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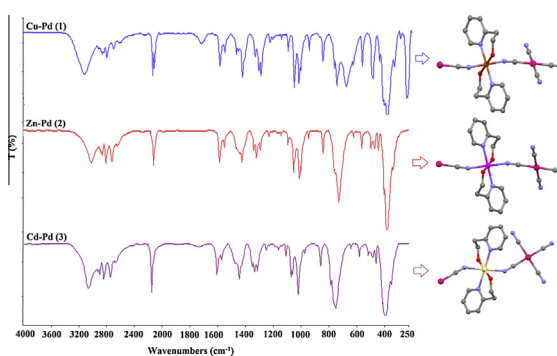
C—H···Pd interactions: One dimensional heteropolynuclear complexes

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HIGHLIGHTS

- 1D heteropolynuclear three cyanide complexes were synthesized and characterized.
- The complexes 1–3 were extended into 2D and 3D by O—H···N and π ·· π interactions.
- The crystal structure of the complexes 1–3 exhibit intermolecular C—H···Pd interactions.

GRAPHICAL ABSTRACT



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ABSTRACT

Three cyanide complexes, $[\text{Cu}(\text{hepH})_2\text{Pd}(\mu\text{-CN})_2(\text{CN})_2]_n$ (**1**), $[\text{Zn}(\text{hepH})_2\text{Pd}(\mu\text{-CN})_2(\text{CN})_2]_n$ (**2**) and $[\text{Cd}(\text{hepH})_2\text{Pd}(\mu\text{-CN})_2(\text{CN})_2]_n$ (**3**) (2-pyridineethanol abbreviated to hepH), have been synthesized and characterized by various techniques (elemental analysis, FT-IR and Raman spectroscopy, thermal analysis and single crystal X-ray diffraction). FT-IR spectroscopy pointed out the existence of terminal and bridged cyanide ligands in the complexes. The crystallographic analyses reveal that complexes **1** and **2** crystallize in the triclinic system, space group $P\bar{1}$ and complex **3** crystallizes in the monoclinic system, space group $P2_1/n$. The palladium atom is coordinated with cyanide-carbon atoms in a square-planar arrangement and the metal(II) atoms are six-coordinated with two cyanide nitrogen, two hepH nitrogen and two hepH oxygen atoms, in a distorted octahedral arrangement. In all the complexes adjacent chains are connected by C—H···Pd, π ·· π and O—H···N hydrogen bonding interactions to form two- and three-dimensional networks. When it comes to thermal analysis, the complexes followed usual decomposition mechanism in which neutral ligands (hepH) are released first, and then cyanide ligands are decomposed. The final decomposition products are found to be the corresponding metal oxides.

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Introduction

Cyanide ligand is versatile due to the nature from its ability to act as both a σ -donor and a π -acceptor, its negative charge, and

its ambidentate feature [1]. In addition, cyanide is an influential ligand for stabilization and the entity of one (1D), two (2D), or three dimensional (3D) structures. Therefore, cyanide complexes have an area of active research because of their areas of usage depending upon the metal center and ancillary ligand used.

Among the cyanide anions, the tetracyanopalladate(II) anion $[\text{Pd}(\text{CN})_4]^{2-}$ used in the syntheses of the cyanide complexes, is an

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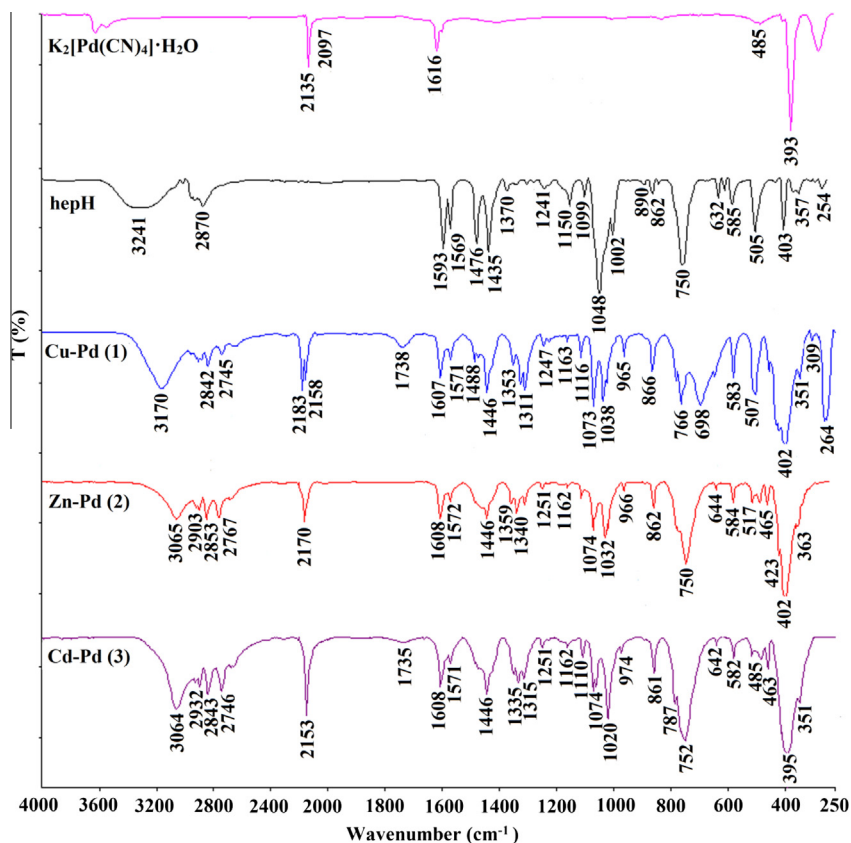


