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Synthesis, Crystal Structure of a Novel Mn Complex with Nicotinoyl-Glycine

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Academic Editor: Helmut Cölfen
Received: 9 November 2016; Accepted: 23 December 2016; Published: 30 December 2016

Abstract: A novel manganese complex, $C_{16}H_{26}MnN_4O_{12}$, was synthesized by the reaction of nicotinoyl-glycine and NaOH in an ethanol/water solution and structurally characterized by elemental analysis, UV-vis spectrum, IR spectrum and single-crystal X-ray diffraction analysis. The crystal of the complex belongs to the triclinic space group P_1 with $a = 7.8192(16)$ Å, $b = 8.8800(18)$ Å, $c = 9.0142(18)$ Å, $\alpha = 83.14(3)^\circ$, $\beta = 65.27(3)^\circ$, $\gamma = 81.67(3)^\circ$, $V = 516.3(2)$ Å^3, $Z = 1$, $Dx = 1.542$ mg·m^{-3}, $\mu = 0.66$ mm^{-1}, $F(000) = 271$, and final $R_1 = 0.0381$, $\omega R_2 = 0.0964$. The nicotinoyl-glycine ligand acts as a bridging ligand to connect the manganese ions by the hydrogen interactions; thus, the complex expands into a 3D supramolecular net structure.

Keywords: nicotinoyl-glycine; manganese complex; synthesis; crystal structure

1. Introduction

Coordination compounds, a class of newly developed porous inorganic-organic hybrid materials, have attracted much attention, due to their diverse and easily tailored structures [1–5], and their tremendous potential applications in nonlinear optics, catalysis, gas absorption, luminescence, magnetism and so on [6–8]. To obtain desired coordination compounds, hydrogen bonds, π-π interactions and Van der Waals interactions must be carefully considered [9]; also, the appropriate use of the well-designed multidentate nitrogen ligands and organic carboxylic acid ligands plays an important role in the synthesis of coordination compounds [10]. The hydrogen bond is an important element in coordination compounds. The strong and directional nature of hydrogen bonds is exploited in the organized self-assembly of molecules in solution and the solid state. Carboxylic acids and amides are two commonly used functional groups in crystal engineering because they generally form robust architectures via O–H...O and N–H...O hydrogen-bonded dimers [11].

In our experiment, we used nicotinoyl-glycine as a ligand. A manganese ion coordination polymer of this ligand was obtained and characterized by elemental analysis, IR, UV-vis and X-ray single-crystal diffraction analysis.

2. Results and Discussion

2.1. Elemental Analysis

The result of the elemental analysis showed that the symmetric unit of the Mn(II) coordination polymer is $C_{16}H_{26}MnN_4O_{12}$, indicating that the Mn(II) coordination compounds conform to a 1:2 metal-to-ligand stoichiometry.

2.2. *Structural Description of* $C_{16}H_{26}MnN_4O_{12}$ (**1**)

The result of the single-crystal X-ray diffraction revealed that complex **1** crystallizes in the triclinic space group P_1. The asymmetric unit consists of half a Mn(II) ion, one nicotinoyl-glycine ligand and two water molecules. The coordination environment of the manganese center is depicted in Figure 1. As shown in Figure 1, each manganese is octahedrally coordinated by two N atoms(N1, N1^i) from two nicotinoyl-glycine ligands at the axial positions, and four O atoms(O1w, O1w^i, O2w, O2w^i) from four coordination water molecules in the equatorial plane. In complex **1**, the nicotinoyl-glycine ligand acts as a bridge to connect two Mn (II) ions by hydrogen-bonding interactions. There are two kinds of element rings in the complex. The two oxygen atoms were linked by hydrogen-bonding interactions (O1w–H1wB...O3, O2w–H2wB...O2), and an element ring was formed. In addition, three oxygen atoms were linked by hydrogen-bonding interactions (O3w–H3wB...O2, O3w–H3wA...O1), and an element ring was formed as well. (Figure 2 shows the two kinds of element rings in the complex.) Furthermore, there are π-π stacking interactions (Figure 3) between the pyridine rings. The complex is extended to a 3D supramolecular net structure by the hydrogen-bond interactions and π-π stacking interactions. The 3D supramolecular net structure is shown in Figure 4. The main bond lengths (Å) and angles (°) for **1** are given in Table 1. The details of the hydrogen bond lengths and angles of the complex are given in Table 2.

