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Two new pyridine-2,3-dicarboxylate coordination polymers prepared from zerovalent metal precursor: Syntheses, luminescent and magnetic properties[☆]

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ABSTRACT

Two new K^+/Cu(II) and Zn(II) coordination polymers with pyridine-2,3-dicarboxylate (pydc), $\{K_2[Cu(\mu\text{-pydc})_2]\cdot 3H_2O\}_n$ (**1**) and $\{[Zn(\mu\text{-pydc})(H_2O)(4\text{-mim})]\cdot H_2O\}_n$ (**2**) (4-mim=4-methylimidazole) have been synthesized from zerovalent metal and characterized by IR, EPR spectroscopy, thermal analysis and single crystal X-ray diffraction techniques. In the sandwiched 3D anionic framework of **1**, pydc ligands exhibit hexadentate coordination; tridentate coordination bond with Cu(II) and tridentate ionic interaction with K^+ ions. $\{K_2[Cu(\mu\text{-pydc})_2]\cdot 3H_2O\}_n$ shows a rare topology consists of three dimensional (3,4,5)-connected network with the point symbol of $\{4^2.6\}_2\{4^2.8^4\}\{4^3.6.8^6\}_2$. The distorted square pyramidal geometry of **2** is completed with an nitrogen atom from 4-mim and aqua ligand to form a 1D polynuclear structure. The hydrogen bonds link the 1D chains into 3D architecture. The temperature dependent magnetic property of complex **1** has been studied. Complex **2** exhibits unusual yellow luminescence in the solid state at room temperature.

1. Introduction

The reasons for combining metal ions and organic ligands into supramolecular coordination networks are countless, they give access to structural diversity and properties likewise small molecule adsorbsion, spectroscopic and magnetic properties, conductivity and catalytic activity that are less common in organic solids [1–5]. Although some highly important coordination polymers have emerged recently, the majority of them are not water soluble. Water-solubility is a very important characteristic of the some field such as electrochemistry, and medical purposes [6–8]. Self-assembly of weaker intermolecular forces such as hydrogen bonds not only are a vital process in the formation of biological architectures but also they are capable of create large complex units into desirable motifs [9–12].

Heterometallic coordination polymers formed by metallic building blocks with different chemical nature (such as alkali metals and transitions metals) are interesting due to their diverse structural functionality [13–18]. It is known that coordination polymers can be synthesized starting from zerovalent metals and this strategy was successfully used to prepare a good deal of heterometallic coordination compounds [17,19–24]. For the formation of a heterometallic or homometallic polynuclear complexes in the presence of polydentate ligands is required as well as the presence of zerovalent metals. Heterocyclic aromatic multicarboxylic acids such as pyridinedicarboxylic acids, are widely exploited to construct polynuclear coordination polymers due to existence of both nitrogen and oxygen atoms [25,26]. Pyridine-2,3-dicarboxylic acid ligand has proved to be versatile ligands and exhibit various coordination modes to furnish various structures with higher dimensionality (Scheme 1) [26–29]. Imidazole ligands with binding capabilities arising from the nitrogen atom for coordination to a metal atom, the N–H group for hydrogen bonding, and the planar aromatic ring for other intermolecular forces have been successfully employed for the construction of supramolecular assemblies with various structures. 4(5)-Methylimidazole and 3(5)-methylpyrazole ligands can exhibit linkage isomerism phenomenon (Scheme 2) [30–32]. The preference of one or another coordination mode of methyl containing imidazole

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[☆] CCDC 933350 and 933351 contain supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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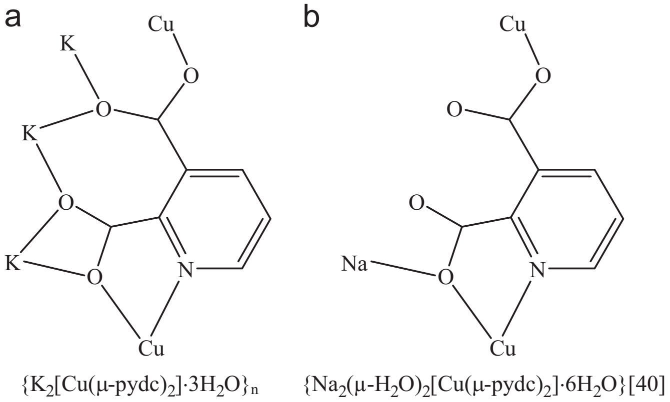
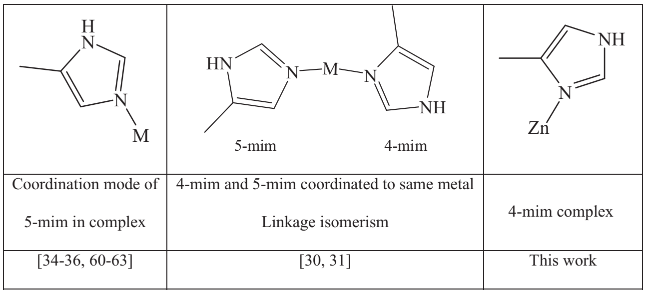


Scheme 1. Coordination mode of pydc in (a) **1** and in (b) {$Na_2(\mu\text{-}H_2O)_2[Cu(\mu\text{-}pydc)_2]\cdot 6H_2O$} complex.



