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Inorganica Chimica Acta 360 (2007) 1466–1473

Inorganica Chimica Acta

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Syntheses and crystal structures of three Mn(II) complexes with 2-hydroxynicotinate

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Received 8 June 2006; accepted 12 August 2006
Available online 24 August 2006

Abstract

Three new Mn(II) complexes $[Mn(HnicO)_2(H_2O)_2]$ (**1**), $[Mn_2(HnicO)_2SO_4(H_2O)_2]_n$ (**2**), and $[NaMn(HnicO)_3]_n$ (**3**) (H_2nicO = 2-hydroxynicotinic acid) have been synthesized and determined by X-ray diffraction. For complex **1**, the mononuclear units with two bidentate $HnicO^-$ ions and two water molecules are assembled into a 3D architecture *via* hydrogen bonding and π–π interactions. For **2**, Mn(II) ions are connected by μ_3-$HnicO^-$ and μ_2-SO_4^{2-} bridging ligands, producing a 2D (6,3) coordination network. For **3**, binuclear Na(I)–Mn(II) units with three carbonyl oxygen bridges are interlinked by carboxylate groups, resulting in a 3D 6-connected coordination network with distorted α-Po topology. The magnetic properties of **2** are discussed.

Keywords: Mn(II) complexes; Hydrogen-bonding; π–π interaction; 2-Hydroxynicotinate; Hydrothermal reactions; Crystal structure

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1. Introduction

In recent years, great efforts have been devoted to the rational design and synthesis of new metal-organic networks in the field of crystal engineering with the driving force of intriguing architectures and novel functionalities such as gas storage [1], photoluminescent [2], and magnetic properties [3]. The goal of crystal engineering is to recognize and design synthons that ensures structural generality and predictability. Within this field, many studies have been concentrated on the utility of supramolecular contacts, particularly, hydrogen bonding and aromatic interactions, to construct multi-dimensional arrays and/or networks [4]. Ligands containing heterocycles and carboxylates, such as 2,3-pyrazinedicarboxylic acid [5], pyrazine-2-carboxylic acid [6], and 2,3-pyrazinedicarboxylic acid [7], have attracted intense attention due to their versatile coordination modes and high structural stability. Besides, interesting multi-dimensional networks may be expected due to the potential noncovalent interactions, since the carboxylate group could act as strong hydrogen bonding donor and/or acceptor. The resulting structures are often influenced by deprotonation of carboxylic acid, coordination modes, and other subtle factors such as the spatial arrangement of the side-chains and the counter ions. Thus, it is possible to synthesize polymeric frameworks with interesting topologies through using of bridging ligand and tuning of the reaction conditions.

However, the systematic investigation of polymeric frameworks constructed from heterocyclic carboxylates bearing a hydroxyl group is rare [3a,8,9]. We choose 2-hydroxynicotinic acid (H_2nicO) as the organic ligand to build up metal-organic networks. The ligand contains multiple coordination sites deriving from both pyridine and carboxylate, and hence is a good candidate that may yield new polymeric networks with specific topologies. As shown in Scheme 1, H_2nicO undertakes enol-ketonic tautomeric

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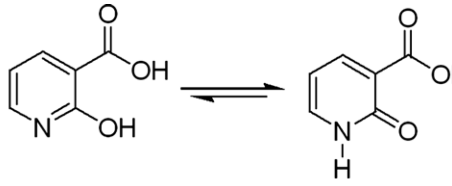
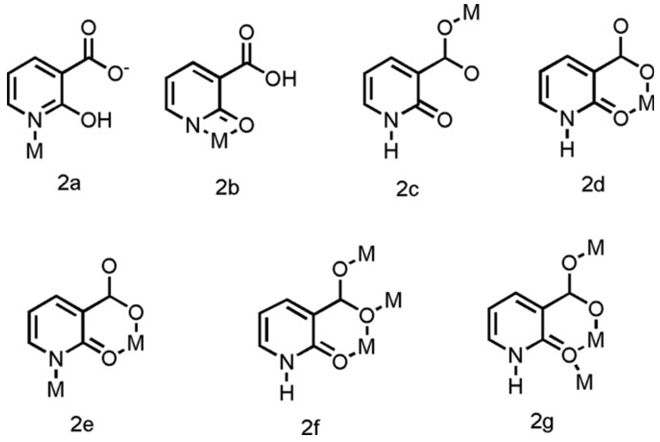
doi:10.1016/j.ica.2006.08.014



Scheme 1. The enol–ketonic tautomerism of H_2nicO.



Scheme 2. The different coordination modes of $HnicO^-$.

transformation [9e] in both phases of solid state and solution, and the ketonic(amide) tautomer is stabilized by the intramolecular hydrogen bonding between the COOH and C=O groups [10]. It can be deprotonated successively to generate $HnicO^-$ and $nicO^{2-}$ in the basic medium [9e]. The different coordination modes of $HnicO^-$ including monodentade [8a], bridging [8b,9b], N,O-chelating [9c,9d], and O,O-chelating (Scheme 2) [8a,9a] could result in a large diversity of coordination compounds.

