of this kind, have present various coordination modes and seemed to be a good choice [27].

On the other hand, because of the weak coordination bonding, many CPs are unstable when separated from their mother solution, which could limit their application. Therefore, to make CPs for practical utilization, stability of the framework is one of the key factors that could not be neglected, especially under tough conditions, for example, high temperature and aqueous environment [28-34].

In this paper, we utilized H_2pip as ligand and presented a series of Mn(II) complexes with structure dimension from 0D, 2D to 3D, namely, $[Mn(Hpip)_2(bipy)_2(H_2O)_2]$ (**1**), $\{[Mn(pip^{2-})(bipb)] \cdot DMA\}_n$ (**2**) and $[Mn(pip)]_n$ (**3**), under hydrothermal conditions. Thermal and aqueous stability of complex **2** and **3** were investigated in this context. Furthermore, magnetic property were also studied, which show that compound **2** and **3** both reveal antiferromagnetic behavior. Herein, we report on the synthesis, crystal structures and properties of these complexes.

2 Experimental Section

2.1 Materials and General Methods

All the chemical reagent of analytical grade were commercially available, and used without further purification. Powder X-ray diffraction (PXRD) data under the 2θ range $5-50^\circ$ were recorded using Cu-K α radiation ($\lambda = 0.1542$ nm) on a Bruker D8A A25 X-ray diffractometer, with the X-ray tube operated at 40 kV and 40 mA at room temperature. The Elementar Vario Micro Cube analyzer was used to carry out the elemental analyses (C, H, N), and a SHIMADZU DTG-60 thermo analyzer was used to perform the thermogravimetric analyses (TGA) from room temperature to 800°C under nitrogen protection with a heating rate of $20^\circ\text{C min}^{-1}$. Infrared (IR) spectrum of the KBr disks dispersed sample powders were measured on a Thermo Nicolet IR 200 FT-IR spectrometer in the range of $4000-500\text{ cm}^{-1}$. Magnetic property were performed using a Quantum Design Squid-VSM magnetometer.

2.2 X-ray Crystallography

X-ray diffraction data for the single crystal sample of **1-3** were collected on a Bruker SMART APEXII CCD diffractometer equipped with a graphite monochromated Mo-K α radiation ($\lambda = 0.71073\text{ \AA}$). The SADABS programs was used to apply the empirical absorption correction [35]. Direct methods and full-matrix least-squares methods on F^2 were performed to solve and refine the structure using the SHELXL 97 [36]. All the crystallographic programs were integrated into a system by using the single suite WINGX [37]. All non-hydrogen atoms were refined anisotropically. Geometrically calculations was implemented to locate the hydrogen atoms, and during the structure refinement, positions and thermal parameters of them were fixed as well. The crystallographic data and details of selected bond lengths and angles are summarized in Table 1 and Table S1, respectively.

2.3.1 Synthesis of $[\text{Mn}(\text{Hpip})_2(\text{bipy})_2(\text{H}_2\text{O})_2]$ (**1**)

A mixture of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.0395 g, 0.2 mmol), H_2pip (0.0243 g, 0.1 mmol) and 4,4'-Bipyridine (4,4'-bipy) (0.0156 g, 0.1 mmol) were dissolved in distilled water (5 ml) and then heated to 160°C for 96 h in a 20 ml stainless steel reactor with a Teflon

liner. The reaction system was then cooled to room temperature slowly. Colorless block crystals of **1** were obtained with low yield and could hardly be purified.

2.3.2 Synthesis of $\{[Mn(pip)(bibp)]\cdot DMA\}_n$ (**2**)

A mixture of $MnCl_2\cdot 4H_2O$ (0.02 g, 0.1 mmol), H_2pip (0.006 g, 0.025 mmol) and 4,4'-Bis(imidazolyl)biphenyl (bibp) (0.007 g, 0.025 mmol) were placed in a vial, followed by the addition of 1 ml N,N' -dimethylacetamide (DMA) and 1 ml H_2O . The reaction system was sealed and then heated to 100 °C for 48 h. After cooled to room temperature slowly, the reactor was unsealed and yellow block crystals of **2** formed. The obtained samples were finally filtered, washed with mother liquid and dried in air (yield: 49 % based on H_2pip). $C_{35}H_{21}MnN_6O_5$ (%): Elemental anal. calcd. (%) C, 63.64; H, 3.20; N, 12.72. Found C, 63.62; H, 3.23; N, 12.69. IR frequencies (KBr, cm^{-1}): 1610(s), 1547(s), 1509(m), 1392(s), 1309(m), 1254(w), 1191(w), 1063(m), 835(w).

