

Two new complexes with 6-methylnicotinic acid ligand: Synthesis, crystal structure and Hirshfeld surfaces



Yang-Hui Luo, Qiu-Xia Mao, Bai-Wang Sun*

School of Chemistry and Chemical Engineering, Southeast University, Nanjing 210096, People's Republic of China

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ABSTRACT

Two new complexes derived from 6-methylnicotinic acid: **1** ($\text{Mn}(\text{C}_7\text{H}_6\text{NO}_2)_2(\text{H}_2\text{O})_2$) and **2** ($[\text{Ni}(\text{C}_7\text{H}_7\text{NO}_2)_2\text{Cl}_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$) have been synthesized and characterized. In complex **1**, the Mn^{II} ion exhibits a distorted octahedral geometry and featured with 1D chain, while the Ni^{II} ion in complex **2** exhibits a regular octahedral geometry and featured with intricate 3D motif. We further compared the molecular Hirshfeld surface and fingerprint plot analysis of ligand 6-methylnicotinic acid in complexes **1** and **2** with the individual 6-methylnicotinic acid, for the purpose of investigating the influence of different metals on the intermolecular interaction around 6-methylnicotinic acid. Which revealed that the closest contacts of these two complexes were dominated by $\text{H} \cdots \text{H}$, $\text{H} \cdots \text{O}$, $\text{N} \cdots \text{H}$, $\text{C} \cdots \text{H}$ and $\pi \cdots \pi$ (C–C) interactions, and the complexation with transition metals lead to the increase of $\text{C} \cdots \text{H}$ interactions while the decrease of $\text{H} \cdots \text{H}$, $\text{N} \cdots \text{H}$, and $\pi \cdots \pi$ interactions.

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1. Introduction

In recent years, great efforts has been devoted to the complexation of nicotinic acid and its derivative ligands with transition metals due to the great coordination potential of these ligands and the potential applications of these metal complexes in the field of biological system and desirable physical and chemical properties, such as conductivity or catalytic activity [1–4]. What's more, metal complexes with abundant hydrogen-bonding capabilities may also be developed as chemotherapeutic compounds [5]. The metal complexes of nicotinic acid and its derivative ligands are just in these case, the reported metal complexes with nicotinic acid [4] as well as 6-methylsubstituted nicotinic acid [3,6] adequately displayed the structural diversity of these ligands. Among these, only three metal complexes with 6-methylnicotinic acid have been reported, two of them with copper(I) and the third one with cobalt(II) ion.

The prediction and computation of molecular crystal structures through the aspect of intermolecular interactions, for the purpose of study the crystal structural features, crystal design and crystal engineering also have aroused much attention in recently years [7–10]. The main approach was through Hirshfeld surfaces [11], which serves as a powerful tool for elucidating molecular crystal structures, gaining additional insight into polymorphs comparison and identifying common features and trends in specific classes of compounds [12]. It is a space partitioning construct that summa-

rizes the crystal packing into a single 3D surface, and the surface can reduced to a 2D fingerprint plot, which summarizes the complex information on intermolecular interactions present in molecular crystals [8]. The principle of Hirshfeld surface and fingerprint plot are reported in other literature [7].

In our previously work [13], we reported the crystal structure of 6-methylnicotinic acid. As part of our systematic studies on the structural features of metal complexes with ligand 6-methylnicotinic acid, in the present work, we reported the synthesis and crystal structures of two new metal complexes derived from 6-methylnicotinic acid (Scheme 1): $\text{Mn}(\text{C}_7\text{H}_6\text{NO}_2)_2(\text{H}_2\text{O})_2$ (complex **1**) and $[\text{Ni}(\text{C}_7\text{H}_7\text{NO}_2)_2\text{Cl}_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ (complex **2**). We also compared the molecular Hirshfeld surface of individual 6-methylnicotinic acid ligand with these in complexes **1** and **2**, for the sake of investigating the influence of different metals on the intermolecular interactions experienced by 6-methylnicotinic acid ligand.