Scheme 2. Coordination mode of 4(5)-methylimidazole ligand.

or pyrazole ligands depends on a relative basicity of the N atoms in the ring and steric factors imposed by the methyl groups. There are many studies in the literature about 4(5)-methylimidazole complexes, but 4-methylimidazole complexes have been rarely observed [33–36]. Furthermore our group described the crystal structure of two complex, which accommodates two binding modes of the 4(5)-methylimidazole ligand in same coordination sphere, which is a very unique example of the linkage isomers namely, $[Zn(4\text{-mim})_2(5\text{-mim})_2]sq\cdot 3H_2O$ and $[Cd(pzdc)(4\text{-mim})(5\text{-mim})_2]\cdot 1/2H_2O$ [30,31] (Scheme 2).

The goal of the present work is the synthesis and spectroscopic, thermal studies (TG, DTG and DTA) and crystal structure of two new coordination polymer of pyridine-2,3-dicarboxylic acid prepared from zerovalent metal. In heterometallic complex of **1** exhibits a 3D sandwich-like framework. The complex **2** is an example containing steric hindranced 4-methylimidazole selected as secondary ligand.

2. Experimental

2.1. Materials and physical measurements

All chemicals used were of analytical grade and were purchased commercially. The IR absorption spectra were recorded in the range of 400–4000 cm^{-1} by means of a Bruker Tensor 27 FT-IR spectrometer with KBr pellets. Elemental analyses for C, H, and N were carried out with Thermo Finnigan Flash EA 1112. The photoluminescence (excitation and emission) spectrum for the solid complex sample of **2** was determined with a Perkin-Elmer LS-55 spectrophotometer. The 10–300 K magnetization measurements were carried out on a Quantum Design PPMS system. χ–T graphs were recorded under the constant magnetic field of 10 kOe. Magnetic data were corrected for the diamagnetic contribution of the sample holder. The EPR powder spectrum was recorded with a Bruker EMX X-band spectrometer (9.8 GHz) with about 20 mW microwave power and 100 kHz magnetic field modulation. The powder X-ray diffraction patterns were collected using a diffractometer (RIGAKU DMAX2500) with Cu $K\alpha$ radiation ($\lambda = 1.5406$ Å).

2.2. Crystallographic analyses

Diffraction measurements were performed at 100 K on a Bruker Smart Apex CCD diffractometer using Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods using the program SHELXS97 [37] with anisotropic thermal parameters for all non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods SHELXL-97 [37]. All the non-hydrogen atoms in the two complexes were refined anisotropically. Most of hydrogen atoms were placed in their calculated positions or from difference Fourier map, respectively. Restrain was applied to water hydrogens to optimize geometry. Molecular drawings were obtained by using Mercury [38]. Details of the refinement are presented in Table 1; the crystallographic information files are deposited with the CCDC as 933350 and 933351.

2.3. Preparation of the complexes

$$\{K_2[Cu(\mu\text{-}pydc)2]\cdot 3H_2O \quad (1)$$

A quantity of 10 mL dimethylformamide solution of pydcH$_2$ (1.00 g, 5.98 mmol) was treated with KOH and metallic copper (0.38 g, 5.98 mmol) under stirring at 80 °C and stirred until total dissolution of the mixture was observed. The mixture turned to blue about 1 h. The clear solution was stirred for 2 h at 80 °C and then cooled to room temperature. Blue crystals were formed and washed with 10 mL of water and then dried in air. The compound is soluble in CH_3OH, DMF, water and is indefinitely stable in air. Yield: 68% (based on Cu) for **1**. Anal. Found: C, 31.40; H, 2.46; N,

Table 1
Crystal data and structure refinement parameters for **1** and **2**.

	1	2
Formula	$C_{14}H_{12}CuK_2N_2O_{11}$	$C_{12}H_{13}N_2O_6Zn$
Formula weight	526.00	346.61
Crystal system	Triclinic	Monoclinic
Space group	$P-1$	$P2_1/c$
a (Å)	6.8309(5)	7.3756(8)
b (Å)	7.8300(6)	11.4198(11)
c (Å)	17.8330(2)	16.8220(2)
α (°)	87.225(4)	90
β (°)	86.004(4)	97.047(7)
γ (°)	67.693(4)	90
V (Å^{-3})	880.05(2)	1406.20(3)
Z	2	4
D_x (Mg m^{-3})	1.985	1.637
μ (mm^{-1})	1.78	1.78
F_{000}	530	708
T (K)	293(2)	101(2)
Crystal dimensions (mm)	0.30 × 0.28 × 0.27	0.25 × 0.23 × 0.20
Index range	$h = -8 \to 9$ $k = -10 \to 10$ $l = -23 \to 23$	$h = -9 \to 9$ $k = -14 \to 15$ $l = -22 \to 18$
Measured reflections	15653	13252
Independent reflections	4291	3511
Reflections with $I > 2\sigma(I)$	3747	2732
$R[F^2 > 2\sigma(F^2)]$	0.046	0.042
$wR(F^2)$	0.132	0.122
$(\Delta/\sigma)_{max}$	0.001	0.001
$\Delta\rho_{max}$	1.06e Å^{-3}	0.67e Å^{-3}
$\Delta\rho_{min}$	$-0.57e$ Å^{-3}	$-0.46e$ Å^{-3}
S	1.16	1.05