Polyhedron 139 (2018) 178–188

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

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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ARTICLE INFO

Article history:
Received 7 August 2017
Accepted 23 September 2017

Keywords:
Cadmium
N-(hydroxyethyl)ethylenediamine
Picrate
p-Nitrobenzoate
Hydrogen bonding interactions

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, $[Cd(H_2O)_6](pic)_2{\cdot}2H_2O$ **1**, $[Cd(N\text{-}hyden)_2](pic)_2$ **2**, $[Cd(N\text{-}hyden)_2](pnb)_2$ **3**, (where N-*hyden* = N-(hydroxyethyl)ethylenediamine, H*pic* = picric acid and H*pnb* = 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, $[Cd(H_2O)_6]^{2+}$ in **1** and $[Cd(N\text{-}hyden)_2]^{2+}$ in **2** and **3**, together with the counter anions *pic*/*pnb*, which are stabilized by a mutual interplay of various hydrogen bonding interactions.

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 $nd^{10}ns^2$, 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 Ca^{2+} and 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 (H*pnb*) and picric acid (H*pic*) are used due to their wide applications in

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https://doi.org/10.1016/j.poly.2017.09.053

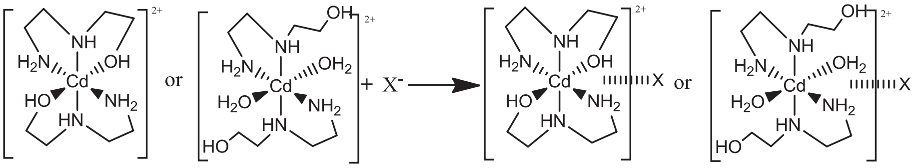


Fig. 1. Schematic representation of second-sphere coordination complexes via hydrogen bonding between the complex cation $[Cd(N\text{-}hyden)_2]^{2+}$ and *pic*/*pnb* anions shown as X in the second coordination sphere.

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 π–π 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, $[Cd(N\text{-}hyden)_2]^{2+}$or $[Cd(N\text{-}hyden)_2(H_2O)_2]^{2+}$ (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: $[Cd_2Cl_7]^{3-}$ and $[Cd_2Br_7]^{3-}$ by using the $[Co(phen)_3]^{3+}$ cation [22(a)]; $[CdBr_4(C_7H_5O_2)]^{3-}$ by using the $[Co(en)_3]^{3+}$ cation [22(b)]; $[Cd_3Br_{10}(H_2O)_2]^{4-}$ by using the $[Co(NH_3)_6]^{3+}$ cation [22(c)]; $[trans\text{-}CdBr_4Cl_2]^{4-}$ and $[CdBr_6]^{4-}$ by using the $[Co(en)_3]^{3+}$ cation [22(d)]; and $[CdI_4]^{2-}$ by using the $[Co(en)_2Cl_2]^{+}$ 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 $[Cd(H_2O)_6](pic)_2{\cdot}2H_2O$ **1** (structure redetermination), $[Cd(N\text{-}hyden)_2](pic)_2$ **2** and $[Cd(N\text{-}hyden)_2](p\text{-}nitrobenzoate)_2$ **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	$[Cd(H_2O)_6](pic)_2{\cdot}2H_2O$	$[Cd(N\text{-}hyden)_2](pic)_2$	$[Cd(N\text{-}hyden)_2](pnb)_2$
Empirical formula	$C_{12}H_{18}CdN_6O_{21}$	$C_{20}H_{28}CdN_{10}O_{16}$	$C_{22}H_{32}CdN_6O_{10}$
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	*Pccn* (No. 56)	$C222_1$ (No. 20)	$P\bar{1}$ (No. 2)
Unit cell dimensions			
a (Å)	25.3723(9)	9.8836(2)	7.1058(2)
b (Å)	7.2691(3)	12.9192(3)	7.5543(2)
c (Å)	13.2050(4)	46.4409(10)	13.0469(4)
α (°)	90	90	102.255(1)
β (°)	90	90	104.976(1)
γ (°)	90	90	98.515(1)
V (Å^3)	2435.5(2)	5930.0(2)	645.69(3)
Z	4	8	1
D_c (Mg m^{-3})	1.944	1.740	1.679
μ (mm^{-1})	1.012	0.829	0.913
F(000)	1432	3152	334
T (K)	296	296	296
Radiation (Å)	Mo Kα; 0.71073	Mo Kα; 0.71073	Mo Kα; 0.71073
Reflections collected/ unique/>2σ(*I*)	24708/4918/ 3192	19643/9056/ 8474	17664/3975/ 3718
R_{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 [$I > 2\sigma(I)$]	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
Δρ (e Å^{-3})	−0.64, 0.48	−1.14, 0.63	−0.29, 0.53

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

2.2. Sample preparation

2.2.1. Synthesis of $[Cd(H_2O)_6](pic)_2{\cdot}2H_2O$, **1**

0.34 g (2 mmol) of cadmium(II) carbonate was suspended in 20 mL of water. To the stirred $CdCO_3$ 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 $[Cd(N\text{-}hyden)_2](pic)_2$, **2**

Method 1: 0.5 g (2 mmol) of $CdCl_2$ was dissolved in 20 mL of ethanol. To the stirred $CdCl_2$ solution, N-(hydroxyethyl)ethylenediamine (4 mmol) was added dropwise. The mixture was stirred for

Table 2
Structural parameters [Å, °] of complexes **1**–**3**.

Complex **1**			
Cd1–O1W	2.249(2)	O1W–Cd1–O2W	84.63(6)
Cd1–O2W	2.297(1)	O1W–Cd1–O3W	90.76(7)
Cd1–O3W	2.225(2)	O2W–Cd1–O3W	86.16(6)
Complex **2**			
Cd1–N1	2.303(4)	N1–Cd1–O1	146.49(1)
Cd1–N2	2.326(4)	N2–Cd1–O1	71.55(1)
Cd1–O1	2.509(4)	N1–Cd1–N2	75.93(1)
		N1–Cd1–O1^{i}	72.89(1)
Cd2–N3	2.279(4)	N3–Cd2–O2	145.59(1)
Cd2–N4	2.298(4)	N4–Cd2–O2	68.62(1)
Cd2–O2	2.642(4)	N3–Cd2–N4	77.13(1)
		N3–Cd2–O2^{ii}	89.48(1)
Equivalent positions: (i) $-x + 1, y, -z + 1.5$; (ii) $x, -y, -z + 2$.			
Complex **3**			
Cd1–N1	2.298(1)	N1–Cd1–N2	77.72(5)
Cd1–N2	2.320(1)	N1–Cd1–O1	89.97(4)
Cd1–O1	2.417(1)	N2–Cd1–O1	75.08(4)

45 min. The mixture was filtered in a filtration unit and dried in vacuum to avoid moisture. 0.5 g of the above dried product, [Cd(N-*hyden*)$_2$]Cl$_2$, was dissolved in a methanol–water solvent mixture (25 mL), then the sodium salt of picric acid was added to the solution in a 1:2 stoichiometry. Precipitation appeared in the solution. The precipitates were filtered and the filtrate was put aside to obtain orange yellow crystals after seven days at room temperature. Complex **2** decomposes at 220 °C. Complex **2** is soluble in water and insoluble in organic solvents like methanol, acetone, chloroform, etc.

