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Synthesis, structural characterization and magnetic property of metal 2,5-pyridine dicarboxylate complex

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Abstract

Four 2,5-pyridine dicarboxylate (pydc) metal (Mn, Mn/K, Zn, and Nd) coordination polymers with 2D and 3D architectures were synthesized, in which pydc ligand exhibits four new coordination modes to link up to seven metal atoms. Magnetic properties of the complexes are also discussed.

Keywords: Manganese; Zinc; Neodymium; Pyridine dicarboxylate; Crystal structure; Magnetism

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Over the past decade there have been considerable interest in the structures and properties of multi-metal or mixed-metal coordination polymers because of their promising application to diverse areas of technology [1–3]. In designing 1-, 2- and 3-dimensional coordination polymers, the selection of appropriate ligand as building block is crucial to determining structural outcome of target polymers. Mixed-linker systems composed of both benzene dicarboxylate and pyridyl ligand have always used for the preparation of novel coordination polymers [4]. We have synthesized several manganese coordination polymers by using phthalic acid or picolinic acid in the presence of pyridyl ligand [5]. Our interest in the manganese complexes stems also from the existence of Mn as a mixed metal cluster together with other redox-inert metal in oxygen evolving complex of photosystem II [6]. 2,5-pyridine dicarboxylate (pydc) is a polydentate ligand having the coordination ability of both dicarboxylate and pyridyl ligands, and is expected to produce new cluster topologies by virtue of its coordinative flexibility. It is noted that pydc has recently been used in the preparation of polymeric Ln(III)/Cu, Ag, Zn mixed metal complexes [7–10]. However, only few transition metal complexes containing pydc have been synthesized [11–17]. In order to develop the metal-pydc coordination chemistry including transition metal, lanthanide and mixed metals, four complexes $[Mn(phen)(pydc)]_n$ (**1**), $[K_2Mn(pydc)_2(H_2O)_5]_n$ (**2**), $[\{Zn(pydc)(H_2O)_2\} \cdot (H_2O)]_n$ (**3**) and $[\{Nd_2(pydc)_2(Hpydc)_2(H_2O)_4\} \cdot 2H_2O]_n$ (**4**) were prepared by both conventional solution syn-

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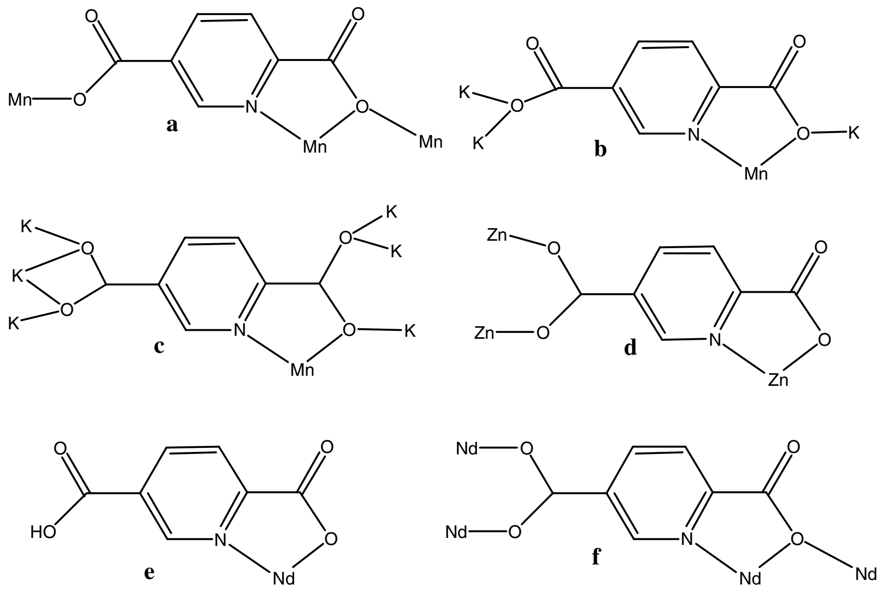

Scheme 1. Coordination modes of pydc ligand in complexes **1** (a), **2** (b,c), **3** (d), and **4** (e,f).

thesis and hydrothermal method. [1] In all the preparations, mixed metal Mn/alkali, Mn/Zn and Mn/Nd materials were adopted to attempt to produce mixed metal pydc complexes. However, only **2** contains mixed MnK_2 metals, while **3** and **4** contain sole Zn and Nd, respectively, indicating that Zn and Nd have better affinity for oxygen than Mn has. As a multifunctional ligand, pydc coordinates to these metal atoms in chelating-bridging modes using up to all the five donor atoms. Scheme 1 exhibits all the coordination modes of the pydc ligand in complexes **1**–**4**. It is worthwhile to explain that the pydc ligand acts as a μ_3-, μ_4- or μ_7-bridge to link 3–7 metal atoms in complexes **1**–**4** (Scheme 1), of which modes a, b, c and f are discovered for the first time in the metal pydc complexes. To our knowledge, in all the pydc metal complexes, only a few contain more than three metal atoms bound simultaneously by one pydc ligand [9,10]. These new coordination modes represent more complicated structures.