Fig. 1. The FT-IR spectra of $K_2[Pd(CN)_4] \cdot H_2O$, free hepH and complexes 1–3.

ideal building block that has rarely been studied [2–5]. Square-planar geometry tetracyanopalladate(II) anions have attracted attention as catalysts in C–C coupling reactions [6]. Since palladium complexes display a behavior as catalyst such as the Suzuki–Miyaura and the Heck–Mizoroki coupling reactions [7–9], cyanide complexes containing palladium central atoms can be used to increase the yield of these reactions.

Among the bonding interactions of the cyanide group, hydrogen bonds can also be included. These hydrogen bonds are played an important role in packing and stabilizing the structures formed, and sometimes they are played an important role as a possible exchange path for magnetic interactions [10]. The C–H...M interactions are relevant with d^8 systems and considered to be of importance for understanding the catalytic reactions [11]. These C–H...M interactions are best described as the three-center four electrons ($3c-4e$). However, the nature of the apical C–H...M interactions in the square-planar complexes of d^8 metal ions is very rare [12,13]. The face-to-face $\pi \cdots \pi$ interaction, where most of the ring-plane area overlaps, is a rare interaction. 2-Pyridineethanol is a good choice in this respect for being able to coordinate itself as chelating or bridging ligand, as well as for possessing OH groups able to participate in hydrogen bondings.

In our previous study, we have reported the tetracyanonickelate(II) complexes with hepH [14]. To the best of our knowledge, neither crystallographic, nor vibrational analysis study of tetracyanopalladate(II) with hepH has been reported yet. As a continuation of our previous study, we carried out the syntheses of $[Cu(hepH)_2Pd(CN)_4]_n$ (1), $[Zn(hepH)_2Pd(CN)_4]_n$ (2) and $[Cd(hepH)_2Pd(CN)_4]_n$ (3) cyanide-bridged coordination polymers with hepH ligand. We report herein their crystal structures, and also their vibrational, thermal and elemental analyses results. According to the obtained results, in complexes 1–3, the adjacent planes are

held together by C–H...Pd, $\pi \cdots \pi$ and O–H...N interactions, forming two- and three-dimensional networks.

Experimental

Materials

All materials such as copper(II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$, 99%), zinc(II) chloride ($ZnCl_2$, 96%), cadmium(II) chloride hemihydrate ($CdCl_2 \cdot 2.5H_2O$, 81%), Palladium(II) chloride ($PdCl_2$, 99%), Potassium cyanide (KCN, 96%) and 2-pyridineethanol (C_7H_9NO , 98%) were used as received.

Syntheses of the complexes

To water solution of $PdCl_2$ (0.177 g, 1 mmol) was added a solution of KCN (0.260 g, 4 mmol) in water (10 mL) solution and $K_2[Pd(CN)_4] \cdot H_2O$ was formed as crystallized. $K_2[Pd(CN)_4] \cdot H_2O$ (0.306 g, 1 mmol) to which was added solid metal chloride ($CuCl_2 \cdot 2H_2O = 0.170$ g, $ZnCl_2 = 0.136$ g or $CdCl_2 \cdot 2.5H_2O = 0.228$ g, 1 mmol) became $M[Pd(CN)_4] \cdot H_2O$. To $M[Pd(CN)_4] \cdot H_2O$ ($Cu[Pd(CN)_4] \cdot H_2O = 0.292$ g, $Zn[Pd(CN)_4] \cdot H_2O = 0.293$ g or $Cd[Pd(CN)_4] \cdot H_2O = 0.340$ g; 1 mmol) solution, hepH (0.246 g, 2 mmol) dissolved in ethanol (10 mL) was added a few drops with continuous stirring approximately for 4 h at 55 °C in a temperature-controlled bath, and then filtered. The resultant solutions were filtered and kept for crystallization at room temperature. The suitable crystals for X-ray measurements were formed by slow evaporation after a week. The freshly prepared complexes were analyzed for C, H and N with the following results: Anal. Calcd. for $C_{18}H_{18}N_6O_2PdCu$ (1) ($M_w = 520.32$ g mol⁻¹): C, 41.48; H, 3.49; N, 16.15%. Found: C,

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