

# Synthesis, characterization and single crystal X-ray structure determination of three cadmium(II) complexes derived from picric acid and p-nitrobenzoic acid in the presence and absence of nitrogen donor ligand N-(hydroxyethyl)ethylenediamine



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## ABSTRACT

Cadmium, an extremely toxic heavy metal, is of a major public health concern and its efficient removal from the environment is a real challenge. This work aims for a deep understanding of stable cadmium(II) chelation with a tridentate ligand to form complex salts being stabilized by cation–anion hydrogen bonding non-covalent interactions in addition to electrostatic interactions. Three new Cd(II) complexes,  $[\text{Cd}(\text{H}_2\text{O})_6](\text{pic})_2 \cdot 2\text{H}_2\text{O}$  **1**,  $[\text{Cd}(\text{N-hyden})_2](\text{pic})_2$  **2**,  $[\text{Cd}(\text{N-hyden})_2](\text{pnb})_2$  **3**, (where N-hyden = N-(hydroxyethyl)ethylenediamine, Hpic = picric acid and Hpnb = p-nitrobenzoic acid) using the appropriate acids in the absence and presence of the tridentate N-hyden ligand have been synthesized and fully characterized by elemental analyses, thermogravimetric analyses and spectroscopic (FT-IR, NMR) techniques. The exact ionic structures of complexes **1–3** have been unambiguously determined using single crystal X-ray diffraction studies. They comprise octahedrally surrounded cationic Cd(II) centers,  $[\text{Cd}(\text{H}_2\text{O})_6]^{2+}$  in **1** and  $[\text{Cd}(\text{N-hyden})_2]^{2+}$  in **2** and **3**, together with the counter anions pic/pnb, which are stabilized by a mutual interplay of various hydrogen bonding interactions.

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## 1. Introduction

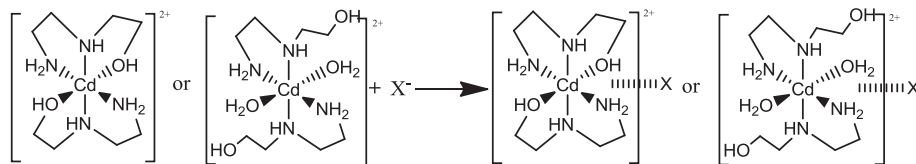
The design and synthesis of novel complexes with toxic metal ions with an appended framework are the fundamental requisites for the discovery of various functional supramolecular devices or technologically useful materials [1]. Recently, a great deal of attention has been paid to the design and construction of organic–inorganic hybrid frameworks from various synthons or building blocks owing to their interesting structural diversity and enormous potential application in chemistry, biology and material science [2,3]. Heavy metals are environmental pollutants due to their non-degradable nature. Although Zn, Cd and Hg belong to the same metal group of the Periodic Table (group 12) with the similar electronic configuration  $\text{nd}^{10}\text{ns}^2$ , their chemical characteristics and potential applications are different. For example, zinc salts/complexes have been extensively studied over the years because a number of zinc containing enzymes are known to exist in

biological species, e.g., Zn-Cu superoxide dismutase, carboxypeptidase, etc. On the other hand, Cd/Hg salts/complexes are known to be highly toxic and can accumulate in the human body leading to renal dysfunction and various other diseases, including cancer, as  $\text{Ca}^{2+}$  and  $\text{Cd}^{2+}$  ions have similar ionic radii. Moreover, cadmium and mercury, having a large size with a half-life of many years in humans, are known to be toxic [7] and show direct or indirect interactions with DNA, hence leading to cancer [8,9].

The cadmium(II) ion exhibits different coordination numbers from 4 to 8 in its coordination complexes with various ligands [4–6]. Despite the harmful effects of cadmium, an outstanding example is the discovery of a cadmium-containing carbonic-anhydrase enzyme from *Thalassiosira weissflogii* that specifically uses cadmium to achieve its biological function, suggesting the impact of cadmium on the global carbon cycle [9]. In order to reduce the toxicity of heavy metals, chelation therapy is an important aspect as metals are removed in the form of stable chelate complexes. So, the design of drugs to overcome the toxicosis requires an in-depth insight into the properties of the ligands employed and the geometry of resultant complexes [9]. Para-nitrobenzoic acid (Hpnb) and picric acid (Hpic) are used due to their wide applications in