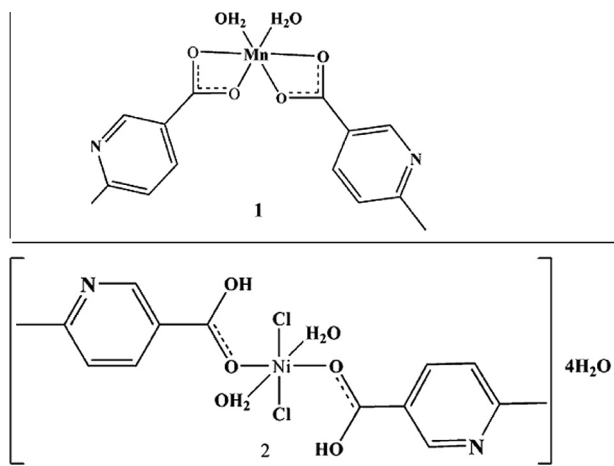
2. Experimental

2.1. General procedure

6-Methylnicotinic acid (purity > 99%, CAS registry number: 3222-47-6), $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (purity > 99%, CAS registry number: 13446-34-96), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (purity > 99%, CAS registry number: 7791-20-0) and all other solvents (reagent grade) were commercially available from Sigma Aldrich and used as received without further purification. Infrared spectras (IR) were recorded on a SHIMADZU IR prestige-21 FTIR-8400S spectrometer in the spectral range 4000 to 400 cm^{-1} , with the samples in the form of

* Corresponding author. Tel./fax: +86 25 52090614.

E-mail address: chmsunbw@seu.edu.cn (B.-W. Sun).



Scheme 1. Molecular structures of complexes **1** and **2**.

potassium bromide pellets. Elemental analyses were performed by a Vario-EL III elemental analyzer for carbon, hydrogen, and nitrogen of the complexes **1** and **2**.

2.2. Synthesis of complexes **1** and **2**

Complex **1** ($\text{Mn}(\text{C}_7\text{H}_6\text{NO}_2)_2(\text{H}_2\text{O})_2$) was prepared as follows: $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.4 mmol, 79.12 mg) was added into a stirring 30 ml methanol solution containing 6-methylnicotinic acid (0.8 mmol, 109.6 mg) at room temperature. The resulting mixture was stirred for 10 min and then filtered. The filtrate was collected and left undisturbed. Blank needles crystals formed after 3 days in high yield (88% based on Mn). Elemental analysis for **1**, *Anal. Calc.*: C, 46.29; N, 7.71; H, 4.44. Found: C, 46.28; N, 7.72; H, 4.442%. IR (KBr pellet, cm^{-1}): 3020, 2920, 2845, 2400, 1915, 1700 1608, 1448, 1380, 1250, 1005, 850, 743.

The colorless prism crystals of complex **2** ($[\text{Ni}(\text{C}_7\text{H}_7\text{NO}_2)_2\text{Cl}_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$) was prepared in the same way as **1** by using $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.4 mmol, 95.04 mg) instead of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and acetonitrile instead of methanol, the final yield is 80% (based on Ni). Elemental analysis for **2**, *Anal. Calc.*: C, 32.97; N, 5.49; H, 4.74. Found: C, 32.98; N, 5.48; H, 4.75%. IR (KBr pellet, cm^{-1}): 3030, 2910, 2854, 2420, 1905, 1720 1618, 1460, 1380, 1245, 1025, 845, 730.

2.3. X-ray crystallographic study

The single-crystal X-ray diffraction data of the complexes **1** and **2** were collected at 293 K with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.071073$ nm), a Rigaku SCXmini diffractometer with the ω -scan technique were used [14]. The lattice parameters were integrated using vector analysis and refined from the diffraction matrix, the absorption correction was carried out by using Bruker SADABS program with multi-scan method. A summary of crystallographic data, data collection, and refinement parameters for complexes **1** and **2** were given in Table 1. The structures of them were solved by full-matrix least-squares methods on all F^2 data, and used the SHELXS-97 and SHELXL-97 programs [15] for structure solution and structure refinement respectively. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms (except the hydrogen atoms of the water molecule) were inserted at their calculated positions and fixed at their positions [16], the hydrogen atoms of water molecules were located in difference Fourier maps and included in the subsequent refinement using restraints [17]. The molecular graphics were prepared by using the DIAMOND program [18] and MERCURY [19].

