



Structures and spectroscopic properties of Ni(II) and Mn(II) complexes based on 5-(3', 5'-dicarboxylphenyl) picolinic acid ligand



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ABSTRACT

Two novel complexes including [Ni(Hdcppa)(H₂O)₄] (**1**) and {[Mn₃(dcppa)₂(H₂O)₆]·2H₂O}_n (**2**) have been synthesized and characterized by single crystal X-ray structure analysis and elemental analysis. Results show that **1** is a mononuclear nickel(II) compound with octahedron coordination geometry, while **2** is a stairs-like 2D layer structure consisting of the trinuclear Mn^{II} units linked through dcppa³⁻. Spectroscopic and electrochemical properties of the complexes **1–2** have also been studied in dimethyl sulfoxide solution at room temperature.

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1. Introduction

The design and synthesis of coordination polymers (CPs) are of great interest, owing to their intriguing esthetic structures as well as their tremendous potential applications in nonlinear optics, gas storage, luminescence, magnetism and catalysis [1,2]. Various CPs built up from polynuclear transition metal clusters and multicarboxylate building blocks have been extensively studied [3,4]. In the past decade, the researches in this field have largely focused on high-symmetry structures ligands to prepare MOFs or coordination polymers with well-regulated network structures [5,6]. In recent years, ligands with coordination groups distributed in an unsymmetrical direction have been extensively used to self-assemble irregular CPs. Yan's group synthesized ten Co(II) complexes using positional isomeric dipyriddy ligands and the phenyl dicarboxylate, and systematically investigate the influence of the positional isomeric ligands on the structures and magnetic properties of their complexes [7a]. Wang's group studied significant positional isomeric effect on structural assemblies of Zn(II) and Cd(II) coordination polymers based on bromoisophthalic acids and various dipyriddy-type coligands, the results revealed that the diverse

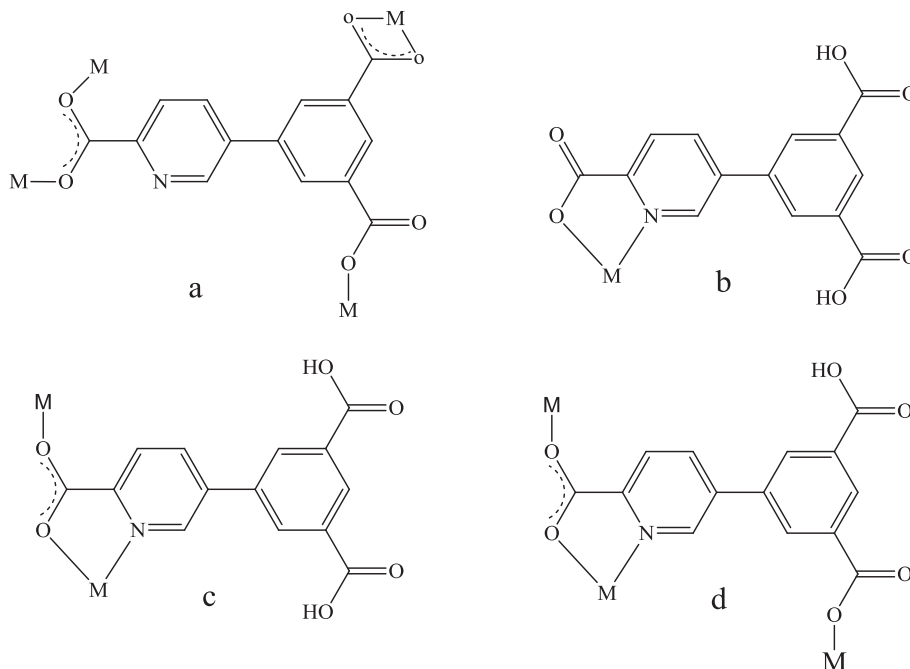
coordination networks of complexes can be adjusted by the different dispositions of the -Br substituent of isophthalate building blocks, as well as the metal ions and the dipyriddy coligands [7b]. In these ligands, biphenyl-3,4',5'-tricarboxylic acid(H₃BPT) has been also started to engage research and a recognized structural component constructing metal-organic frameworks. For example, a unique independent one-dimensional green luminescent coordination polymer nanotube based on an unsymmetric tricarboxylate linker was synthesized by Hong and coworker [8a]. The first near-infrared luminescent ytterbium metal-organic framework has been acquired successfully by Zhang's group and realized for the highly selective and sensitive sensing of small molecules [8b]. Wang's group reported four compounds with four kinds of different topologies based on H₃BPT ligand [8c]. These research works showed that the frameworks based on unsymmetrical linkers may exhibit many novel structures and unique properties. The existence of carboxylate groups in different orientations on the aromatic backbone of some multicarboxylate acids may have significant effects on the assembly of coordination networks [9].