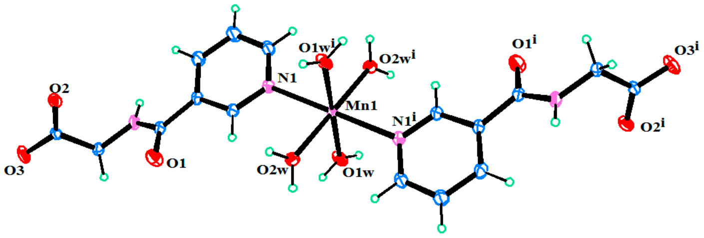

Figure 1. Coordination environment around the Mn(II) ion of complex **1** with labeling scheme at 30% ellipsoidal probability.

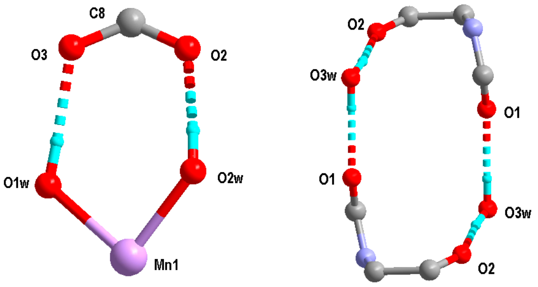

Figure 2. Two kinds of the element rings in the complex.

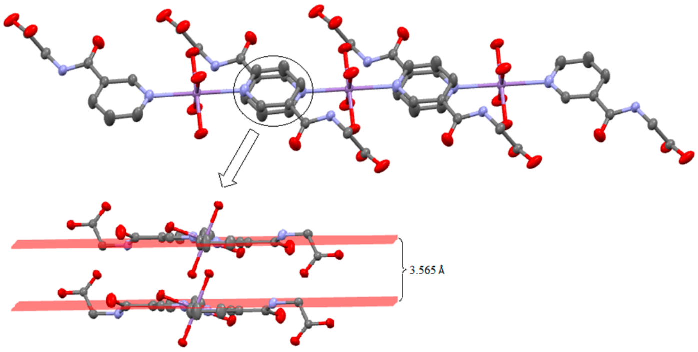

Figure 3. The π-π stacking interactions of **1**.