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

Compound	1	2
Formula	$\text{C}_{14}\text{H}_{16}\text{MnN}_2\text{O}_6$	$\text{C}_{14}\text{H}_{24}\text{Cl}_2\text{N}_2\text{NiO}_{10}$
Formula weight	363.23	509.96
Crystal system	monoclinic	triclinic
Space group	$C2/c$	$P\bar{1}$
a (Å)	22.814(5)	7.1113(14)
b (Å)	5.5122(11)	7.3888(15)
c (Å)	16.662(3)	11.530(2)
α (°)	90	86.61(3)
β (°)	131.81(3)	78.80(3)
γ (°)	90	65.29(3)
V (Å ³)	1561.8(5)	539.71(24)
Z	4	1
D_{calc} (Mg m^{-3})	1.545	1.569
T (K)	293(2)	293(2)
μ (mm^{-1})	0.877	1.198
Crystal dimensions	$0.46 \times 0.24 \times 0.15$	$0.40 \times 0.20 \times 0.20$
No. of reflections collected	1793	2442
No. of unique reflections	1389	2158
Goodness-of-fit (GOF) on F^2	0.984	1.122
R_1, wR_2 ($I > 2\sigma(I)$)	0.0395, 0.0826	0.0845, 0.2420
R_1, wR_2 (all data)	0.0543, 0.0869	0.0935, 0.2534
CCDC No.	888965	889300

2.4. Hirshfeld surface calculations

Molecular Hirshfeld surfaces calculations of individual 6-methylnicotinic acid and 6-methylnicotinic acid ligand in complexes **1** and **2** were performed by using the CRYSTALEXPLORER 2.0 program [20]. The 3D d_{norm} surfaces are mapped over a fixed color scale of -0.75 (red) to 1.1 Å (blue), *Shape index* mapped in the color range of 0.6 – 2.6 Å and *Curvedness* in the range of 0.73 – 2.5 Å. The 2D fingerprint plots displayed by using the standard 0.6 – 2.6 Å view with the d_e and d_i distance scales displayed on the graph axes.

3. Results and discussion

3.1. Structural description

Crystal structures of complexes **1** and **2** were shown in Figs. 1 and 2, selected bond distances and angles were tabulated in Table 2, and geometrical parameters for hydrogen bonds interactions were summarized in Table 3. Single crystal X-ray diffraction analysis of **1** reveals the formation of a complex of stoichiometry $\text{Mn}(\text{C}_7\text{H}_6\text{NO}_2)_2(\text{H}_2\text{O})_2$. It crystallizes in the monoclinic $C2/c$ space group with $Z = 4$, the asymmetric unit (ASU) consisting of half a manganese atom, an entire molecule of 6-methylnicotinic acid as well as a coordinated water molecule (Fig 1), with the water molecule almost perpendicular to the 6-methylnicotinic acid plane with a dihedral angle of 94.01° . The Mn atom is hexa-coordinated in a distorted octahedral geometry defined by two water oxygen atoms and four ligand oxygen atoms. The equatorial plane of the octahedral geometry is composed of three ligand oxygen atoms (O1, O2 and O1A) and one coordinated water O3A with Mn–O distances are found to be $\text{Mn1–O1} = 2.222$ Å, $\text{Mn1–O2} = 2.267$ Å and $\text{Mn1–O3} = 2.132$ Å. The axial positions of the octahedral geometry are occupied by one ligand oxygen atom (O2A) and one water oxygen atom (O3), with the O–Mn–O angles are found to be $\text{O1–Mn1–O3} = 101.49^\circ$, $\text{O2–Mn1–O3} = 99.38^\circ$, $\text{O1–Mn1–O2} = 58.25^\circ$, $\text{O1–Mn1–O3A} = 98.41^\circ$, $\text{O1–Mn1–O2A} = 109.74^\circ$, $\text{O1–Mn1–O1A} = 165.30^\circ$, $\text{O2–Mn1–O2A} = 85.16^\circ$ and $\text{O3–Mn1–O3A} = 95.91^\circ$.

Single crystal X-ray diffraction analysis of **2** reveals the formation of a complex of stoichiometry $\text{NiCl}_2(\text{C}_7\text{H}_7\text{NO}_2)_2(\text{H}_2\text{O})_2 \cdot 4(\text{H}_2\text{O})$. It crystallizes in the triclinic $P\bar{1}$ space group with $Z = 1$, the ASU consisting of half a nickel atom on the crystallographic inversion

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