5-3',5'-dicarboxylphenyl picolinic acid (H₃dcppa) is unsymmetrical substituted linkers with three carboxylates and N–O chelator. H₃dcppa can be partially or fully deprotonated to generate H₂dcppa⁻, Hdcppa²⁻ or dcppa³⁻ at different pH values. As shown in Scheme 1, the tricarboxylate anions can display more versatile coordination modes than biphenyl-3,4',5'-tricarboxylic acid.

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Scheme 1. Some possible representative coordination modes of H₃dcpa ligand.

Therefore, it can coordinate with metal centers in multicoordinated ways to form a series of coordination polymers with interesting topologies (1D helical chain, 2D layer and 3D MOFs) and properties.

Herein, we report the syntheses and features of the two new structures containing H₃dcpa with different metal centers, namely [Ni(Hdcpa)(H₂O)₄] and {[Mn₃(dcpa)₂(H₂O)₆]·2H₂O}_n.

2. Experimental

2.1. Materials and instrumentation

H₃dcpa was received from Jinan Camolai Trading Company, China. Other reagents and solvents were of analytical reagent and directly used without further purification. Elemental analyses (C, H and N) were performed on a Perkin–Elmer 240 CHN elemental analyzer. UV–vis spectra were recorded on a Puxi TU-1901 double-beam spectrophotometer (Beijing, China). Luminescence spectrum was recorded on a CARY Eclipse fluorescence spectrophotometer at room temperature. A CHI 660E electrochemical workstation (Shanghai CH Instrument Company, China) was used for all of the electrochemical measurements. A glassy carbon electrode (GCE) of 3-mm diameter was used as working electrode; a platinum wire and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively.

2.2. X-ray diffraction study

Single-crystal X-ray diffraction data for the complexes **1–2** were collected on a Bruker Apex CCD area-detector diffractometer (Cu K α , $\lambda = 1.54184$ Å). Absorption corrections were applied by using multiscan program SADABS. The structures were solved with direct methods and refined with a full-matrix least-squares technique with the SHELXTL program package [10,11]. All non-H atoms were refined anisotropically, then hydrogen atoms attached to C atoms were placed geometrically and refined using a riding model approximation, with C–H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. H atoms of water molecules were located from the difference Fourier map

and placed in the structural model with the O–H distances restraint to O–H distances of 0.80–0.85 Å. Crystallographic data of the complexes are shown in Table 1. Selected bond lengths and bond angles were given in Table S1. The geometrical parameters of the hydrogen bonds are listed in Table S2.

2.3. Syntheses of 1 and 2

The complexes **1–2** were prepared by self-assembly of

Table 1
Crystallographic data and structural refinement details of complexes 1 and 2.

Parameter	1	2
CCDC number	1412056	1412057
M	831.96	873.31
empirical formula	C ₂₈ H ₃₀ N ₂ Ni ₂ O ₂₀	C ₂₈ H ₂₄ Mn ₃ N ₂ O ₂₀
Temperature (K)	296(2)	296(2)
Crystal system	monoclinic	triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1
<i>a</i> (Å)	14.3976(10)	6.8045(9)
<i>b</i> (Å)	6.9895(8)	9.1648(9)
<i>c</i> (Å)	15.7865(14)	14.8222(16)
α (deg)	90	103.797(9)
β (deg)	95.148(8)	100.792(10)
γ (deg)	90	101.415(9)
<i>V</i> (Å ³)	1582.2(3)	852.81(17)
Crystal size (mm)	0.35 × 0.33 × 0.30	0.35 × 0.32 × 0.30
<i>Z</i>	4	1
<i>D</i> _{calc} (g cm ⁻³)	1.746	1.552
μ (mm ⁻¹)	2.34	9.70
<i>F</i> ₀₀₀	856	441
Theta range (deg)	3.1–68.5	3.22–70.46
GOOF(<i>F</i> ²)	1.08	1.17
Reflections measured	3075	5228
Reflections Unique	1715	3246
<i>R</i> _{int}	0.092	0.059
Final <i>R</i>	<i>R</i> ₁ = 0.053	<i>R</i> ₁ = 0.0783
[<i>I</i> > 2 σ (<i>I</i>)]	ω R ₂ = 0.114	ω R ₂ = 0.2107
<i>R</i> (all data)	<i>R</i> ₁ = 0.085, ω R ₂ = 1.03	<i>R</i> ₁ = 0.1067 ω R ₂ = 0.2405
$\Delta\rho_{\max}/\Delta\rho_{\min}$ (e Å ³)	0.42, -0.36	1.82, -0.680

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