Complex **1** is the second example of the Mn pydc complex family [12]. The Mn(II) center is coordinated by one phen and three pydc ligands (Fig. 1), to form a distorted octahedral geometry. Fig. 1 also shows the coordination mode of the pydc linking three Mn atoms in a chelating-bridging mode (Scheme 1(a)). The carboxylate oxygen atom in the chelating ring links neighboring Mn(II) ion to form $[(phen)_2Mn_2(\mu\text{-}O_{carboxylate})_2]$ subunit with the Mn···Mn distance of 3.552 Å, which is connected to other subunit by a long bridge via pyridyl ring, constructing a two-dimensional sheet structure. [2] Complex **2** is a mixed metal (Mn/K) pydc complex containing a basic Mn unit $[Mn(pydc)_2(H_2O)_2]^{2-}$ which is connected to two K^+ ions

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[1] A mixture of H_2pydc (0.34 g, 2 mmol), KOH (0.23 g, 4 mmol) $Mn(OAc)_2 \cdot 4H_2O$ (0.49 g, 2 mmol), phen (0.40 g, 2 mmol) in 15 ml of $MeOH/H_2O$ (v/v, 1:1) was sealed in a 25-ml stainless-steel reactor with a teflon liner and was heated at 453 K for 72 h under autogenous pressure. Slow cooling to room temperature yielded 0.42 g (yield 52%) of block yellow crystals of **1**. Anal. Calc. for $C_{19}H_{11}MnN_3O_4$ (%): C, 56.97; H, 2.75; N, 10.49. Found (%): C, 57.14; H, 2.56; N, 10.36. Complex **4** was prepared according to preceding procedure in the absence of phen using $Mn(NO_3)_2 \cdot 4H_2O$ (1 mmol) and $Nd(NO_3)_3$ (0.5 mmol) as metal reagents. Light purple block crystals (0.15 g, yield 57%) were obtained. Anal. Calc. for $C_{28}H_{24}Nd_2N_4O_{22}$ (%): C, 31.79; H, 2.27; N, 5.30. Found (%): C, 31.54; H, 2.31; N, 5.25. Complexes **2** and **3** were prepared in 25 mL of $EtOH/H_2O$ (v/v, 2:1) by stirring a mixture of $Mn(acac)_3$ (2 mmol) and KOH (5 mmol) for **2** or $ZnCl_2$ (5 mmol) for **3**. After crystallization and filtration the yields were 65% and 63%, respectively. Anal. Calc. for **2** ($C_{14}H_{16}MnK_2N_2O_{13}$) (%): C, 30.36; H, 2.89; N, 2.53. Found (%): C, 30.44; H, 2.81; N, 2.59; for **3** ($C_7H_9NO_7Zn$) (%): C, 29.52; H, 3.16; N, 2.46. Found (%): C, 30.18; H, 3.22; N, 2.57.

[2] Crystal data: **1**, $M_r = 400.25$, monoclinic, $C2/c$, $a = 21.4834(3)$, $b = 10.6324(2)$, $c = 16.3063(4)$ Å, $\beta = 116.222(1)°$, $V = 3341.37(11)$ Å^3, $Z = 8$, $D_c = 1.591$ g/cm^3, $\mu = 0.822$ mm^{-1}. $R_1 = 0.0379$, $wR_2 = 0.0897$. Observed reflections 2353 [$I > 2\sigma(I)$]. **2**, $M_r = 553.43$, triclinic, $P\bar{1}$, $a = 7.4203(7)$, $b = 10.4709(9)$, $c = 13.7730(12)$ Å, $\alpha = 77.607(2)$, $\beta = 83.790(2)$, $\gamma = 76.267(2)°$, $V = 1013.46(16)$ Å^3, $Z = 2$, $D_c = 1.814$ g/cm^3, $\mu = 1.135$ mm^{-1}. $R_1 = 0.0594$, $wR_2 = 0.1277$. Observed reflections 2194 [$I > 2\sigma(I)$]. **3**, $M_r = 284.52$, orthorhombic, $P2_12_12_1$, $a = 7.3509(2)$, $b = 9.4432(3)$, $c = 13.8586(2)$ Å, $V = 962.01(4)$ Å^3, $Z = 4$, $D_c = 1.964$ g/cm^3, $\mu = 2.575$ mm^{-1}. $R_1 = 0.0337$, $wR_2 = 0.0718$. Observed reflections 1422 [$I > 2\sigma(I)$]. **4**, $M_r = 1059.01$, monoclinic, $P2_1$, $a = 9.1280(1)$, $b = 19.8299(4)$, $c = 9.2715(1)$ Å, $\beta = 101.563(1)°$, $V = 1644.15(4)$ Å^3, $Z = 2$, $D_c = 2.139$ g/cm^3, $\mu = 3.227$ mm^{-1}. $R_1 = 0.0247$, $wR_2 = 0.0609$. Observed reflections 4055 [$I > 2\sigma(I)$]. The number of Friedel pairs in datasets is 1252.