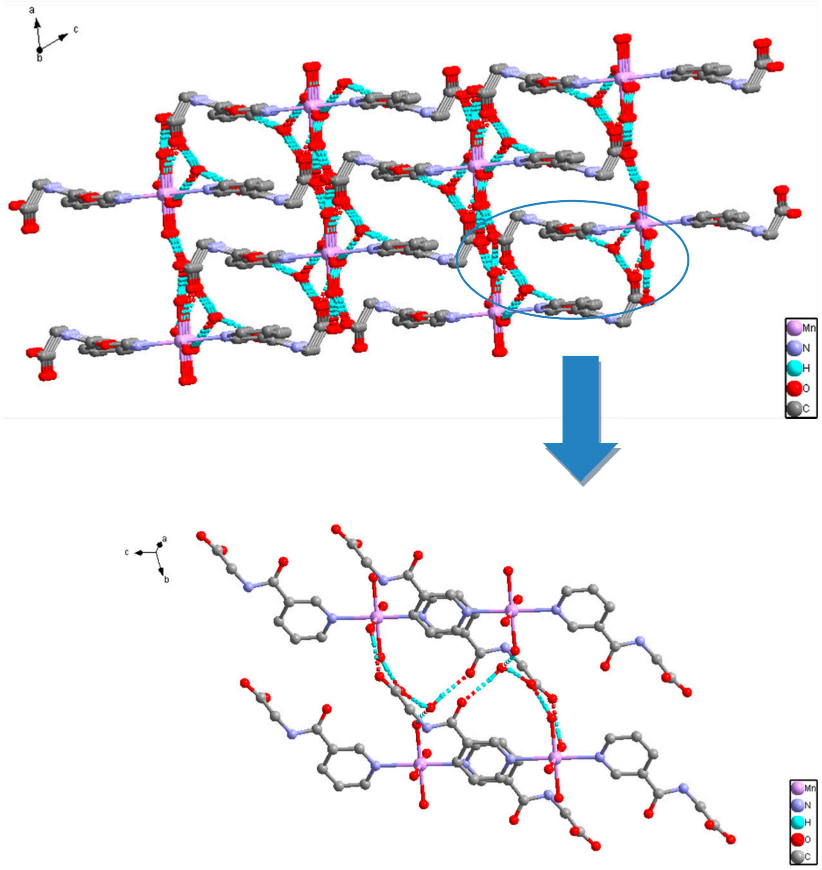

Figure 4. The 3D supramolecular net structure of **1**.

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

Bond	Distance	Bond	Distance
Mn1–O1w	2.1309 (13)	O2–C8	1.241 (2)
Mn1–O1w^{i}	2.1309 (13)	O3–C8	1.253 (2)
Mn1–O2w	2.1444 (13)	O3w–H3wB	0.851
Mn1–O2w^{i}	2.1444 (13)	O3w–H3wA	0.8491
Mn1–N1	2.3489 (16)	N2–H2B	0.86
Mn1–N1^{i}	2.3489 (16)	O1W–H1wB	0.8515
N1–C5	1.339 (2)	O1W–H1wA	0.8449
N1–C1	1.340 (3)	O1–C6	1.222 (2)
N2–C6	1.334 (2)	O2w–H2wA	0.8518
N2–C7	1.445 (2)	O2w–H2wB	0.8592
Angle		Angle	
O1w^{i}–Mn1–O2w^{i}	90.01 (6)	O2w–Mn1–O2w^{i}	180
O1w–Mn1–N1	90.58 (6)	O1w^{i}–Mn1–N1	89.42 (6)
O2w–Mn1–N1	89.20 (6)	O2w^{i}–Mn1–N1	90.80 (6)
O1w–Mn1–N1^{i}	89.42 (6)	O1w–Mn1–N1^{i}	90.58 (6)
O2w–Mn1–N1^{i}	90.80 (6)	O2w^{i}–Mn1–N1^{i}	89.20 (6)
N1–Mn–N1^{i}	180.00 (7)	O1–C6–N2	121.78 (16)
C5–N1–Mn1	121.76 (12)	O1–C6–C4	121.07 (16)
C1–N1–Mn1	121.05 (12)	N2–C6–C4	117.11 (15)
C6–N2–C7	121.44 (15)	N2–C7–C8	114.59 (14)
Mn1–O1w–H1wB	121.2	Mn1–O1w–H1wA	129.9

Symmetry code: (i) −x + 1, −y + 2, −z.

Table 2. Lengths (Å) and angles (°) of hydrogen bonds data for **1**.

	Donor–H...Acceptor	**D–H**	**H...A**	**D...A**	**∠D–H...A**
1	O1w–H1wB...O3	0.85	1.82	2.6711 (5)	176
2	O1w–H1wA...O3	0.84	1.87	2.6882 (6)	163
3	O2w–H2wA...O3w	0.85	1.83	2.6718 (5)	169
4	O2w–H2wB...O2	0.86	1.81	2.6671 (6)	175
5	O3w–H3wB...O2	0.85	1.92	2.7589 (6)	167
6	O3w–H3wA...O1	0.85	1.89	2.7345 (6)	171
7	Intra C5–H5A...O1	0.93	2.50	2.8144 (6)	100

