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Hydrogen bonding networks and proton transfer compounds of cobalt(II) and copper(II) with pyridine-2,5-dicarboxylate

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ABSTRACT

Three Co(II) and Cu(II)-pyridine-2,5-dicarboxylate (pydc) proton transfer compounds with 1,4-butanediamine (ben) and 2,2-dimethylpropane-1,3-diamine (dmpen), *trans*-$(H_2ben)[Co(pydc)_2(H_2O)_2]\cdot 4H_2O$ (**1**), *trans*-$(H_2dmpen)[Co(pydc)_2(H_2O)_2]\cdot 2H_2O$ (**2**) and $(H_2ben)_2[Cu_2(\mu\text{-}pydc)_4(H_2O)_2]$ (**3**) have been synthesized and characterized by the methods of elemental, spectroscopic (IR and UV–Vis), thermal (TG/DTG, DTA) analysis, magnetic measurement and single crystal X-ray diffraction. The crystallographic analysis revealed that the complexes consist of $[Co(pydc)_2(H_2O)_2]^{2-}$ anion, bis(protonated) diamine cation (H_2ben for **1** and H_2dmpen for **2**) and four and two crystal water molecules, respectively. The Co(II) ions are coordinated by two pydc and two aqua ligands. The bis(deprotonated) pydc ligands coordinate to the Co(II) ions through the nitrogen atom of pyridine ring and the oxygen atom of carboxylate group, creating a chelate ring. The distorted octahedral geometries are completed by two *trans* aqua ligands at axial positions. The molecular structure of the complex **3** consists of dinuclear $[Cu_2(\mu\text{-}pydc)_4(H_2O)_2]^{4-}$ units and bis(protonated) 1,4-butanediammonium cation. In the structure, each Cu(II) ion is coordinated by two nitrogen and two oxygen atoms from two pydc ligands and one oxygen atom from aqua ligand, forming a distorted square pyramidal geometry.

1. Introduction

"*The most general and important reaction in chemistry*" [1] has been defined as the reaction which involves transfer of a proton from one atom to another. Depending on the situation, the proton-transfer reactions can be intramolecular or intermolecular. Recently, a large number of theoretical and experimental studies have been carried out to enrich the information regarding the possible mechanisms of proton-transfer, tautomeric equilibria, and relevant properties associated with proton-transfer processes [2]. This elementary reaction plays a fundamental role in innumerable chemical and biochemical processes including acid–base neutralization, electrophilic addition, enzyme mechanisms, contributing to the catalytic power of enzymes etc. [3,4]. For example, many living systems modulate the strength of hydrogen bonds, promoting hydrogen tunneling to affect enzyme catalysis [5]. The understanding of proton transfer in hydrogen bonded systems has been a longstanding issue because it is one of the fundamental processes in nature and plays significant roles in a wide range of dynamic processes such as solvation, proton conduction in polymer electrolyte, acid–base reaction, catalysis and enzymatic reaction [6]. Proton transfer leads to strong and directional interactions, sometimes giving rise to interesting properties such as non-linear optical behavior [4]. Water soluble pharmaceutically important carboxylic acids or amines salts and some ionic liquids are examples for which proton transfer strategy is utilized [7]. Recent investigations have addressed to the use of molecules that have an inherently rigid spacer such as pyridine-2,5-dicarboxylate (pydc). Pyridine-2,5-dicarboxylic acid forms stable chelates with simple metal ions and can display a widely varying coordination behavior functioning as a multidentate ligand [8–15]. The other isomeric pyridinedicarboxylic acids, e.g., pyridine-2,3- 2,4- and 2,6-dicarboxylic acids act as bidentate or bridged (chelating) N,O donors with different d–f metal ions [16–24]. Furthermore, their complexes are also of great interest due to their potential applications in many areas such as fluorescence [25–29], magnetism [14,15,30–32], enzyme inhibition [33], aqueous solution chemistry [34], surface chemistry [35], and catalysis [11]. According to our knowledge, synthesized proton-transfer compounds with pyridine-2,5-dicarboxylic acid, $[(Him)_2[Co(pydc)_2(H_2O)_2]\cdot 4H_2O$ [36], $(H_2pipz)_{1.5}[Cd(pydc)_2(Hpydc)]\cdot 3H_2O$ [37], $\{(H_2pipz)[Zn(pydc)_2(H_2O)]\cdot 2H_2O\}_n$ [38], $(H2a3mpy)_2[Ni(pydc)_2(H_2O)_2]\cdot 2H_2O$ [39], $(H2a3mpy)_2[Co(pydc)_2(H_2O)_2]\cdot 2H_2O$, $(H2a6mpy)_2[Co(pydc)_2(H_2O)_2]\cdot 2H_2O$ [40], $(H2a6mpy)_2[Zn(pydc)_2(H_2O)_2]\cdot 2H_2O$ [41], $(Hdma)_2[Cu(pydc)_2]$ [42], $(bipy)[Zn(pydc)_2(H_2O)_2]$ [43] (pydc = pyridine-2,5-dicarboxylic acid, im =

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imidazole, pipz = piperazine, 2a3mpy = 2-amino-3-methylpyridine, 2a6mpy = 2-amino-6-methylpyridine, dma = dimethylamine, bipy = 4,4′-bipyridine) were also reported. In the present study, we describe the syntheses, spectroscopic (UV–Vis and IR spectra) and thermal analyses, crystal structures, Co(II) and Cu(II)-pydc complexes of $(H_2ben)[Co(pydc)_2(H_2O)_2]\cdot 4H_2O$ (**1**), *trans*-$(H_2dmpen)[Co(pydc)_2(H_2O)_2]\cdot 2H_2O$ (**2**) and $(H_2ben)_2[Cu_2(\mu\text{-}pydc)_4(H_2O)_2]$ (**3**) with 1,4-butanediamine and 2,2-dimethylpropane-1,3-diamine.