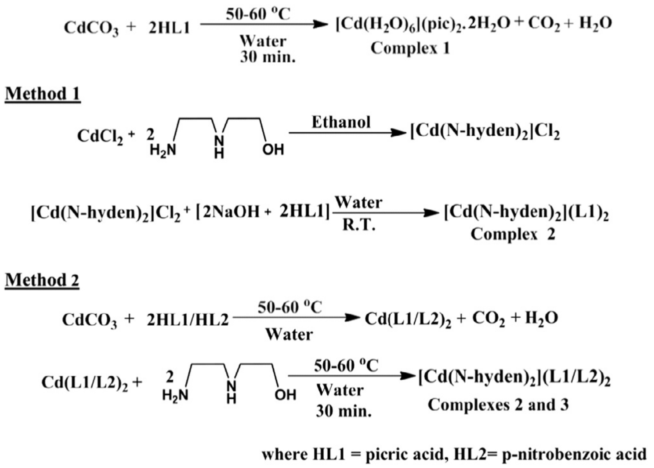
Method 2: 0.34 g (2 mmol) of cadmium(II) carbonate was suspended in 20 mL of water. To the stirred CdCO$_3$, in the temperature range 50–60 °C, 0.91 g (4 mmol) of picric acid was added slowly. The mixture was stirred for 20 min at 50–60 °C until the effervescence ceased completely, indicating the formation of cadmium picrate. To the resultant solution, still in the temperature range 50–60 °C, N-*hyden* (4 mmol) was added slowly. The solution was stirred at 60 °C for 30 min. The resultant reaction mixture was filtered and the filtrate was put aside to obtain orange yellow block shaped crystals after seven days of evaporation at room temperature. Complex **2** decomposes at 220 °C. Complex **2** is also sparingly soluble in water and insoluble in organic solvents like methanol, acetone, chloroform, etc. *Anal.* Calc. (%): C, 30.84; H, 3.59; N, 17.99; Cd, 14.39. Found (%): C, 30.97; H, 3.32; N, 18.10; Cd, 14.51.

2.2.3. Synthesis of [Cd(N-hyden)$_2$](pnb)$_2$, 3

Complex **3** was synthesized similarly to method 2 employed for the synthesis of complex **2**. 0.34 g (2 mmol) of cadmium(II)

Table 3
Hydrogen bond parameters [Å, °] of complexes **1**–**3**.

D–H···A	***d*(D–H)**	***d*(H···A)**	***d*(D···A)**	**∠DHA**
Complex **1**				
O1W–H1···O4W	0.96	1.81	2.755(2)	166.4
O1W–H2···O5	0.96	1.92	2.875(2)	170.3
O2W–H1···O1^{i}	0.96	1.92	2.874(2)	176.7
O2W–H2···O7^{ii}	0.96	2.03	2.915(2)	151.9
O3W–H1···O4W^{iii}	0.96	1.79	2.754(2)	178.1
O3W–H2···O1^{iv}	0.96	1.97	2.892(2)	160.6
O4W–H1···O1^{ii}	0.96	2.25	2.929(2)	126.6
O4W–H1···O7^{ii}	0.96	2.04	2.892(2)	146.5
O4W–H2···O2W^{v}	0.96	2.12	2.992(2)	149.8
C3–H3···O3^{iv}	0.93	2.60	3.418(2)	147.2
C3–H3···O6^{vi}	0.93	2.57	3.189(2)	124.3
C5–H5···O3^{vii}	0.93	2.64	3.261(2)	124.6
Equivalent positions: (i) $x - 0.5, y + 0.5, -z + 1$; (ii) $x - 0.5, -y + 1, -z + 1.5$; (iii) $x, -y + 1.5, z - 0.5$; (iv) $-x + 1.5, -y + 1.5, z$; (v) $-x + 1, y - 0.5, -z + 1.5$; (vi) $-x + 1.5, y, z - 0.5$; (vii) $-x + 1.5, y, z + 0.5$.				
Complex **2**				
N1–H9···O3^{ii}	0.89	2.31	3.051(6)	140.8
N1–H9···O9A^{ii}	0.89	2.37	3.154(8)	146.4
N1–H9···O9B^{ii}	0.89	2.31	3.071(18)	143.5
N2–H11···O5^{iii}	0.98	2.39	3.166(6)	135.7
N2–H11···O13^{iii}	0.98	2.49	3.320(6)	142.1
O1–H12···O3	0.930(1)	1.81(1)	2.710(5)	163.4(8)
N3–H21···O10^{v}	0.89	2.24	3.004(6)	144.2
N3–H21···O12A^{v}	0.89	2.51	3.270(7)	143.1
N3–H21···O12B^{v}	0.89	2.62	3.418(12)	150.0
N3–H22···O15A^{vi}	0.89	2.51	3.254(10)	141.0
N4–H23···O6^{iv}	0.98	2.29	3.218(6)	158.3
N4–H23···O16A^{iv}	0.98	2.51	3.093(7)	117.8
N4–H23···O16B^{iv}	0.98	2.61	3.257(14)	123.9
O2–H24···O10^{i}	0.930(1)	1.86(1)	2.772(6)	166.7(9)
C4–H7···O9B^{i}	0.97	2.58	3.33(3)	134.6
C4–H7···O14	0.97	2.63	3.442(9)	141.7
C5–H13···O16A^{iv}	0.97	2.37	2.978(9)	120.5
C6–H16···O7^{iv}	0.97	2.65	3.247(7)	120.0
C6–H16···O15A^{iii}	0.97	2.41	3.205(7)	139.2
Equivalent positions: (i) $x + 0.5, y + 0.5, z$; (ii) $-x + 1, y, -z + 0.5$; (iii) $x + 0.5, y - 0.5, z$; (iv) $x + 1, y, z$; (v) $x + 0.5, -y + 1.5, -z$; (vi) $x + 1, -y + 2, -z$.				
Complex **3**				
N1–H9···O2^{ii}	0.89	2.24	3.088(2)	160.3
N1–H10···O2^{iii}	0.89	2.27	3.027(2)	142.6
N2–H11···O2^{iv}	0.98	2.30	3.087(2)	136.9
O1–H12···O3	0.78(2)	1.83(2)	2.598(2)	171(2)
C1–H2···O4^{i}	0.97	2.60	3.508(2)	155.1
C7–H14···O3^{v}	0.93	2.58	3.359(2)	141.9
Equivalent positions: (i) $x + 1, y, z - 1$; (ii) $-x + 2, -y + 1, -z + 1$; (iii) $x + 1, y, z$; (iv) $-x + 1, -y + 1, -z + 1$; (v) $x - 1, y, z$				