2.3. IR Spectrum

Figure 5 shows the IR spectrum of the Mn(II) complex. From Figure 5, the bond observed at 3250 cm^{-1} is related to the N–H deformation stretching vibration [12–14], the asymmetrical stretching vibration and symmetrical stretching vibration of C–H in methylene at 2943 cm^{-1} and 2882 cm^{-1}, respectively [15,16]. The symmetrical stretching vibration of C–N is at 1243 cm^{-1}. At 1297 cm^{-1} is the characterized absorption peak of C–O [17,18]. In addition, 1601 cm^{-1}, 1553 cm^{-1}, 1547 cm^{-1}, 1466 cm^{-1} are the characterized absorption peaks of pyridine [19–21]. The deformation stretching vibration of C=O is clearly seen at about 1650 cm^{-1} in the IR spectrum of the complex which confirms the presence of an amidic moiety in the structure of the complex [22–25].

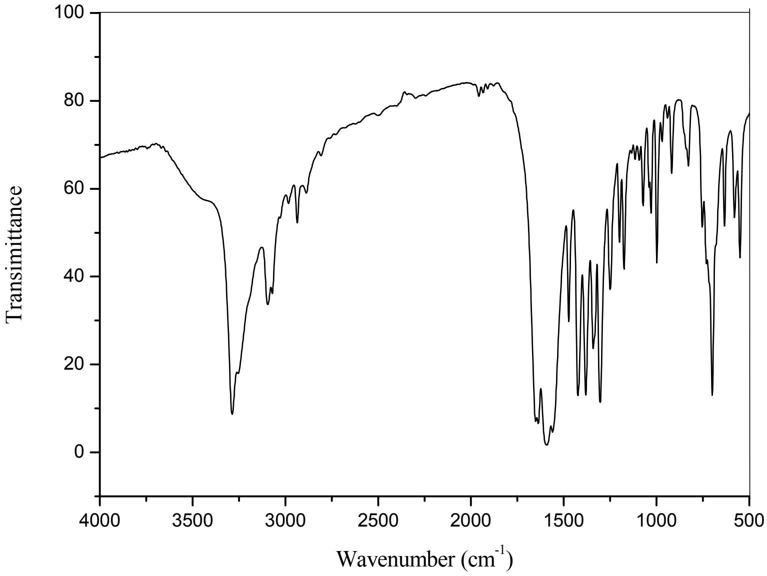

Figure 5. IR spectrum of complex **1**.

2.4. UV-Vis Spectrum

Figure 6 shows the UV-vis spectrum of the Mn(II) complex. From Figure 6, we can see the maximum absorption peak of the coordination compound at 201 nm. This indicates that there are large π-conjugated systems in the complex [26].

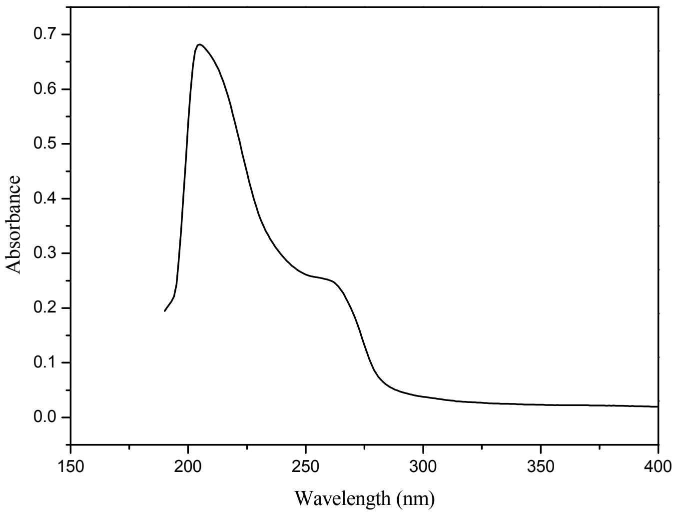

Figure 6. UV-vis spectrum of complex **1**.

