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Syntheses and characterization of two copper pyridine-dicarboxylate compounds containing water clusters

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ABSTRACT

A new homonuclear and heterodinuclear pyridine-2,6-dicarboxylate complexes, formulated as $(enH_2)[Cu(dipic)_2]\cdot 2.5H_2O$ (**1**) and $[Cu(\mu\text{-}dipic)_2Zn(H_2O)_5]\cdot 2H_2O$ (**2**) (en = ethylenediamine, dipic = pyridine-2,6-dicarboxylate) were synthesized according the reactions between the three species of copper(II) and zinc(II) nitrate, ethylenediamine and pyridine-2,6-dicarboxylic acid. Complexes have been characterized by the methods of elemental, spectroscopic (IR and UV–Vis), thermal (TG/DTG, DTA) analysis, magnetic measurement and single crystal X-ray diffraction. Correlation coefficient, activation energies, E^*; pre-exponential factor, A; entropies, S^*; enthalpies, H^* and Gibbs free energies, G^* of the thermal decomposition reactions have been calculated under the derivations from thermogravimetric (TG) and differential thermogravimetric (DTG) curves, using the Coats–Redfern and Horowitz–Metzger methods. Complex **1** belonged to a six-coordinate behavior with a distorted octahedral geometry around Cu(II), that the structure contains two pyridine-2,6-dicarboxylate species as a tridentate ligands and ethylenediaminium cation as a counter ion as well as 2.5 uncoordinated water molecules. On the other hand complex **2** contains six-coordinated Cu(II) and Zn(II) ions, which are linked by two O atoms of the same carboxyl group from dipicolinic acid. The dipicolinate dianions again behave as tridentate ligands in **2**. Two uncoordinated water molecules are also present in the structure. The structure units of **1** and **2** are mutually held by the hydrogen bonds and π···π interactions. There is also a C–O···π interaction in **2**. The Cu(II) complexes are connected to one another via O–H···O hydrogen bonds, forming water clusters, which play an important role in the stabilization of the crystal structure. In the water clusters, the water molecules are trapped by the cooperative association of coordination interactions as well as hydrogen bonds.

1. Introduction

Pyridine-2,6-dicarboxylic acid (also known as 2,6-dicarboxypyridine and as dipicolinic acid, H_2dipic) is a water-soluble, commercially available, cheap and versatile N,O-chelator possessing diverse coordination modes, with a recognized biological function in the body metabolism [1], and in a variety of processes as an enzyme inhibitor [2], plant preservative [3] and food sanitizer [4]. The complexation of transition metal ions from dipicolinic acid has been the subject of numerous reports. The reasons for this interest are the ability of the ligand so it gave stable chelates with different coordination modes [5], affinity to form strong hydrogen bonds and its biological activity in human metabolism [6]. Although lots of dipicolinate complexes of transition metals are known and reported [5,7–12], heterodinuclear pyridine-2,6-carboxylate complexes are limited [8]. Furthermore, proton transfer property is one of the most important fundamental in physics, chemistry and biochemistry. A large number of proton transfer compounds have been constructed by pyridine-2,6-dicarboxylic acid [9–18]. Water clusters have been the focus of intense research interests [19–26]. With the development of research, water clusters have been classified as three classes: discrete water clusters, polymeric water clusters and metal–water clusters [26]. The structural elucidation of discrete and polymeric water clusters provides detailed knowledge of hydrogen-bonding and their fluctuations determined the properties of bulk water. As known, metal–water clusters not only involved the hydrogen-bonding interactions between water molecules, but also the coordination bonds between metal atoms and water clusters. In this sense, the design and synthesis of metal–water clusters is more important than discrete or polymeric clusters.

In this study, we have successfully designed and synthesized two homo- and heteronuclear complexes containing discrete water

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clusters. The crystal structures, FT-IR and thermal properties of Cu(II) and Cu(II)/Zn(II) complexes derived from pyridine-2,6-dicarboxylic acid with ethylenediamine, $(enH_2)[Cu(dipic)_2]\cdot 2.5H_2O$ (**1**) and $[Cu(dipic)_2Zn(H_2O)_5]\cdot 2H_2O$ (**2**) were analyzed and interpretive. In the crystal lattice of complexes **1** and **2**, two kinds of water clusters have been observed.

2. Experimental

2.1. Materials and general methods

All chemicals were commercially available and used without further purification. C, H and N elementals were performed on a Carlo Erba 1106 microanalyzer. Infrared spectra were recorded as KBr discs using Perkin–Elmer 100 FT-IR spectrometer (4000-400 cm^{-1}). Magnetic susceptibility measurements were performed using a Sherwood Scientific MXI model Gouy magnetic balance at room temperature. The absorption spectroscopy measurements were performed using a Shimadzu UV-3150 spectrometer at room temperature (22 ± 1 °C). The spectra were recorded between 300 and 900 nm in water (1.0×10^{-3} M). Thermal analyses were performed on a Diamond TG/DTA thermal analyzer under air from 30 to 600 °C at heating rate of 10 °C/min.

2.2. Synthesis

2.2.1. Synthesis of $(enH_2)[Cu(dipic)_2]\cdot 2.5H_2O$

A solution of pyridine-2,6-dicarboxylic acid (0.852 g, 5 mmol) in water (25 mL) was neutralized with NaOH (0.4 g, 10 mmol). The mixture of $Cu(NO_3)_2\cdot 5H_2O$ (0.760 g, 2.5 mmol) in water (20 mL) was added to this solution. The resulting solution was stirred for 3 h at 60 °C. Then the ethylenediamine ligand (0.601 g, 10 mmol) in water (10 mL) was added dropwise to this solution. The clear solution was stirred for 2 h at 50 °C and then cooling to room temperature violet crystals were formed and collected. *Anal*. Calcd. for $C_{16}H_{26}CuN_4O_{13}$: C, 35.20; H, 4.80; N, 10.26. Found: C, 35.23; H, 4.81; N, 10.18%.