Scheme 1. Schematic representation of the syntheses of complexes **1**–**3**.

carbonate was suspended in 20 mL of water. To the stirred solution 4 mmol of p-nitrobenzoic acid was added slowly. The mixture was stirred for 20 min in the temperature range 50–60 °C until the effervescence completely ceased, indicating the formation of cadmium p-nitrobenzoate. To the resultant solution at 50–60 °C, N-*hyden* (4mmol) was added slowly. The solution was stirred at 50–60 °C for 30 min. The resultant reaction mixture was filtered and the filtrate was put aside to obtain light yellow needle shaped crystals after 12 days of evaporation at room temperature. Complex **3** decomposes at 193 °C. Complex **3** is sparingly soluble in water and insoluble in organic solvents like methanol, acetone, chloroform, etc. *Anal.* Calc. (%): C, 40.40; H, 4.89; N, 12.86; Cd, 17.20. Found (%): C, 40.32; H, 5.01; N, 12.72; Cd, 17.32.

2.3. X-ray crystallography

X-ray diffraction experiments were carried out on a Bruker X8 APEXII Kappa CCD area-detector diffractometer (Mo-Kα, λ = 0.71073 Å), with the help of the APEX2 GUI program suite [26]. For the respective complexes **1**–**3**, a total number of 24708, 19643 and 17664 data were collected at 296(2) K and processed using the standard software programs implemented in the APEX2 suite [26], including integration, reduction together with multi-scan absorption corrections, and merging with SAINT, SADABS and XPREP, respectively. The structures were solved by the intrinsic phasing method with SHELXTL XT [27] and were refined anisotropically by full matrix least-squares on F^2 with SHELXTL XLMP [28]. All H atom positions were calculated geometrically and treated with a riding model. Exceptions are the H-atoms of water molecules in **1** and the –OH group of the N-*hyden* groups in **2** and **3** which were initially located from the difference Fourier electron density maps and then restrained with 'AFIX 3' for the water H-atoms. For **2**, a two-fold disorder of the nitro oxygen atoms of the *pic* anions was found from the difference Fourier maps. The 1,3-distances between the two oxygen atoms were restrained to 1.12 Å, similar to the adjacent fully ordered NO_2 groups, and the displacement parameters of both sites A and B were set to be equal. Note, the present data quality of **1** is comparable to that of Natarajan et al. [29], however, the preparation of **1** from both sources are different, see Section 3.1. Further details of the crystal data and refinement statistics, structural parameters and H-bond parameters of complexes **1**–**3** are given in Tables 1–3 respectively.

3. Results and discussion

3.1. Synthesis

Complexes **1**–**3** were synthesized using the appropriate reactants, as shown in Scheme 1. Complex **1** was isolated in the form of yellow block shaped crystals when an aqueous reaction mixture of cadmium(II) carbonate and picric acid was allowed to stir at 50–60 °C for 30 min and put aside for evaporation at room temperature. It is worth noting that in the previous structure determination of complex **1**, colorless rod-shaped crystals were obtained strangely from a saturated aqueous solution of 1:1 $CdCl_2$-picric acid [29]. The formation of same complex **2** by employing different methods, 1 and 2, was indicated by melting point, elemental analyses and spectroscopic techniques (FT-IR and NMR). Complex **3** was isolated in the form of light yellow needle shaped crystals when the reaction mixture was allowed to evaporate at room temperature after 12 days. The structures of all the newly synthesized complexes **1**–**3** have been unambiguously determined by single crystal X-ray diffraction.

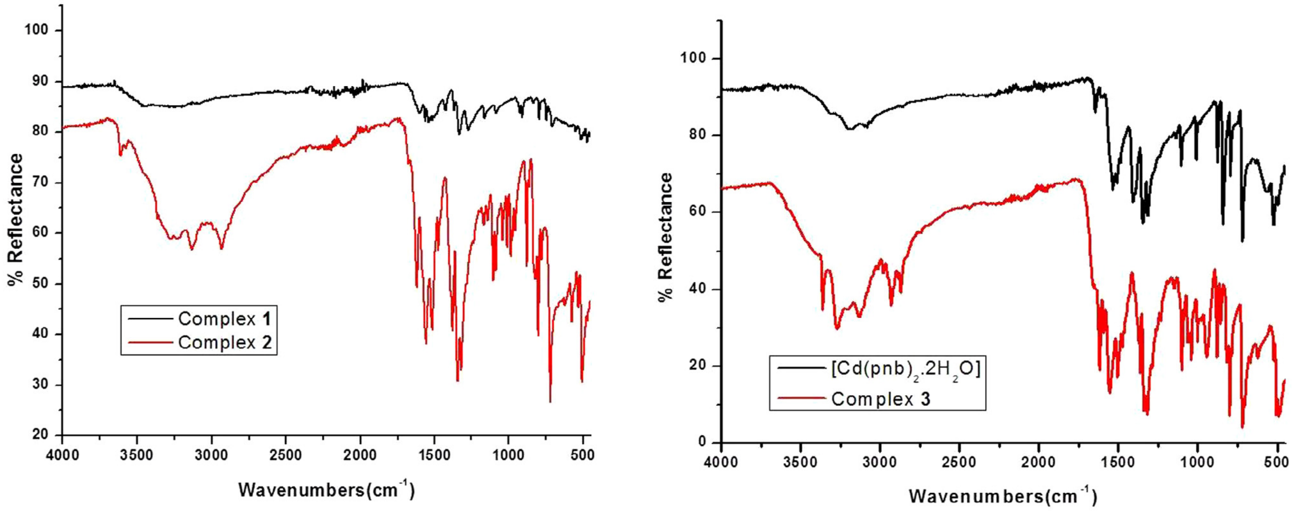


Fig. 2. FT-IR spectra of complexes **1**–**3**.

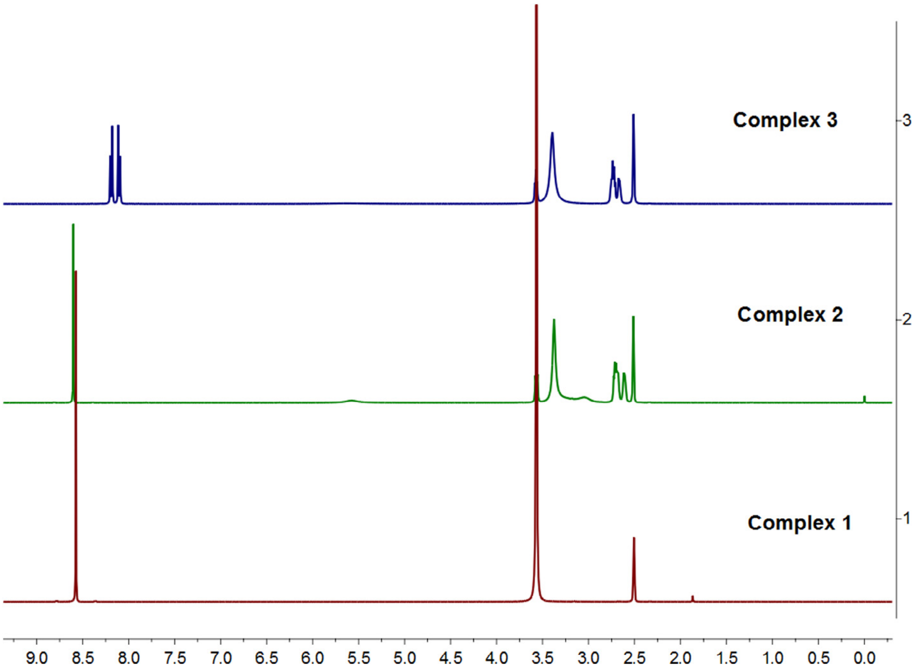


Fig. 3. ^{1}H NMR spectra of complexes **1**–**3**.