3. Experimental Section

3.1. Materials and Instrumentation

Nicotinoyl-glycine ligand, sodium hydroxide (NaOH) and solvents were purchased commercially and used without further purification. The IR spectrum was recorded in the range 4000–400 cm^{-1} on a Infrared Spectrophotometer (Beijing Purkinje General Instrument, Beijing, China). Elemental analysis for carbon, hydrogen and nitrogen was performed on the Elementar Vario EL III elemental analyzer. UV-Vis spectrum was measured using UV-Visible Spectrophotometer (Beijing Purkinje General Instrument, Beijing, China). Single-crystal data of $C_{16}H_{26}MnN_4O_{12}$ were collected by a Bruker smart CCD diffractometer (Bruker, Billerica, MA, USA).

3.2. Synthesis of $C_{16}H_{26}MnN_4O_{12}$ (1)

A mixture of nicotinoyl-glycine ligand (180 mg, 1.0 mmol), and NaOH (40 mg, 1.0 mmol) were dissolved in 15 mL mixed solvents of water (H_2O):ethyl alcohol (CH_3CH_2OH) (v:v = 1:2). And the mixture was stirred for 6 h at 60 °C, then colorless crystals were collected and dried in the air.

3.3. Data Collection, Structural Determination, and Refinement

A colorless single crystal of the complex **1** with dimensions of 0.20 mm × 0.19 mm × 0.18 mm was selected and mounted on a glass fiber for data collection. The X-ray diffraction data were measured at 293(2) K on a Bruker smart CCD diffractometer with a graphite-monochromatized MoKα (λ = 0.71073 Å) radiation. The structure was solved by direct methods with SHELXL-97 [27] and refined on F^2 by full-matrix least-squares procedures with SHELXTL-97 [27]. The non-hydrogen atoms were located refined anisotropically, and hydrogen atoms were added according to theoretical models. The crystal data of **1** are given in Table 3.

Table 3. Summary of crystal result for sodium complex.

Empirical Formula	$C_{16}H_{26}MnN_4O_{12}$
Temperature/K	293 (2)
Crystal system	Triclinic
Space group	P_1
a/Å	7.8192 (16)
b/Å	8.8800 (18)
c/Å	9.0142 (18)

Table 3. *Cont.*

$\alpha/°$	83.14 (3)
$\beta/°$	65.27 (3)
$\gamma/°$	81.67 (3)
Volume/Å^3	561.3 (2)
Z	1
Dx (mg/m^{-3})	1.542
μ/mm^{-1}	0.66
S	1.06
F(000)	271
Index ranges	$-10 \le h \le 10$ $-11 \le k \le 11$ $-11 \le l \le 11$
Reflections collected	5481
Reflections with $I > 2\sigma(I)$	2467
Independent reflections	2559 [R(int) = 0.027]
Data/restraints/parameters	2559/6/151
Goodness-of-fit on F^2	1.061
Final R indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0381, wR_2 = 0.0964
Final R indexes [all data]	R_1 = 0.0388, wR_2 = 0.0969
Largest diff. peak/hole/e Å^{-3}	0.41/−0.38

4. Conclusions

In this study, we successfully synthesized and structurally characterized the Mn(II) complex $C_{16}H_{26}MnN_4O_{12}$. The structural analyses show that the asymmetric unit of the mononuclear complex consists of half a manganese ion, one nicotinoyl-glycine ligand and two coordinated H_2O molecules. The nicotinoyl-glycine ligand is a bridging ligand that connects manganese ions by the hydrogen-bond interaction, so the complex expands to a 3D supramolecular net structure.

Supplementary Materials: The supplementary materials can be accessed at www.mdpi.com/2073-4352/7/1/3/s1.

Acknowledgments: The authors would like to thank the National Natural Science Foundation of China (No. 21553002), and the Basic Research Project of Qinghai Province (No. 2016-ZJ-753).

Author Contributions: Bi Qing Chen designed the method. Xin Wang and Min He analyzed the crystal data for the Mn(II) coordination compounds.

Conflicts of Interest: The authors declare no conflict of interest.

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