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**Fig. 1.** Schematic representation of second-sphere coordination complexes via hydrogen bonding between the complex cation  $[\text{Cd}(\text{N-hyden})_2]^{2+}$  and *pic/pnb* anions shown as X in the second coordination sphere.

nuclear chemistry, biology and the pharmaceutical industry [10,11]. Moreover, arylcarboxylates (*pnb* here) can be employed as building blocks in crystal engineering because of the versatility of their coordination modes (monodentate, symmetric/asymmetric chelating and bidentate/monodentate bridging) and ability to form strong directional hydrogen bonds with predictable/desirable properties [10–12]. On the other hand, picric acid easily forms salts with metal ions due to its strong acidity. Its lead salt is widely used as a primary explosive [13–15]. Picric acid, with three nitro groups, can form crystalline complexes with various organic molecules with the help of ionic, non-covalent hydrogen bonding and  $\pi$ - $\pi$  interactions, and has been widely applied as a supramolecular heterosynthon in the design of new complexes [16–18].

It is envisaged that complexation of the cadmium(II) ion with the N-donor ligand *N-hyden*, which possesses two N–H groups and one O–H group, could form stable chelated cations,  $[\text{Cd}(\text{N-hyden})_2]^{2+}$  or  $[\text{Cd}(\text{N-hyden})_2(\text{H}_2\text{O})_2]^{2+}$  (Fig. 1), depending on whether a tridentate or bidentate coordination mode of the ligand is adopted. This doubly-positively charged cation possesses eight (six N–H and two O–H) hydrogen bond donors and has a stable structural framework onto which anionic components can be assembled [19–21] by various hydrogen bonding interactions.

Our research group has successfully isolated new anionic cadmium(II) complex salts with the help of large cationic cobalt(III) species:  $[\text{Cd}_2\text{Cl}_7]^{3-}$  and  $[\text{Cd}_2\text{Br}_7]^{3-}$  by using the  $[\text{Co}(\text{phen})_3]^{3+}$  cation [22(a)];  $[\text{CdBr}_4(\text{C}_7\text{H}_5\text{O}_2)]^{3-}$  by using the  $[\text{Co}(\text{en})_3]^{3+}$  cation [22(b)];  $[\text{Cd}_3\text{Br}_{10}(\text{H}_2\text{O})_2]^{4-}$  by using the  $[\text{Co}(\text{NH}_3)_6]^{3+}$  cation [22(c)];  $[\text{trans-CdBr}_4\text{Cl}_2]^{4-}$  and  $[\text{CdBr}_6]^{4-}$  by using the  $[\text{Co}(\text{en})_3]^{3+}$  cation [22(d)]; and  $[\text{CdI}_4]^{2-}$  by using the  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$  cation [22(e)]. In continuation of our interest in the structural chemistry of metal-arylcarboxylates [23,24] with nitrogen donor ligands, the present work reports the synthesis, characterization and single crystal X-ray structure determination of the cadmium(II) complexes  $[\text{Cd}(\text{H}_2\text{O})_6](\text{pic})_2 \cdot 2\text{H}_2\text{O}$  **1** (structure redetermination),  $[\text{Cd}(\text{N-hyden})_2](\text{pic})_2$  **2** and  $[\text{Cd}(\text{N-hyden})_2](\text{p-nitrobenzoate})_2$  **3**.

## 2. Experimental

### 2.1. Materials and physical measurements

Analytical grade reagents were used without any further purification. Carbon, hydrogen and nitrogen contents were measured micro-analytically with an automatic Perkin Elmer 2400 CHN elemental analyzer and the cadmium content was determined gravimetrically [25]. FT-IR spectra were recorded using a PERKIN ELMER SPECTRUM RXFT-IR system. Conductance measurements were performed with a Pico Conductivity Meter (Model CNO4091201, Lab India) in aqueous medium at 25 °C, using double distilled water. Multinuclear NMR spectra were recorded on BRUKER AVANCE II 400 MHz spectrophotometer. Thermo-gravimetric (TG) analyses of complexes **1–3** were carried out by a Simultaneous Thermal Analyzer (STA), manufactured and supplied by METTLER TOLEDO, Model Mettler Toledo 851e. The samples were subjected to heating from 25 to 1000 °C at a heating rate 10 °C/min under a nitrogen atmosphere.

**Table 1**

Crystal data and refinement parameters of complexes **1–3**.