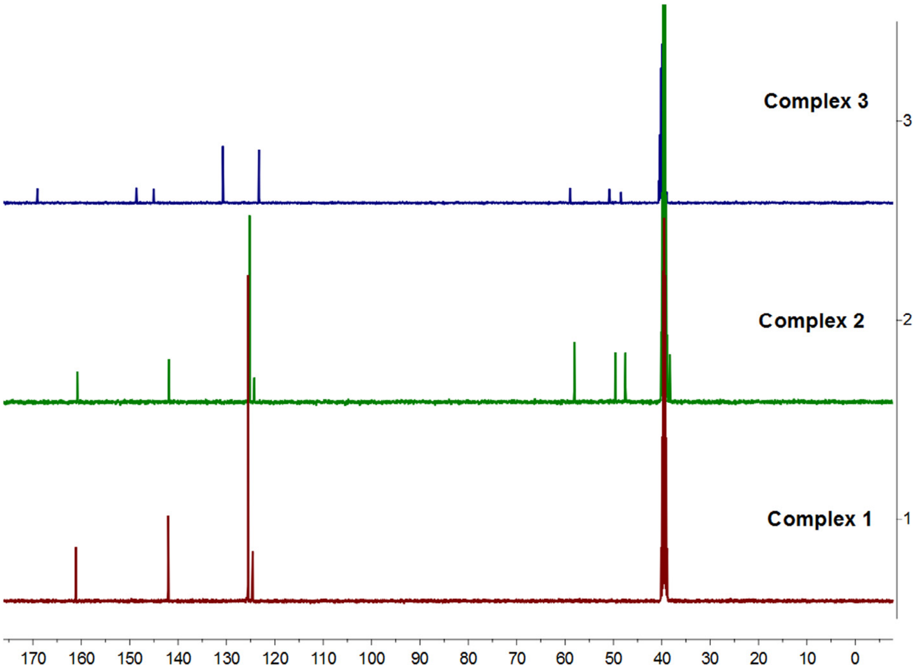


Fig. 4. ^{13}C NMR spectra of complexes **1**–**3**.

3.2. Spectroscopic characterization

3.2.1. Infrared spectroscopy

The infrared spectra of complexes **1**–**3** (neat) were recorded in the region 4000–400 cm^{-1} and tentative assignments were made on the basis of earlier reports in the literature [30–32] (Fig. 2). The broad band in the region 3500–3300 cm^{-1} in the spectrum of complex **1** indicated the presence of water molecule, while the absence of a broad absorption peak in the region 3500–3100 cm^{-1} for the O–H bond stretching of water in complexes **2** and **3** showed their anhydrous nature. The strong bands at 3289 and 3293 cm^{-1} may be attributed to the O–H group of coordinated N-*hyden* in complexes **2** and **3**, respectively which is less than the free O–H stretching frequency. The absorption peaks in the region 3110–3210 cm^{-1} corresponds to –NH$_2$ and –NH stretching vibrations of the coordinated ligand. The sharp bands varying in intensity from weak to medium in the region 3000–2750 cm^{-1} were assigned to –C–H(ν_{as}), –C–H(ν_s) of the ligand and –C=C–H(s, aromatic) of the aromatic anionic group. The sharp absorption bands in the regions 1580–1550 and 1390–1360 cm^{-1} were due to $\nu_{as(COO)}$ and $\nu_{s(COO)}$ of the aromatic carboxylate anions in complex **3**, with $\Delta\nu$ = 171–165 cm^{-1}, corresponding to ionic

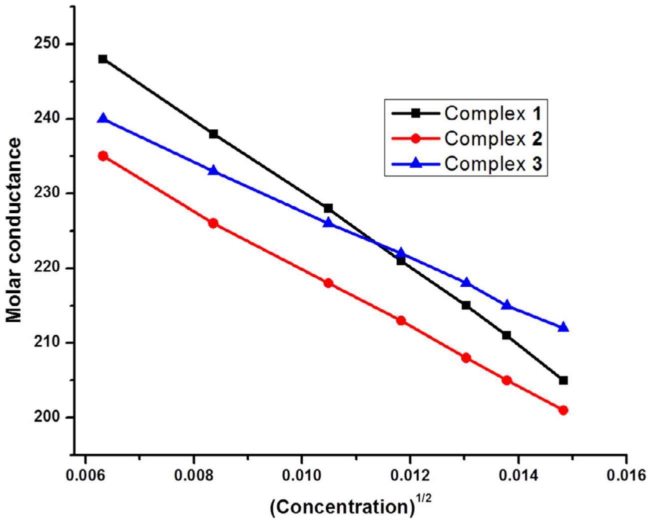


Fig. 5. Molar conductance of complexes **1**–**3**.

mode of carboxylate coordination [31]. In complexes **1** and **2**, the peaks for C–O coordination in the picrate moiety appeared in the range 1090–1050 cm^{-1} and the peaks for the nitro group of the picrate anion appeared in the region 1595–1520 cm^{-1} [31]. IR spectral peaks in the regions 535–520 and 490–475 cm^{-1} indicated the presence of Cd-O and Cd-N stretching frequencies. These types of stretching vibration showed that the N-donor ligand N-*hyden* acts as a chelating agent towards the metal center.

3.2.2. Nuclear magnetic resonance spectroscopy

The ^{1}H and ^{13}C NMR spectra of the complexes were recorded in DMSO-d$_6$ (Figs. 3 and 4). The peak assignments for various protons and carbon atoms of complexes **1**–**3** were assigned on the basis of literature reports [33].

