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One dimensional coordination polymers: Synthesis, crystal structures and spectroscopic properties

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ABSTRACT

Two new one dimensional (1D) cyanide complexes, namely $[M(4\text{-aepy})_2(H_2O)_2][Pt(CN)_4]$, (4-aepy = 4-(2-aminoethyl)pyridine M = Cu(II) (**1**) or Zn(II) (**2**)), have been synthesized and characterized by vibrational (FT-IR and Raman) spectroscopy, single crystal X-ray diffraction, thermal and elemental analyses techniques. The crystallographic analyses reveal that **1** and **2** are isomorphous and isostructural, and crystallize in the monoclinic system and *C2* space group. The Pt(II) ions are coordinated by four cyanide-carbon atoms in the square-planar geometry and the $[Pt(CN)_4]^{2-}$ ions act as a counter ion. The M(II) ions display an N_4O_2 coordination sphere with a distorted octahedral geometry, the nitrogen donors belonging to four molecules of the organic 4-aepy that act as unidentate ligands and two oxygen atoms from aqua ligands. The crystal structures of **1** and **2** are similar each other and linked via intermolecular hydrogen bonding, Pt···π interactions to form 3D supramolecular network. Vibration assignments of all the observed bands are given and the spectral features also supported to the crystal structures of the complexes.

1. Introduction

Cyanide metal complexes have attracted great interest because of a variety of desired features, depending on the used metal centers and auxiliary ligands. Therefore, these complexes show high structural variability due to binding to metal atom with different coordination numbers of the cyanide ligand. This structural variability was explored previously in the syntheses of various types of cyanometallates [1,2]. Cyanometallates have useful building blocks for various dimensional coordination polymeric networks such as the dicyanides in linear geometry $[M(CN)_2]^-$ (M = Cu, Ag, Au), the tetracyanides in square planar geometry $[M(CN)_4]^{2-}$ (M = Ni, Pd, Pt) and the hexacyanides in octahedral geometry $[M(CN)_6]^{3-}$ (M = Ti, V, Cr, Mn, Fe, Co) [3]. To the best of our knowledge, there are a few reports related with the tetracyanoplatinate(II) complexes [4–8]. In the literature, structural properties of cyanide metal complexes synthesized using these building blocks are usually examined such as $[Cu(hydeten)_2Pt(CN)_4]$ (hydeten = *N*-(2-hydroxyethyl-ethylenediamine) [9], $\{[Cu(tmen)][Pt(CN)_4]\}_n$ (tmen = tetramethylethylenediamine) [10], $[Zn(hepH)_2Pt(\mu\text{-}CN)_2(CN)_2]_n$ (hepH = 2-pyridineethanol) [11] and $Cd(H_2O)_2(\mu\text{-ampy})Pt(\mu\text{-}CN)_2(CN)_2]_n$ (ampy = 4-aminomethylpyridine) [12].

These building blocks of cyanometallates have useful functional properties, and they can act as clathrate hosts [13] and single molecular magnets [14], and may also exhibit electrical conductivity [1]. Cyanide metal supramolecular structures can occur by non-covalent interactions, such as electrostatic interactions, hydrogen bond interactions, π-π, C-H···M, C-H···π, M···π interactions. Hydrogen bond interactions may plays a crucial role in packaging and stabilizing of the molecular cluster and may also play an important role as a possible exchange path for the magnetic interactions [15–17]. On the other hand, hydrogen bond interactions are effective in forming to supramolecular structures of the metalloligands [18].

We report here the synthesis, elemental analyses, spectral (FT-IR and Raman) properties and thermal analyses of two new one dimensional (1D) cyanide complexes, $[Cu(4\text{-aepy})_2(H_2O)_2]$