Table 1
IR spectral data of **1**–**3** (cm^{-1}).[a]

Assignment	1	2	3
$\nu(OH)$	3198 s, br	3337 s, br	3350 s, br
$\nu(NH)$	3027 s	3028 s	3036 s
$\nu(C–H)$	2943 w	2971 w	2964 w
$\nu(COO)_{uncoord.}$	1739 s	1739 s	1739 s
$\nu(C{=}C) + \nu(C{=}N)$	1629 s	1584 s	1637 s
$\nu_{as}(COO)$	1580 vs	1530 vs	1589 vs
	1544 vs	1443 vs	1564 vs
$\nu_s(COO)$	1353 vs	1229 vs	1353 vs
	1380 vs	1356 vs	1385 vs
$\delta(OCO)$	764 m	760 m	753 m
$\gamma(py)$	692 m	692 m	682 m
M–O	517 w	517 w	534 w
M–N	434 w	461 w	452 w

[a] *Abbreviations:* w – weak; m – medium; s – strong; vs – very strong, and br – broad.

2. Experimental

2.1. Materials and measurements

All chemicals and solvents used for the syntheses were of reagent grade. Pyridine-2,5-dicarboxylic acid, 1,4-diaminobutane, 2,2-dimethylpropane-1,3-diamine, CH_3OH, C_2H_5OH, $Co(CH_3COO)_2\cdot 4H_2O$ and $Cu(CH_3COO)_2\cdot H_2O$ (Aldrich) were used as received. Elemental analysis (C, H, and N) were performed using a Vario EL III CHNS elemental analyzer. Magnetic susceptibility measurements were performed at room temperature using a Sherwood Scientific MK1 model Gouy magnetic balance. UV–Vis spectra were obtained in the water solutions (10^{-3} mol/L) of the complexes with a Shimadzu Pharmaspec UV-1700 spectrometer within the range of 1000–190 nm. FT-IR spectra were recorded in the 4000–400 cm^{-1} region with a Bruker Optics, Vertex 70 FT-IR spectrometer using

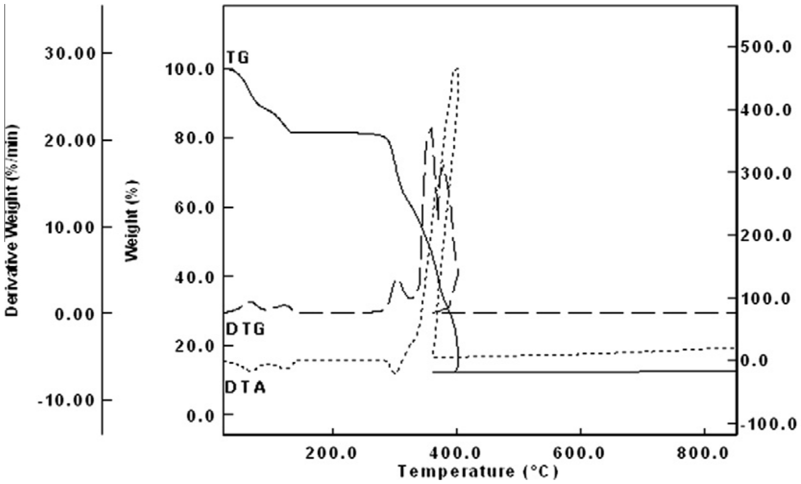

Fig. 1. TG–DTA–DTG curves of **1**.

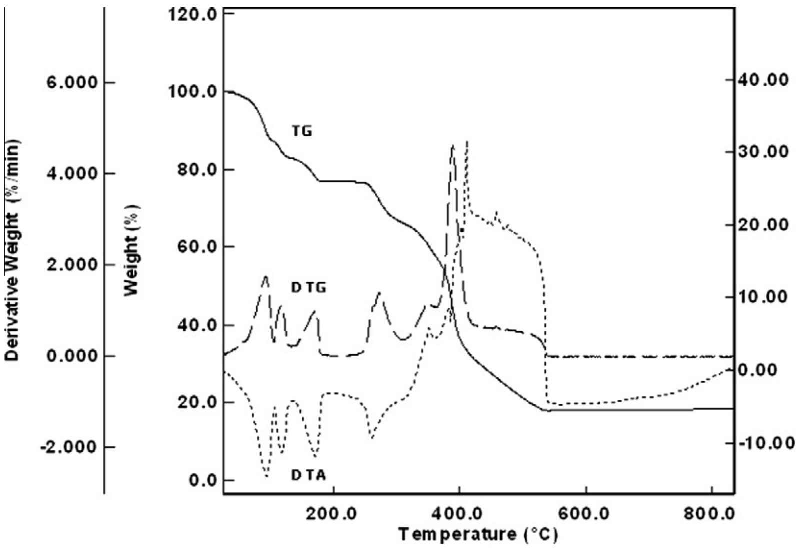

Fig. 2. TG–DTA–DTG curves of **2**.