3.2.2.1. ^{1}H NMR spectra. In the proton NMR spectrum of complex **1**, the peaks observed at δ 8.57 (4H, s) ppm were assigned to four aromatic protons of two *pic* anions. In proton NMR spectrum of complex **2**, one sharp peak observed at δ 8.6014 (4H, s) ppm might be assigned to four aromatic protons of two *pic* anions. The remaining observed peaks in the proton NMR spectrum correspond to protons present in the counter cation [Cd(N-*hyden*)$_2$]$^{2+}$. The methylene protons adjacent to the hydroxyl group of the ligand appeared more deshielded, appeared at δ 3.566 ppm as a triplet, due to the electron withdrawing nature of the adjacent oxygen atom. The eight methylene protons adjacent to the middle N–H group of two N-*hyden* ligands were observed at δ 2.7009 ppm. The remaining four methylene protons adjacent to the –NH$_2$ group of the two N-*hyden* ligands were observed at δ 2.512 ppm. The remaining six protons of one/two –NH and two –NH$_2$ groups of two moieties of N-*hyden*

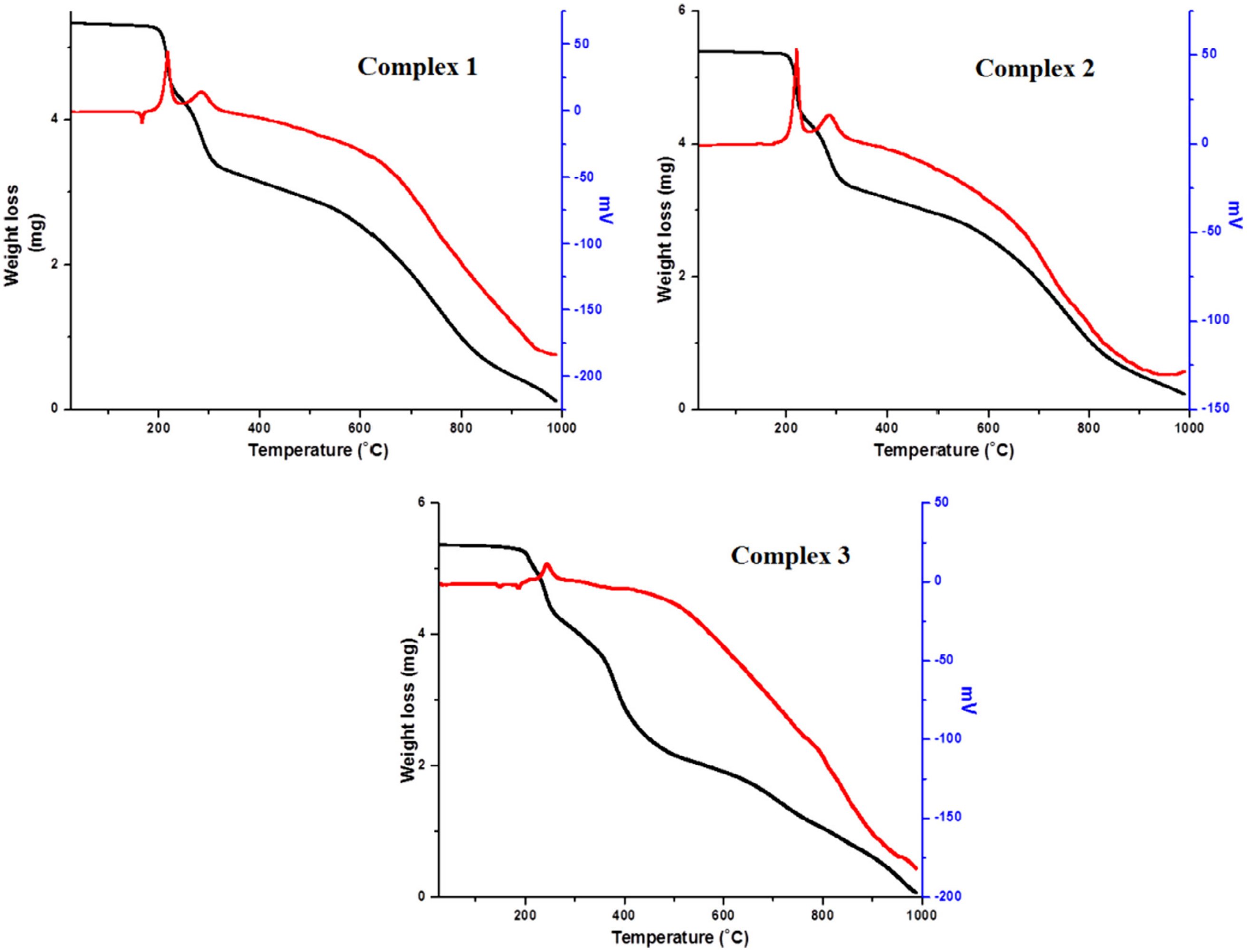


Fig. 6. TGA-DTA curves of complexes **1**–**3**.

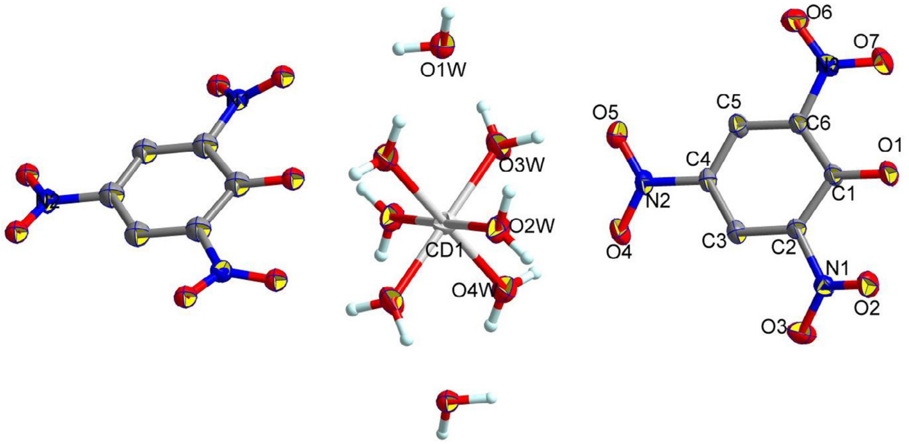


Fig. 7. ORTEP diagram of the ionic complex **1**, [Cd(H_2O)$_6$](*pic*)$_2$·2H_2O (40% probability level). Hydrogen atoms of the picrate anions are omitted for clarity.