2.3.3 Synthesis of $[Mn(pip)]_n$ (**3**)

A mixture of $MnCl_2\cdot 4H_2O$ (0.0395 g, 0.2 mmol) and H_2pip (0.0243 g, 0.1 mmol) were placed in a 20 ml stainless steel reactor with a Teflon liner, followed by the addition of distilled water (5 ml). The reaction system was sealed and then heated to 160 °C for 96 h. After cooled to room temperature slowly, the reactor was unsealed and colorless block crystals of **3** formed. The obtained samples were finally filtered, washed with H_2O and dried in air (yield: 53 % based on H_2pip). $C_{13}H_7MnNO_4$ (%): Elemental anal. calcd. (%) C, 52.72; H, 2.38; N, 4.73. Found C, 52.69; H, 2.39; N, 4.72. IR frequencies (KBr, cm^{-1}): 3437(s), 2343(w), 1635(m), 1376(w), 1109(m), 990(w), 785(w), 612(m), 552(m).

3 Results and Discussion

3.1 Structural description

$[Mn(Hpip)_2(bipy)_2(H_2O)_2]$ (**1**). Single-crystal X-ray diffraction analysis showed that complex **1** crystallized in the triclinic $P-1$ space group. In **1**, each Mn(II) ion is six coordinated by two O atoms of carboxylate from two different pip^{2-} ligands, two N atom of pyridyl from two different 4,4'-bipy ligands and two O atoms from water

molecules (Fig. 1a). However, each anionic pip^{2-} ligand bonds with one Mn(II) (Fig. 4a) using only one carboxylate group in a monodentate mode, and meanwhile, each 4,4'-bipy connects with only one Mn(II) as well by one of the pyridyl group. As a result, complex **1** shows a 0D mononuclear structure rather than infinite frameworks through coordination. These mononuclear molecules could be further joined together via two kinds of hydrogen bonds interactions (Fig. 1b and Table 2) (O-H...N, between the O-H groups from coordinated water molecules and the N atoms from pyridyl of pip^{2-} ligand; O-H...N, between the O-H groups from carboxylate of the pip^{2-} ligands and the N atoms from pyridyl of 4,4'-bipy) into 3D supramolecular structures (Fig. 1c), though. The Mn-O bond distances are in the range of 2.1691(13)-2.2133(15) (Å), and the Mn-N bond distance is 2.2976(16) (Å). The bond angles between the donor atoms around the Mn(II) center range from 87.80(6) to 180.00(9) (deg) (Table S1).

(Insert Fig.1, Table 1, Table 2)

$\{[Mn(\text{pip})(\text{bibp})]\cdot\text{DMA}\}_n$ (**2**). Structural analysis showed that compound **2** belongs to the *P-1* space group of triclinic system. In complex **2**, there contains one independent Mn^{2+} center, one pip^{2-} ligand and one bibp ligand in the asymmetric unit. Every Mn1 cation is six-coordinated with a MnN_2O_4 octahedral geometry containing four carboxylate O atoms from three pip^{2-} ligands and two imidazole N atoms from two bibp ligands (Fig. 2a). Each anionic pip^{2-} ligand bounds three Mn^{2+} ions (Fig. 4b). As shown in Fig. 2 (b), two adjacent Mn(II) are bonded together to generate a $\text{Mn}_2(\text{COO})_4\text{N}_4$ SBU, and each pip^{2-} ligand binds three SBUs to form a 1D chain with a ladder shape. These chains are further linked by bibp ligands generating the final 2D layer structure. Moreover, different layers are stacked together leading to the formation of 1D channels along *a* axis, which were filled with DMA molecules. The effective free void volume is estimated to be 25.5 % by PLATON [38] (402.8 Å^3 out of the 1579.2 Å^3 per unit cell volume). Besides, the Mn-O bond distances are in the range of 2.099(2)-2.335(2) (Å) while the Mn-N bond distance is between 2.256(3)-2.272(3) (Å). The bond angles between the donor atoms around the Mn(II) center range from 57.37(7) to 167.96(10) (deg) (Table S1).

