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Two dimensional heteropolynuclear Zn(II) and Cd(II)-tetracyanopalladate(II) complexes with the 1-ethylimidazole ligand exhibiting C–H· · ·Pd interactions

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ABSTRACT

The cyano-bridged heteronuclear complexes $[Zn(etim)_2Pd(\mu\text{-}CN)_4]_n$ (**1**) and $[Cd(etim)_2Pd(\mu\text{-}CN)_4]_n$ (**2**) (etim = 1-ethylimidazole), have been synthesized and characterized by FT-IR, Raman spectroscopy, thermal and elemental analyses. The crystal structures of the complexes have been determined by X-ray single crystal diffraction. In the complexes, the Pd(II) ion is coordinated by four cyano ligands, forming a square-planar geometry, and the Zn(II) or Cd(II) ions are coordinated by six N atoms from four bridging cyano ligands and two etim ligands in a distorted octahedral geometry. The most important features of the complexes are the presence of C–H···Pd hydrogen-bonding interactions between the Pd(II) ion and the hydrogen atoms of the etim ligand.

1. Introduction

The synthesis and rational design of coordination polymers are being given considerable attention owing to their interesting structural properties and potential applications [1–3]. Recently, cyano bridged coordination polymers, together with their diverse bonding and structural chemistry, have had widespread applications in the field of chemistry, pharmacy and industry, therefore they have been attracting increasing attention from scientists and chemists [4–6].

For many years there has been considerable interest in the activation of C–H bonds by transition metal complexes. In this connection, many examples of transition metal complexes showing agostic or anagostic C–H···M interactions have been recognized [7–13]. In simpler terms, agostic and anagostic interactions describe two electron three-center bonding interactions, and hydrogen bonding describes a four electron three-center interaction, respectively [14]. Recently a few examples of three-center four-electron anagostic interactions have been reported [7,11,15–18]. This hydrogen bonding interaction plays a crucial role in constructing supramolecular networks [19]. In the literature, four electron three-center interactions with Ni(II) in square planar $[Ni(CN)_4]^{2-}$ complexes have been studied [11,17,20], but knowledge of these interactions with Pd(II) are scarce.

In previous studies, cyano complexes were obtained using imidazol and imidazole derived ligands [12,21–26]. As a part of our continuing research on the syntheses and characterizations of cyano complexes containing imidazole and imidazole derivative ligands, the 1-ethylimidazol ligand having CH groups, was used. Furthermore, the main purpose for the preparation of these complexes, using Pd(II) metal with a d^8 system and forming a square planar geometry, was to analyze the effect of C–H· · ·M interactions in the crystal packing. We define in this study, the syntheses, spectral (FT-IR and Raman), thermal and elemental analyses of the complexes $[Zn(etim)_2Pd(\mu\text{-}CN)_4]_n$ (**1**) and $[Cd(etim)_2\ Pd(\mu\text{-}CN)_4]_n$ (**2**). The molecular and crystal structures of the cyano-bridged heteronuclear polymeric complexes **1** and **2** have been designated by X-ray single crystal diffraction. The thermal decomposition behaviors of the complexes were followed up in the temperature range 30–700 °C in a static air atmosphere.

2. Experimental

2.1. Materials and instrumentation

Zinc(II) chloride ($ZnCl_2$, 98%), cadmium(II) chloride hemipentahydrate ($CdCl_2{\cdot}2.5H_2O$, 98%), palladium(II) chloride ($PdCl_2$, 99%), 1-ethylimidazole ($C_5H_8N_2$, 95%) and potassium cyanide (KCN, 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 4000–400 cm^{-1} (2 cm^{-1} resolution) on a

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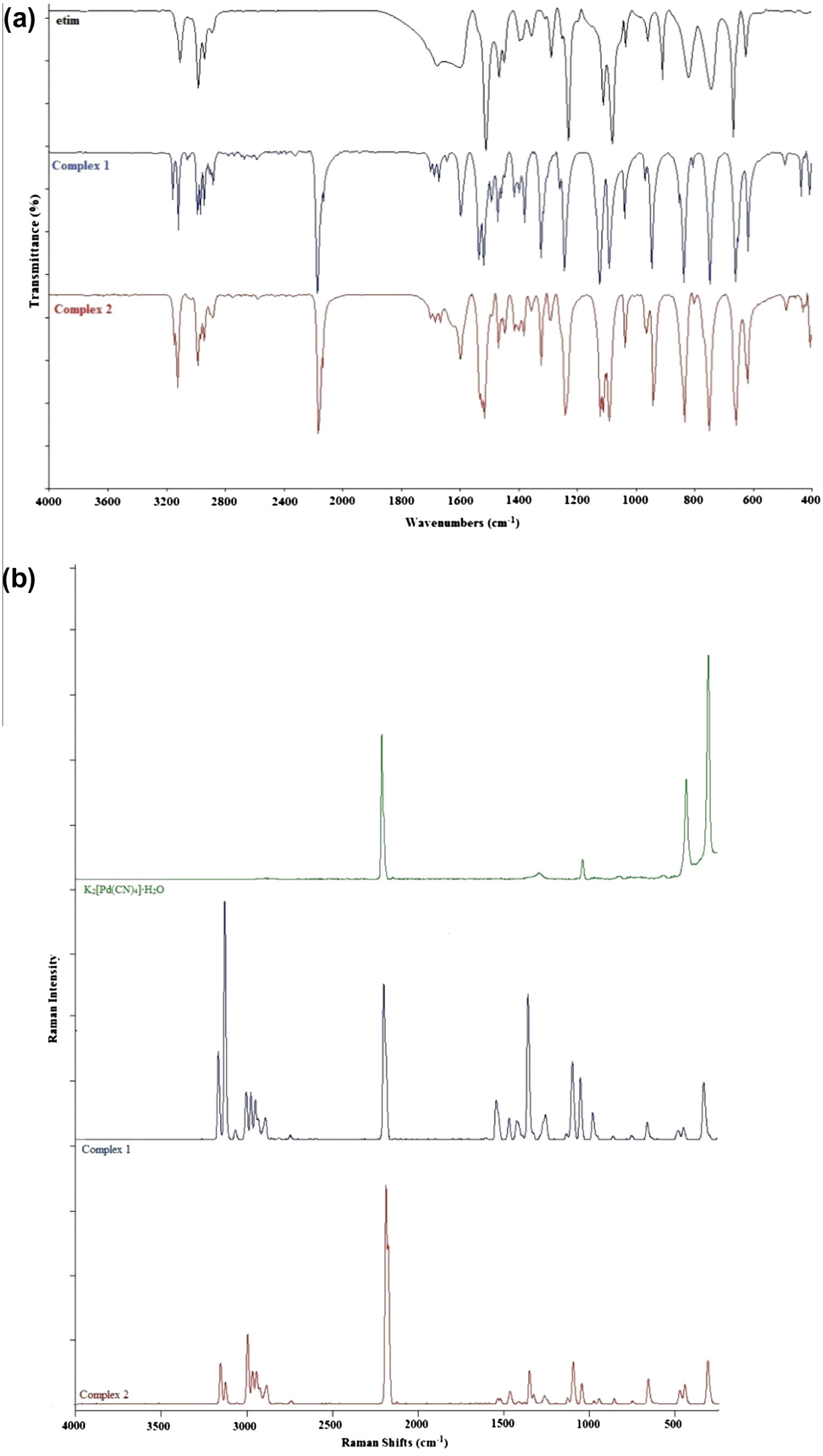

Fig. 1. (a) The FT-IR spectra of etim and the complexes and (b) Raman spectra of the complexes.