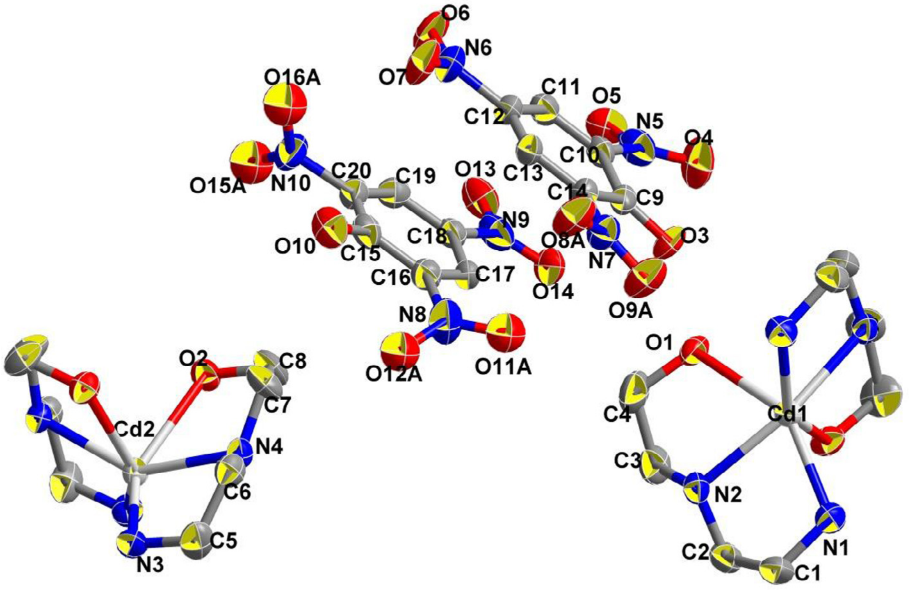


Fig. 8. ORTEP diagram of the ionic complex **2**, [Cd(N-*hyden*)$_2$](*pic*)$_2$ (40% probability level). Hydrogen atoms of the picrate anions are omitted for clarity.

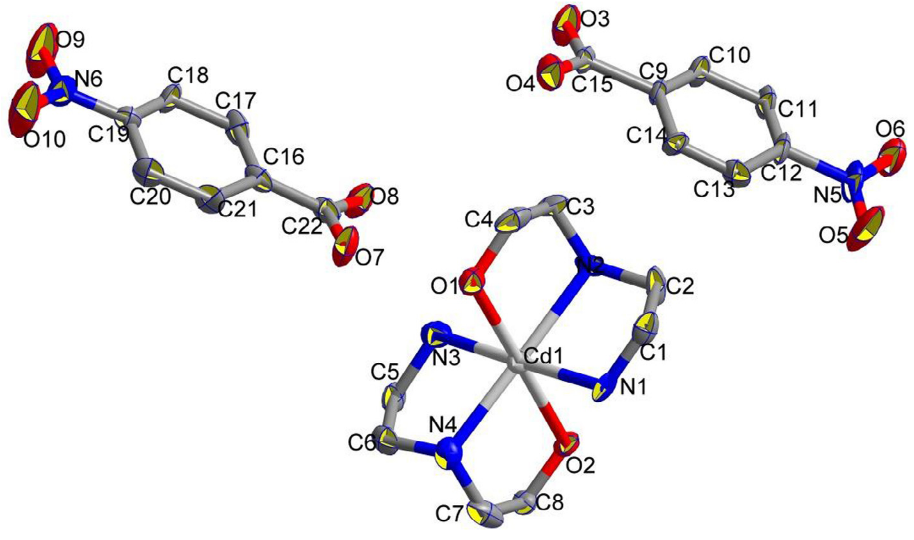


Fig. 9. ORTEP diagram of the ionic complex **3**, [Cd(N-*hyden*)$_2$](*pnb*)$_2$ (40% probability level). Hydrogen atoms of the picrate anions are omitted for clarity.

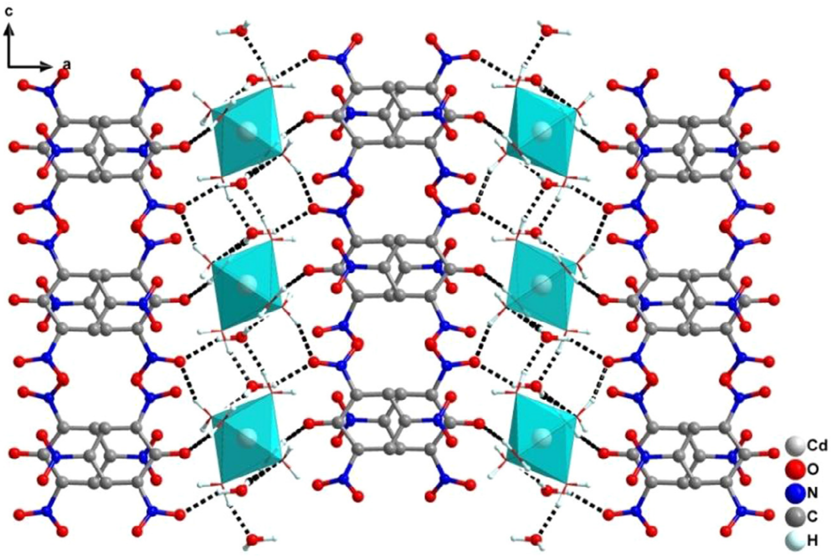


Fig. 10. Packing diagram of complex **1**, showing a strong network of O—H···O hydrogen bonding interactions between the cationic $[Cd(H_2O)_6]^{2+}$ and anionic *pic* units.

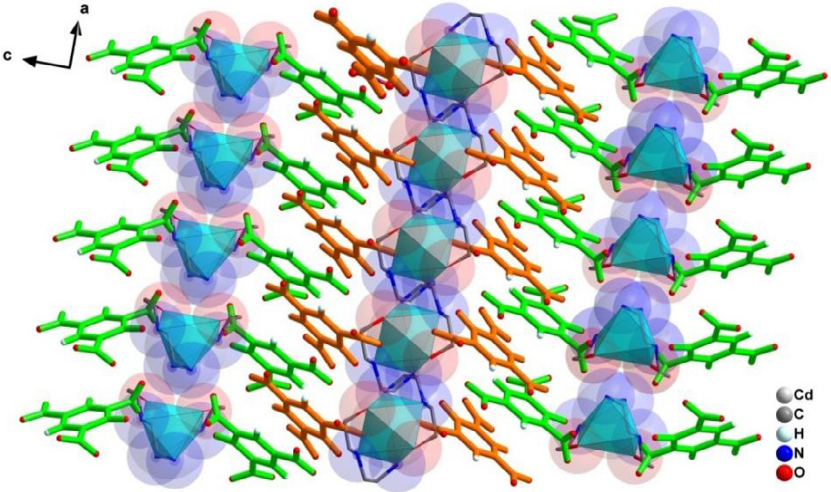


Fig. 11. Crystal lattice of complex **2**, showing an alternate arrangement of cationic and anionic layers.

appeared at δ 3.044 ppm as a broad peak. The two –OH protons of similar ligands appeared at δ 5.573 ppm as a broad peak. Similar to complex **2**, the ^{1}H NMR spectrum of complex **3** showed eight aromatic protons for the two *pnb* anions, which appeared at δ 8.18 ppm as a doublet. The observed peaks for the cationic region of complex **3** were observed at similar δ values as those observed for the complex cation in complex **2** (Fig. 3).