Herein we report the syntheses and structural characterization of three new Mn(II) complexes $[Mn(HnicO)_2(H_2O)_2]$ (**1**), $[Mn_2(HnicO)_2SO_4(H_2O)_2]_n$ (**2**), and $[NaMn(HnicO)_3]_n$ (**3**). The 3D architectures of these complexes are sustained with coordination bonds and π–π interactions and/or hydrogen bonding. Magnetic investigations revealed antiferromagnetic interactions in **2** but no obviously magnetic interactions in **3**.

2. Experimental

2.1. Materials

All the starting chemicals were of AR grade and used as purchased without further purification.

2.2. Synthesis of $[Mn(HnicO)_2(H_2O)_2]$ (1)

A mixture of $MnSO_4 \cdot H_2O$ (0.25 mmol, 0.042 g), H_2nicO (0.5 mmol, 0.070 g), NaOH solution (0.2 M, 0.6 mL), Me_4NOH solution (10%, 0.3 mL), and H_2O (10 mL) was sealed in a 25-mL stainless steel reactor with a Teflon liner and heated at 150 °C for 3 days, then cooled to room temperature. Colorless crystals were collected by filtration, washed quickly with water and ethanol, and dried in air. The final pH value of the reaction mixture is 6. Yield: (0.028 g) 30.0%. *Anal.* Calc. for $C_{12}H_{12}N_2MnO_8$ (**1**) (Fw: 367.17): C, 39.25; H, 3.29; N, 7.63. Found: C, 39.06; H, 3.46; N, 7.55%. Main IR bands (cm^{-1}): 3368m, 3124m, 1634vs, 1606vs, 1575s, 1462m, 1431m, 1380m, 1318m, 1238m, 903m, 781m, 660m.

2.3. Synthesis of $[Mn_2(HnicO)_2SO_4(H_2O)_2]_n$ (2)

A mixture of $MnSO_4 \cdot H_2O$ (0.50 mmol, 0.085 g), H_2nicO (0.25 mmol, 0.035 g), NaOH solution (0.2 M, 0.3 mL), Me_4NOH solution (10%, 0.2 mL), and H_2O (10 mL) was sealed in a 25-mL stainless steel reactor with a Teflon liner and heated at 150 °C for 3 days, then cooled to room temperature. Colorless crystals were collected by filtration, washed quickly with water and ethanol, and dried in air. The final pH value of the reaction mixture is 7. Yield: (0.119 g) 46.0%. *Anal.* Calc. for $C_{12}H_{12}N_2Mn_2O_{12}S$ (**2**) (Fw: 518.18): C, 27.82; H, 2.33; N, 5.41. Found: C, 28.00; H, 2.67; N, 5.34%. Main IR bands (cm^{-1}): 3295m, 3090m, 1633vs, 1593vs, 1556s, 1464m, 1420m, 1386m, 1231m, 1105vs, 910m, 782m, 664m.

2.4. Synthesis of $[NaMn(HnicO)_3]_n$ (3)

A mixture of $MnCl_2 \cdot 4H_2O$ (0.4 mmol, 0.079 g), H_2nicO (0.4 mmol, 0.056 g), NaN_3 (1 mmol, 0.065 g), and H_2O (5 mL) was sealed in a 25-mL stainless steel reactor with a Teflon liner and heated at 150 °C for 3 days, then cooled to room temperature. Light yellow crystals were collected by filtration, washed quickly with water and ethanol, and dried in air. The final pH value of the reaction mixture is 8. Yield: (0.142 g) 72.3%. *Anal.* Calc. for $C_{18}H_{12}N_3NaMnO_9$ (**3**) (Fw: 492.24): C, 43.92; H, 2.46; N, 8.54. Found: C, 43.86; H, 2.55; N, 8.73%. Main IR bands (cm^{-1}): 3083m, 3002m, 1652vs, 1601m, 1555s, 1465m, 1426m, 1377m, 1317m, 1146vs, 904m, 792m, 660m.

2.5. Physical measurements

Elemental analyses (C, H, N) were performed on an Elementar Vario EL analyzer. IR spectra were recorded on a Nicolet Magna-IR 750 spectrometer equipped with a Nic-Plan Microscope. Magnetic properties of the complexes **2** and **3** were carried out on a Quantum Design MPMS XL-5 SQUID system. Diamagnetic corrections were made with Pascal's constants [11].

2.6. Crystallographic studies

Diffraction intensity data of the single crystals were collected at room temperature on a Nonius Kappa CCD diffractometer, equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Empirical absorption corrections were applied using the Sortav program [12].