	Complex 1	Complex 2	Complex 3
Abbreviated formula	$[\text{Cd}(\text{H}_2\text{O})_6](\text{pic})_2 \cdot 2\text{H}_2\text{O}$	$[\text{Cd}(\text{N-hyden})_2](\text{pic})_2$	$[\text{Cd}(\text{N-hyden})_2](\text{pnb})_2$
Empirical formula	$\text{C}_{12}\text{H}_{18}\text{CdN}_6\text{O}_{21}$	$\text{C}_{20}\text{H}_{28}\text{CdN}_{10}\text{O}_{16}$	$\text{C}_{22}\text{H}_{32}\text{CdN}_6\text{O}_{10}$
Crystal habit	rod, yellow	rod, yellow	needle, light yellow
Crystal size (mm)	0.24 × 0.24 × 0.30	0.14 × 0.22 × 0.30	0.15 × 0.15 × 0.40
$M_w$	694.40	776.93	652.95
Crystal system	orthorhombic	orthorhombic	triclinic
Space group	<i>Pccn</i> (No. 56)	<i>C222</i> <sub>1</sub> (No. 20)	<i>P</i> $\bar{1}$ (No. 2)
Unit cell dimensions			
<i>a</i> (Å)	25.3723(9)	9.8836(2)	7.1058(2)
<i>b</i> (Å)	7.2691(3)	12.9192(3)	7.5543(2)
<i>c</i> (Å)	13.2050(4)	46.4409(10)	13.0469(4)
$\alpha$ (°)	90	90	102.255(1)
$\beta$ (°)	90	90	104.976(1)
$\gamma$ (°)	90	90	98.515(1)
<i>V</i> (Å <sup>3</sup> )	2435.5(2)	5930.0(2)	645.69(3)
<i>Z</i>	4	8	1
$D_c$ (Mg m <sup>-3</sup> )	1.944	1.740	1.679
$\mu$ (mm <sup>-1</sup> )	1.012	0.829	0.913
<i>F</i> (000)	1432	3152	334
<i>T</i> (K)	296	296	296
Radiation (Å)	Mo K $\alpha$ ; 0.71073	Mo K $\alpha$ ; 0.71073	Mo K $\alpha$ ; 0.71073
Reflections collected/ unique > 2 $\sigma$ ( <i>I</i> )	24708/4918/ 3192	19643/9056/ 8474	17664/3975/ 3718
$R_{\text{int}}$	0.0344	0.0214	0.0325
Data/parameters	4918/188	9056/424	3975/182
Goodness on fit	1.020	1.094	1.044
$R_1, wR_2$ [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0343, 0.0847	0.0394, 0.0994	0.0257, 0.0569
$R_1, wR_2$ [all data]	0.0609, 0.0980	0.0427, 0.1012	0.0296, 0.0584
$\Delta\rho$ (e Å <sup>-3</sup> )	−0.64, 0.48	−1.14, 0.63	−0.29, 0.53

**CAUTION!** Although we have experienced no problems in handling picric acid complexes, these should be handled with great caution, because of their explosive nature.

### 2.2. Sample preparation

#### 2.2.1. Synthesis of $[\text{Cd}(\text{H}_2\text{O})_6](\text{pic})_2 \cdot 2\text{H}_2\text{O}$ , **1**

0.34 g (2 mmol) of cadmium(II) carbonate was suspended in 20 mL of water. To the stirred  $\text{CdCO}_3$  suspension at 50–60 °C, 0.91 g (4 mmol) of picric acid was added slowly. The mixture was stirred for 20 min in the temperature range 50–60 °C until the effervescence ceased completely, indicating formation of cadmium picrate. The resultant reaction mixture was filtered and put aside for slow solvent evaporation at room temperature. Yellow block shaped crystals were harvested after a few days. Complex **1** decomposes at 236 °C. Complex **1** is sparingly soluble in water and insoluble in organic solvents like methanol, acetone, chloroform, etc. *Anal. Calc.* (%): C, 20.73; H, 2.59; N, 12.09; Cd, 16.18. *Found* (%): C, 20.81; H, 2.51; N, 12.25; Cd, 16.24.

#### 2.2.2. Synthesis of $[\text{Cd}(\text{N-hyden})_2](\text{pic})_2$ , **2**

**Method 1:** 0.5 g (2 mmol) of  $\text{CdCl}_2$  was dissolved in 20 mL of ethanol. To the stirred  $\text{CdCl}_2$  solution, *N*-(hydroxyethyl)ethylenediamine (4 mmol) was added dropwise. The mixture was stirred for

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