3.2.2.2. ^{13}C NMR spectra. The three complexes contain aromatic carbon atoms, i.e., the *pic* moiety in complexes **1** and **2**, and the *pnb* moiety in **3**. In complex **1**, the δ values at 161.10, 142.03, 125.51, 124.55 ppm were assigned to the aromatic carbon atoms of the *pic* moiety. For complex **2**, the δ 160.83, 141.85, 125.21, 124.24 ppm peaks might be assigned to different carbon atoms of the *pic* anion. The peak at δ 160.83 ppm corresponds to the carbon atom which is coordinated to the phenoxo oxygen atom. The peaks with less intensity in the aromatic region (δ = 120–170 ppm) correspond to the quaternary carbon atoms, to which the nitro group is attached. The peaks observed at δ 58.7, 49.60, 47.52 ppm corresponded to aliphatic carbon atoms in the ligand N-*hyden*. In complex **3**, the peak at δ 169.04 ppm corresponded to the carboxylate carbon atom. The other peaks at δ 148.61, 145.029, 130.74, 123.264 ppm might be assigned to different aromatic carbons of the *pnb* anion. The peaks of the ligand N-*hyden* in complex **3** were similar to those in complex **2** (Fig. 4).

3.3. Molar conductance measurements

Conductivity measurements of complexes **1**–**3** were carried out in aqueous medium at 25 °C. The limiting molar conductance at infinite dilution was calculated by plotting Λ (molar conductance) versus $C^{1/2}$ (square root of concentration). When the concentrations were extrapolated to zero, they gave Λ_o values of 261, 243 and 250 S cm^2 mol^{-1}, respectively for complexes **1**–**3** (Fig. 5). These values fall into the range observed for 1:2 electrolytes [34]. Therefore, the conductance measurements revealed that complexes **1**–**3** behave as 1:2 electrolytes in aqueous medium, supporting the ionic formulation of the complexes.

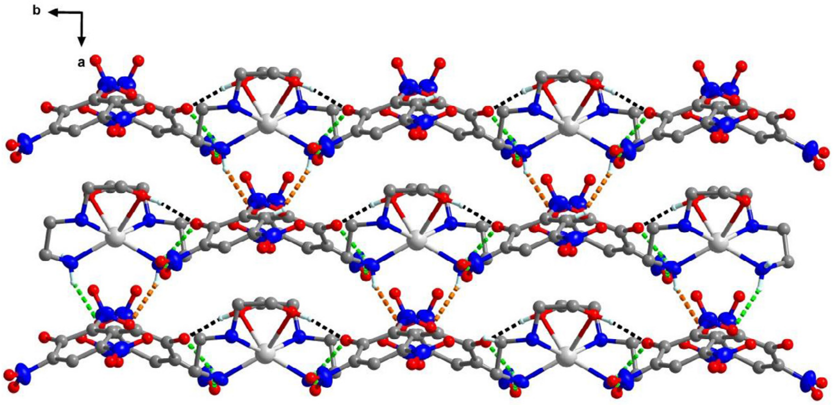
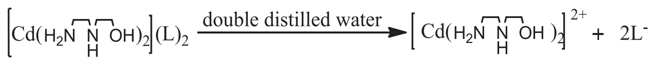


Fig. 12. Hydrogen bonding network in complex **2**.



$$\left[\mathrm{Cd}(\mathrm{H_2N}\ \underset{\mathrm{H}}{\mathrm{N}}\ \mathrm{OH})_2\right](\mathrm{L})_2 \xrightarrow{\text{double distilled water}} \left[\mathrm{Cd}(\mathrm{H_2N}\ \underset{\mathrm{H}}{\mathrm{N}}\ \mathrm{OH})_2\right]^{2+} + 2\mathrm{L}^-$$

where L= picrate or p-nitrobenzoate

3.4. Thermogravimetric analyses

In order to study thermal stability of synthesized complexes, thermogravimetric analyses were carried out for all complexes **1**–**3** under a nitrogen atmosphere. The first weight loss in complex **1** corresponded to the loss of seven water molecules, as revealed from the DTA peak (endothermic loss) in the temperature range 130–150 °C (Fig. 6). The second weight loss for complex **1**, in the temperature range 170–320 °C, was simultaneous to the first weight loss and corresponds to the exothermic loss of picrate counter anions. For complexes **2** and **3**, the first weight loss in the temperature range 170–320 °C corresponded to loss of counter anions, i.e., *pic* and *pnb*, respectively. After 320 °C, the observed continuous weight loss indicated the formation of some malleable impurities at high temperatures in all the complexes **1**–**3** (Fig. 6).

3.5. X-ray crystallography

3.5.1. Coordination geometry of $[Cd(H_2O)_6]^{2+}$, $[Cd(N\text{-}hyden)_2]^{2+}$ and pic/pnb

Complex **1** crystallizes in the orthorhombic crystal system with the space group *Pccn*. The asymmetric unit comprises half a complex cation, $[Cd(H_2O)_6]^{2+}$, with the cadmium (Cd1) ion sitting on a special position, one anionic *pic* moiety and one lattice water molecule. Hence the complete structure and formula of complex **1** is $[Cd(H_2O)_6](pic)_2{\cdot}2H_2O$ (Fig. 7). The central Cd(II) ion is octahedrally surrounded by oxygen atoms of coordinated water molecules. The corresponding Cd–Ow distances are in the range 2.225 (2)–2.297(1) Å (Table 2). The ORTEP diagram of complex **1** from this work agrees with the previous structure determination [29]. However, the crystal packing of **1** was not described at all previously [29], and hence is analyzed and compared in detail in this report with the crystal packing of complexes **2** and **3**, see Section 3.5.2.

The presence of the tridentate N-*hyden* ligand makes different scenarios in complexes **2** and **3**. Complex **2** crystallizes in the orthorhombic crystal system with the space group $C222_1$. The asymmetric unit consists of two complex $[Cd(N\text{-}hyden)_2]^{2+}$ cations, each of which sits on a special position (with two-fold rotation symmetry), and two *pic* anionic moieties (Fig. 8). The central Cd (II) ion adopts a distorted *trans*-octahedral geometry which is composed of two tridentate ligand N-*hyden* coordinated through two nitrogen atoms and one oxygen atom. The bond lengths and bond angles observed for the N-*hyden* ligand closely resemble with those observed in related N-*hyden* complexes [19–21]. The structural parameters of the *pic* anion are similar to those observed in salts containing *pic* ions. Complex **3** crystallizes in the triclinic crystal system with the space group $P\overline{1}$. The asymmetric unit comprises one *trans*-octahedral complex cation, $[Cd(N\text{-}hyden)_2]^{2+}$, and two *pnb* anionic moieties (Fig. 9). The bond lengths and bond angles of the N-*hyden* ligand and the *pic* and *pnb* anions in complexes **1**–**3** are very similar to those reported previously [35–46].