(Insert Fig.2)

$[Mn(pip)]_n$ (**3**). Structural analysis showed that compound **3** belongs to the $P4_32_12$ space group of tetragonal system. As shown in Fig. 3a, there contains one independent Mn^{2+} center and one pip^{2-} ligands in the asymmetric unit of **3**. Every Mn1 cation is five-coordinated with a $MnNO_4$ trigonal biyramid geometry containing four carboxylate O atoms from four pip^{2-} ligands and one pyridyl N atom from another pip^{2-} ligand. Each anionic pip^{2-} ligand bounds five Mn^{2+} ions (Fig. 4c), and the coordination of carboxylate groups with Mn^{2+} ions result in the formation of 1D metal chains, which are further linked by the ligands generating the final 3D framework [39] (Fig. 3b). The Mn-O bond distances are in the range of 2.1195(12)-2.1541(12) (Å) while the Mn-N bond distance is 2.2239(15) (Å). The bond angles between the donor atoms around the Mn(II) center range from 84.63(5) to 179.84(6) (deg) (Table S1). Additionally, the effective free void volume is estimated to be only 1.7 % by PLATON (38.4 Å³ out of the 2238.9 Å³ per unit cell volume), indicating the low porosity of this compound.

(Insert Fig.3)

Structural modulation. From the above analysis, it could be seen that H_2pip ligand presents two different coordination types between compound **1** and **3**. In **1**, only one O atom participate in the coordination, and no N atoms coordinate with Mn^{2+} ions in the structure. As for **3**, four O atoms and one N atoms all take part in the coordination with Mn^{2+} ions, forming a $\eta^1:\eta^1:\eta^1:\eta^1:\eta^1:\mu_5$ coordination mode. Possible reason for the structure differences of **1** and **3** with similar synthetic method but having completely different coordination mode, might be attributed to the addition of N-donor ligand, 4,4'-bipy in **1**, which could remarkably influence the coordination environment of Mn^{2+} ions and block the coordination between Mn^{2+} and N atoms from the H_2pip ligand. However, when adding bibp as auxiliary ligand at the same condition, no good crystals that are suitable for X-ray diffraction were obtained. Therefore, we changed the method into solvothermal reaction at low temperature, which resulted in the formation of **2**. In the structure of **2**, four O atoms from the two carboxylate groups of H_2pip ligand are all coordination atoms revealing a $\eta^1:\eta^1:\eta^1:\eta^1:\mu_3$ mode and no N atoms participate in the coordination. Moreover,

through auxiliary ligand and reaction condition modulation, it finally led to the different structures of these compounds from 0D mononuclear structure, 2D layer structure to 3D networks, which also demonstrating the various conformations of H₂pip in the assembly system.

(Insert Fig.4)

3.2 TGA and PXRD

Compound **2** with binuclear SBUs and **3** with internal metal chains encouraged us to evaluate its thermal and water stability. On one hand, TG analyses were performed to assess the thermal stability of compound **2** and **3**. Before measurement, the samples were dried under 50 °C for several hours in order to remove the solvent of the surface. As shown in Fig. 5, the weight loss is 6.8% from 140 to 440 °C for compound **2**, which is much lower than the calculated value for one DMA solvent molecule in the layers (13.2%), indicating the removal of about one half DMA per formula unit (calcd 6.6%). After 440 °C, the structure of **2** begin to collapse, and the final 16.0% residue might be assigned to the formation of MnO (calcd 13.2%). While no weight loss was observed for the pretreated samples of **3**, indicating the complete removal of solvent molecules. Furthermore, TGA curve revealed that **3** could be stable up to about 460 °C which is a little higher than compound **2**, and then complex **3** starts to decompose. Finally, the 25.2% residue of the samples could be concluded to be the formation of MnO (calcd 24.0%).

(Insert Fig.5)

One the other hand, PXRD patterns of compound **2** and **3** under different conditions were carried out, as shown in Fig. 6. Firstly, simulated PXRD patterns of **2** and **3** both agree well with their respective as-synthesized one, indicating the purity of the two compounds. After treated by soaking the samples into EtOH and boiling water for 72 h, the main peaks of PXRD patterns for the two compounds could still match well with their simulated ones, respectively, although some slight changes were observed due to distortion of the crystal lattice in response to solvent exchanges, suggesting the good stability of **2** and **3** against solvents.

(Insert Fig.6)

3.3 Magnetic Properties

Magnetic properties were measured on crystalline samples of compounds **2** and **3**. In **2**, the obtained data suggests antiferromagnetic coupling between adjacent Mn^{II} ions of one Mn^{II} cluster and negligible Mn^{II}...Mn^{II} couplings between the neighboring Mn^{II} clusters. The obtained data indicates antiferromagnetic coupling between adjacent Mn^{II} ions of one Mn^{II} chain in **3** and negligible Mn^{II}...Mn^{II} couplings between the neighboring Mn^{II} chains. The magnetic behaviors as detail discussed below.