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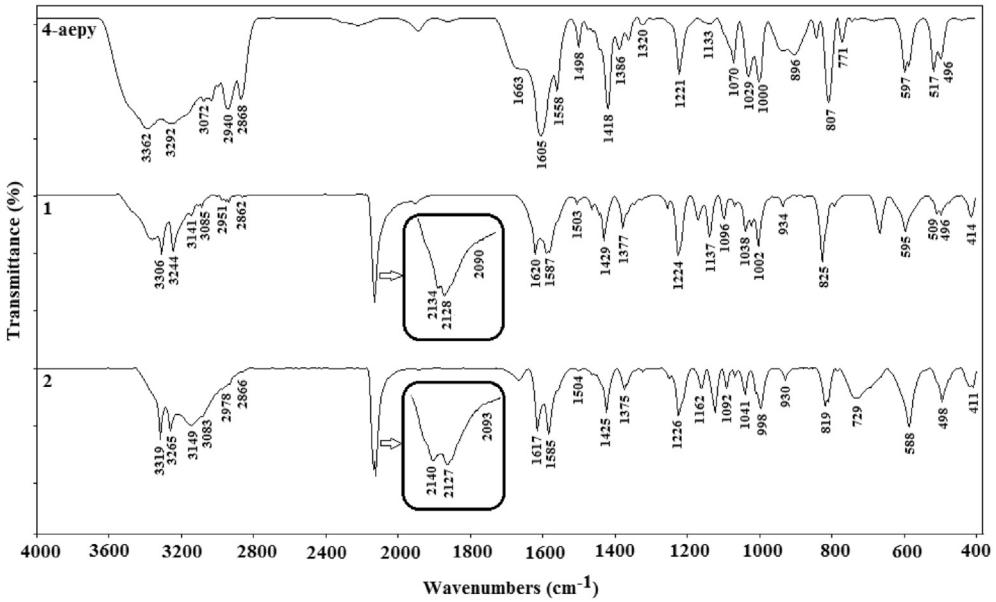

Fig. 1. The FT-IR spectra of 4-aepy and the complexes.

$[Pt(CN)_4]$ (**1**) and $[Zn(4\text{-aepy})_2(H_2O)_2][Pt(CN)_4]$ (**2**) (4-aepy = 4-(2-aminoethyl)pyridine). The crystal structures of the complexes have been determined by X-ray single crystal diffraction. The spectral data are structurally consistent with those of obtained from single crystal X-ray studies. According to the obtained results, in complexes **1** and **2**, 1D coordination polymer occurs with a combination of metalloligands and adjacent 1D coordination polymers are connected by O-H···N hydrogen bonds. The crystal packing of the complexes are stabilized through the hydrogen bonds and Pt···π interactions, resulting in a 3D framework.

2. Experimental

2.1. Material and instrumentation

Copper (II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$, 99%), zinc(II) chloride ($ZnCl_2$, 96%), platinum (II) chloride ($PtCl_2$, 99%), potassium cyanide (KCN, 96%) and 4-(2-aminoethyl)pyridine ($C_7H_{10}N_2$, 96%) were purchased from commercial sources and used without further purification. The FT-IR spectra of the complexes were recorded as KBr pellets in the range of 4000–400 cm^{-1} (2 cm^{-1} resolution) on a

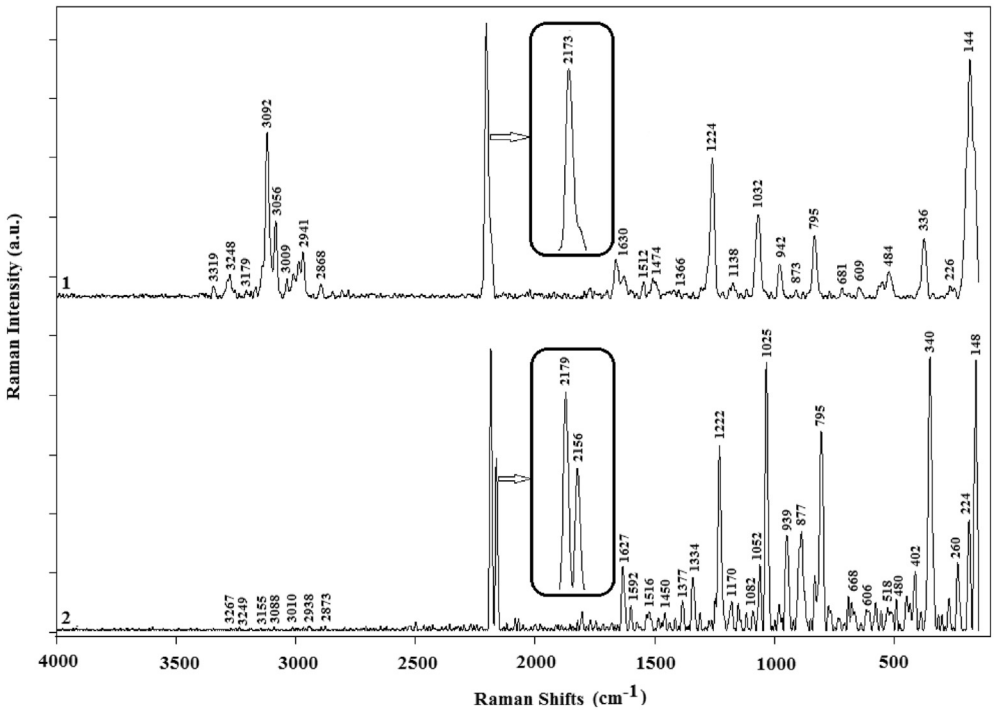

Fig. 2. The Raman spectra of the complexes.