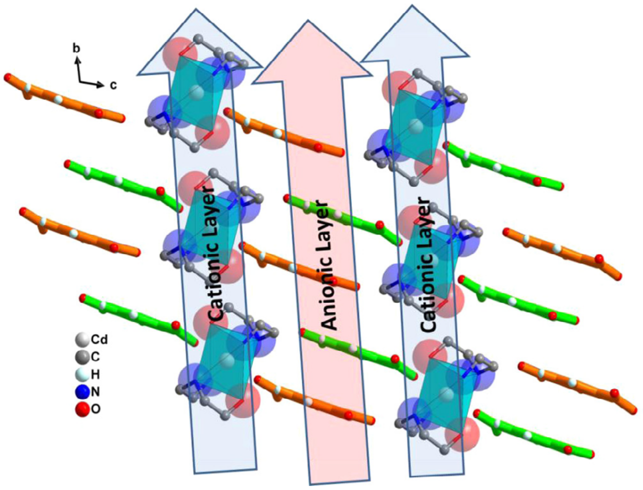


Fig. 13. Crystal lattice of complex **3**, showing an alternate arrangement of cationic and anionic layers.

3.5.2. 3D arrangements of complexes 1–3

The crystal lattice of complex **1** showed a layered arrangement of cationic $[Cd(H_2O)_6]^{2+}$ and anionic *pic* moieties (Fig. 10). The six water molecules coordinated to the Cd(II) ion act as hydrogen bond donors to the oxygen atoms of the nitro and phenoxo groups of the *pic* anions. The adjacent anionic layers are arranged in an opposite fashion in order to reduce steric repulsion between the functional groups. The *pic* moieties act as hydrogen bond acceptors, giving rise to O–H···O and C–H···O extensive hydrogen bonding network (Table 3).

The crystal lattices of complexes **2** and **3**, both having a common *trans*-octahedral $[Cd(N\text{-}hyden)_2]^{2+}$ complex cation and *pic* and *pnb* anionic counterparts respectively, being stabilized by second-sphere non-covalent interactions. Complex **2** showed a layered arrangement of cations and anions, in which layers of *pic*

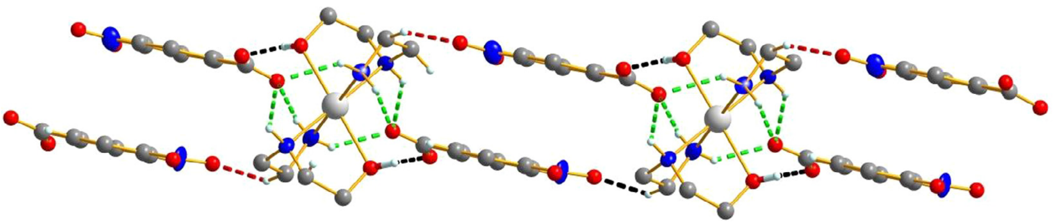
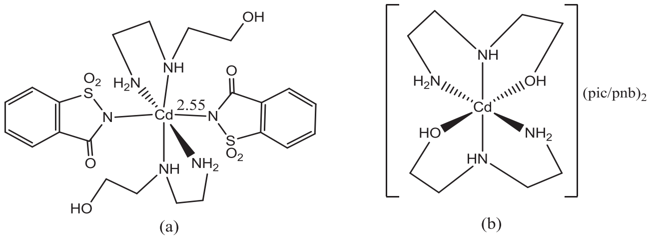


Fig. 14. Network of C–H···O, N–H···O and O–H···O hydrogen bonds in complex **3**.



(a) (b)

Fig. 15. Influence of anions or co-ligands on the chelation mode of the tridentate N-*hyden* ligand to the Cd(II) metal center: (a) saccharinates induce a bidentate chelation; (b) *pnb* and *pic* induce a tridentate chelation.

anions are sandwiched between layers formed by [Cd(N-*hyden*)$_2$]$^{2+}$ moieties (Fig. 11). The C–H groups of the N-*hyden* ligands act as hydrogen bond donors to the *pic* oxygen atoms. The N–H group of the ligand showed hydrogen bonding interactions with the nitro oxygen atom of the *pic* anions (Table 3). The extensive hydrogen bonding network in complex **2** has been depicted in Fig. 12.

Similarly, complex **3** also showed a layered arrangement of cations and anions (Fig. 13). A network of C–H···O, N–H···O and O–H···O hydrogen bonds and π–π interactions have been displayed in Fig. 14. Note that neither π–π nor C–H···π interactions have been observed in either complex **1** or **2** because of the steric crowding from the *pic* nitro groups, which are not parallel stacked, but are disoriented.

It is observed from the literature that ligand coordination to a cadmium center depends not only upon the denticity of ligand, but also upon the participating counter anion or co-ligands under different reaction conditions [47]. For example, the saccharinate anion forces the tridentate N-*hyden* ligand to coordinate to the cadmium center in a bidentate mode [48], whilst the picrate and *p*-nitrobenzoate anions facilitate a tridentate coordination mode of the N-*hyden* ligand (Fig. 15).

4. Conclusions

Three new complexes of cadmium(II), [Cd(H$_2$O)$_6$](*pic*)$_2$·H$_2$O **1**, [Cd(N-*hyden*)$_2$](*pic*)$_2$ **2** and [Cd(N-*hyden*)$_2$](*pnb*)$_2$ **3**, where N-*hyden* = N-(hydroxyethyl)ethylenediamine, *pic* = picrate and *pnb* = *p*-nitrobenzoate, have been successfully synthesized and fully characterized by various physicochemical techniques. The vital role of the non-covalent intermolecular interactions on the stability of complexes **1**–**3** has been revealed by single crystal X-ray analysis. In complex **1**, six water molecules form an octahedral environment around Cd(II) ion, which is counter-balanced by two anionic *pic* moieties. In contrast, the presence of the tridentate N-*hyden* ligand in complexes **2** and **3** gives a distorted *trans*-octahedral arrangement around the Cd(II) metal center, resulting in the complex cation [Cd(N-*hyden*)$_2$]$^{2+}$ which is counter-balanced by two anions, namely, *pic* and *pnb* units respectively. The cationic [Cd(N-*hyden*)$_2$]$^{2+}$ moieties and anionic *pic* (**2**) and *pnb* (**3**) moieties are arranged in an alternate layered pattern in the crystal lattice, being stabilized by various hydrogen bonding interactions, such as C–H···O, N–H···O and O–H···O, etc. The present structural study suggests that the tridentate N-*hyden* ligand may find application to chelate the toxic cadmium(II) ion for its removal from water and living organisms.

Acknowledgments

The authors RPS and SK acknowledge the financial support from UGC, New Delhi (India) as a UGC Emeritus and BSR Meritorious Fellowship respectively. PV thanks the DST PURSE program of Panjab University, Chandigarh. Dr. P.K. Soni, TBRL, Chandigarh, India is also acknowledged for his help in the thermogravimetric analyses. TA is grateful to the Ratchadaphiseksomphot Endowment Fund, Chulalongkorn University (CU-58-021-FW).

Appendix A. Supplementary data

CCDC nos. 1562435, 1562436 and 1562437 contain the supplementary crystallographic data for complex **1**, **2** and **3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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