The magnetism of **2** and **3** was studied by solid state magnetic susceptibility measurements in the 2-300 K range at a field of 1 kOe. The magnetic properties for **2** in the form of $\chi_m T$ vs. T and χ_m^{-1} vs. T plots are shown in Fig. 7(a). The value of $\chi_m T$ at room temperature is 6.50 cm³·mol⁻¹·K, which is larger than the expected value (4.375 cm³·mol⁻¹·K) for one magnetically isolated Mn^{II} ion ($S = 5/2$, $g = 2.0$). As the temperature decreases, the value of $\chi_m T$ slowly increases down to a 6.32 cm³·mol⁻¹·K at 100 K, while decreases rapidly below 100 K and reaches a minimum value of 0.72 cm³·mol⁻¹·K at 2 K. Mentioned above indicates antiferromagnetic coupling between adjacent Mn^{II} ions of one Mn^{II} cluster. Fitting the data at 2-300 K with the Curie-Weiss law [$\chi_m = C/(T-\theta)$] gives $C = 6.79$ cm³·mol⁻¹·K and $\theta = -8.34$ K. The small negative value of θ further confirms the overall antiferromagnetic couplings between neighboring Mn^{II} ions. The $\chi_m T$ vs T curve could be analyzed by equation 1, which is based on the Hamiltonian: $\hat{H} = -2J\hat{S}_{Mn1}\hat{S}_{Mn1A}$.

$$\chi = \frac{Ng^2\beta^2}{2kT} \times \frac{10 + 35A + 84B + 165C + 286e^{32J/KT}}{4 + 6A + 8B + 10C + 12e^{32J/KT}} \quad \text{Equation 1}$$

$$\chi_m = \frac{\chi}{1 - (2zj'/Ng^2\beta^2)\chi} \quad \text{Equation 2}$$

The best fitting gives $J = -0.60$ cm⁻¹, $g = 1.80$, $zj' = -0.06$ cm⁻¹. The J value is reasonable and suggests weak antiferromagnetic interaction between the Mn^{II} ions. It is noteworthy that the magnetic interactions between the adjacent Mn^{II} clusters are negligible, attributing to the far distances of Mn^{II}...Mn^{II} ions. Therefore, complex **2** exhibits antiferromagnetic behavior.

As for **3**, the magnetic properties are presented in the form of $\chi_m T$ vs T and χ_m^{-1} vs T plots in Fig. 7(b). The resulted $\chi_m T$ value is $4.22 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ at room temperature, which is slightly smaller than the theoretical value ($4.375 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$) for one magnetically isolated Mn^{II} ion ($S = 5/2$, $g = 2.0$). Along with temperature declining, the value of $\chi_m T$ presents a slowly downward trend at the beginning with a decrease of only $0.23 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ at 100 K, while a sharp decrease is observed below 100 K and it reaches a minimum value of $0.29 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ at 2 K. Based on the above analysis, it reveals that antiferromagnetic coupling exists between adjacent Mn^{II} ions of one Mn^{II} chain. The data at 14-300 K was fitted by using the Curie-Weiss law [$\chi_m = C/(T-\theta)$], and the value of C and θ was given as $4.48 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ and -13.51 K , respectively. As a result, the overall antiferromagnetic couplings could be further confirmed existing between neighboring Mn^{II} ions by the negative value of θ . It is noteworthy that the magnetic interactions between the adjacent Mn^{II} chains are negligible, attributing to the far distances of $\text{Mn}^{\text{II}} \cdots \text{Mn}^{\text{II}}$ ions. Therefore, complex **3** also exhibits antiferromagnetic behavior.

(Insert Fig.7)

Conclusions

In summary, three novel complexes $[\text{Mn}(\text{Hpip})_2(\text{bipy})_2(\text{H}_2\text{O})_2]$ (**1**), $\{[\text{Mn}(\text{pip})(\text{bibp})] \cdot \text{DMA}\}_n$ (**2**) and $[\text{Mn}(\text{pip})]_n$ (**3**) were constructed based on 6-(3-pyridyl) isophthalic acid (H_2pip) and befitting metal salt under hydrothermal conditions. **1** displays a 0D mononuclear structure. In **2**, the binuclear $\text{Mn}_2(\text{COO})_4\text{N}_4$ secondary building units (SBUs) are linked by neighboring ligands to result in a 2D layer. Moreover, the contiguous 1D chains are interlinked through the carboxylate groups of the H_2pip ligands, extending the chains into 3D network in **3**. Notably, complex **2** and **3** shows high performance on thermal and aqueous stability. Also, complexes **2** and **3** exhibit antiferromagnetic behavior.