2.2.2. Synthesis of $[Cu(dipic)_2Zn(H_2O)_5]\cdot 2H_2O$

A solution of pyridine-2,6-dicarboxylic acid (0.852 g, 5 mmol) in water (25 mL) was neutralized with NaOH (0.4 g, 10 mmol). The mixture of $Cu(NO_3)_2\cdot 5H_2O$ (0.760 g, 2.5 mmol) in water (20 mL), $Zn(NO_3)_2\cdot 6H_2O$ (0.727 g, 2.5 mmol) was added to this solution. The resulting solution was stirred for 3 h at 60 °C. After cooling to room temperature violet crystals were formed and collected. *Anal*. Calcd. for $C_{14}H_{20}N_2O_{15}CuZn$: C, 28.73; H, 3.44; N, 4.79. Found: C, 28.71; H, 3.37; N, 4.81%.

2.3. Crystallography

Diffraction experiments were carried out at 170(1) K on a Rigaku RAPIDII diffractometer. The structures were solved by direct methods and refined using the programs SHELXS97 and SHELXL97 [27]. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods [27]. The hydrogen atoms were placed in geometrically idealized positions and refined as riding atoms. Data collection: PROCESS-AUTO [28], cell refinement: PROCESS-AUTO, data reduction: CRYSTALSTRUCTURE [28]; program(s) used for molecular graphics: MERCURY programs [29]. Details of crystal structures are given in Table 1.

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

	1	2
Empirical formula	$C_{16}H_{21}CuN_4O_{10.50}$	$C_{14}H_{16}CuN_2O_{13}Zn\cdot 2(H_2O)$
Formula weight	500.91	585.24
T (K)	170(1)	
Wavelength (Å)	0.71075 Mo Kα	0.71075 Mo Kα
Crystal system	monoclinic	monoclinic
Space group	*C*2/*c*	*P*2$_1$/*c*
a (Å)	16.7775(3)	8.35571(17)
b (Å)	16.3344(3)	27.0317(5)
c (Å)	15.1908(3)	9.71370(18)
β (°)	110.5211(7)	98.3436(7)
V (Å^3)	3898.87(13)	2170.80(7)
Z	8	4
Absorption coefficient (mm^{-1})	1.19	2.16
D_{calc} (Mg m^{-3})	1.707	1.791
θ Range for data collection (°)	3.1–30.0	3.1–30.0
Measured reflections	31,120	32,840
Independent reflections	5664	6306
Absorption correction	multi-scan (ABSCOR; Higashi, 1995)	
Refinement method	full-matrix least-squares on F^2	
R_{int}	0.023	0.020
$R[F^2 > 2\sigma(F^2)]$	0.030	0.021
$wR(F^2)$	0.092	0.056
Goodness-of-fit (GOF) on F^2	1.08	1.04
$\Delta\rho_{max}$ (e Å^{-3})	0.82	0.47
$\Delta\rho_{min}$ (e Å^{-3})	−0.73	−0.31

3. Results and discussion

3.1. UV–Vis spectra and magnetic properties

The electronic spectra of water solutions of the complexes display broad absorption bands at 587 nm (= 93 L mol^{-1} cm^{-1}) and 783 nm (= 97 L mol^{-1} cm^{-1}) respectively, which are assigned to the $E_g \rightarrow T_{2g}$ transition. The strong absorption bands below

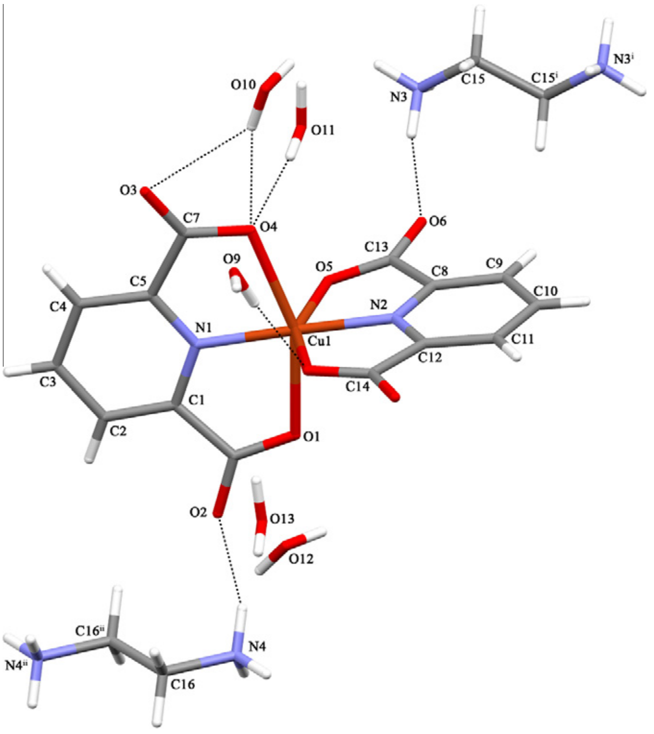

Fig. 1. The molecular structure of **1** showing the atom numbering scheme ((i) −*x*, 1 − *y*, 1 − *z*; (ii) 1 − *x*, 1 − *y*, −*z*).