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Appendix A. Supplementary material

CCDC 1483304 (for **1**), CCDC 1524839 (for **2**) and CCDC 1483353 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033).

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Captions to Figure and Tables

Fig. 1 (a) Coordination environment of the Mn (II) in **1**.

(b) The packing diagram of **1** showing the hydrogen bonding interactions. (pink dashed lines).

(c) 3D supramolecular structures formed by the hydrogen bonding interactions of **3**. (pink dashed lines) (H atoms omitted for clarity)

Symmetry codes: #1 1-x, 1-y, 2-z

Fig. 2 (a) Coordination environment of the Mn(II) in **2**.

(b) View of formation of 2D layer structure in compound **2**. (H atoms omitted for clarity)

(c) View of the DMA-filled stacking channels of compound **2**.

Symmetry codes: #1 -x, 1-y, 2-z; #2 -1+x, y, 1+z; #3 1-x, 1-y, 2-z;

Fig. 3 (a) Coordination environment of the Mn(II) in **3**.

(b) 3D frameworks of **3** connected by 1D chains. (H atoms omitted for clarity)

Symmetry codes: #8 1+x, y, z; #9 3/2-y, 1/2+x, -1/4+z; #10 1/2-x, -1/2+y, 7/4-z; #11 x, y, 2-z

Fig. 4 Coordination modes of pip^{2-} in **1-3**: (a) for **1**, (b) for **2** and (c) for **3**.

Fig. 5 The TGA curves of compound **2** and **3**.

Fig. 6 PXRD patterns of **2** (a) and **3** (b) and after being treated under different conditions for 72h.

(Simulated pattern derived from the X-ray single crystal data of compound **2** and **3**)

Fig. 7 Plots of χmT vs. T ($\circ$) and χm^{-1} vs. T ($\diamond$) (red part for the Curie-Weiss fitting) for **2** (a) and **3** (b).

Table 1 Crystal data and structure refinement parameters for compounds **1-3**.

Table 2. Hydrogen bond lengths ($\text{\AA}$) and bond angles ($^\circ$) for compound **1**.

Fig. 1.

(a)

(b)

(c)

Fig. 2.

(a)

(b)

Fig. 3.

Fig. 4.

Fig. 5.

(a)

(b)

Fig. 6.

(a)

(b)

Fig. 7.

Table 1

Compound	1	2	3
Empirical formula	C ₄₆ H ₃₆ MnN ₆ O ₁₀	C ₃₅ H ₂₁ MnN ₆ O ₅	C ₁₃ H ₇ MnNO ₄
Formula weight	885.73	660.52	296.14
Crystal system	monoclinic	triclinic	tetragonal
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> 4 ₃ 2 ₁ 2
Unit cell dimensions			
a (Å)	8.1130(10)	10.129(6)	8.2020(10)
b (Å)	9.2350(10)	13.293(8)	8.202
c (Å)	14.8010(10)	13.295(8)	33.281(2)
α (deg)	83.9990(10)	101.373(11)	90
β (deg)	79.4700(10)	101.661(11)	90
γ (deg)	68.6890(10)	109.825(10)	90
Volume (Å ³)	1014.84(18)	1579.2(16)	1757
Z	1	2	8
Calculated density (g/cm ³)	1.449	1.389	2.238
F(000)	457	676	1192
θ range for data collection (°)	2.37 to 27.48	3.26 to 53.94	2.45 to 27.47

Goodness-of-fit on F^2	1.012	1.062	1.140
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0415 wR2 = 0.0898	R ₁ = 0.0520 wR ₂ = 0.1334	R ₁ = 0.0223 wR ₂ = 0.0608
R indices (all data)	R1 = 0.0596 wR2 = 0.1004	R1 = 0.0742 wR2 = 0.1486	R1 = 0.0227 wR2 = 0.0610
Largest diff. peak and hole ($e \cdot \text{\AA}^{-3}$)	0.302 and -0.332	0.68 and -0.38	0.404 and -0.618

Table 2

	D-H $\cdots$ A	d(D-H)	d(H $\cdots$ A)	d(D $\cdots$ A)	<(DHA)
Complex 1	O(1W)-H(1W)...O(2)	0.86(3)	1.83(3)	2.657(2)	163(3)
	O(1W)-H(2W)...N(2)#2	0.89(3)	1.95(3)	2.815(2)	166(3)
	O(3)-H(3S)...N(3)#3	0.82	1.83	2.645(2)	176.9
Symmetry codes: #2 -x+2,-y+1,-z+2 #3 x,y-1,z-1					