

Spectral and Geometrical Study of Two Cadmium Complexes, *mer-R,S*-[Cd(aepn)₂]X₂ (X: Γ, Cl⁻, aepn: *N*-(2-Aminoethyl)-1,3-propanediamine) Supported by Solution Experiments

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ABSTRACT. In this research, two new complexes of *N*-(2-aminoethyl)-1,3-propanediamine (aepn), [Cd(aepn)₂]₂ (**1**) and [Cd(aepn)₂]Cl₂·H₂O (**2**), were prepared and identified by elemental analysis, FT-IR, Raman spectroscopy and single-crystal X-ray diffraction. Geometry around the cadmium atom in two complexes by coordination of six nitrogen atoms of two aepn is distorted octahedral. If distortion in the *mer*-[Cd(aepn)₂]²⁺ cation is disregarded, it has a C₂ axis and C₂ symmetry. The cyclic voltammetry experiments were carried out to study the complexation process. Two structural surveys on coordination modes and complexes of aepn are presented. A study was carried out using CSD data to estimate the averages of bond lengths for different types of the Cd–N bonds. It was found that the intermolecular N–H···I, C–H···I hydrogen bonds in **1** and N–H···Cl, N–H···O, C–H···O, O–H···Cl in **2** stabilized the crystal networks.

Key words: Cadmium complex, Chiral center, Diastereomer, Cyclic voltammetry, X-ray crystal structure

INTRODUCTION

N-(2-Aminoethyl)-1,3-propanediamine (aepn) is a rather common tridentate amine ligand. It usually forms three coordination bonds with the same central atom^{1–2} and only rarely aepn adopts bridging function.³ Of particular interest from the coordination chemistry perspective of the asymmetrical aepn ligand is that six diastereomers are possible in complexation,⁴ facials and meridionals (*Table 1*). The meridional conformation has a nonsuperimposable mirror image shown in *Table 1*. Although the study of geometrical isomerism in octahedral complexes has been a subject of cutting-edge research, the facial and meridional isomerism has been given less attention mainly due to the difficulties in the syntheses of these compounds.⁵

In this work preparation of two cadmium complexes [Cd(aepn)₂]X₂ (X: Γ, Cl⁻) of aepn (*Scheme 1*) were presented. These complexes were characterized by elemental analysis, FT-IR, Raman spectroscopy and X-ray crystallography. Cyclic voltammetry experiments were carried out in order to study the complexation process in DMSO solution.

The coordination geometry of the cadmium atom and the nature of the ligands results in the coordination numbers of the cadmium atom in range of 2–10.⁶ In this paper, we endeavor to introduce new coordination aspects of the tridentate aepn with cadmium atom.

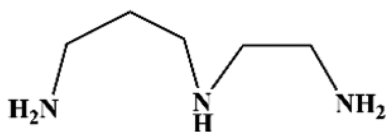
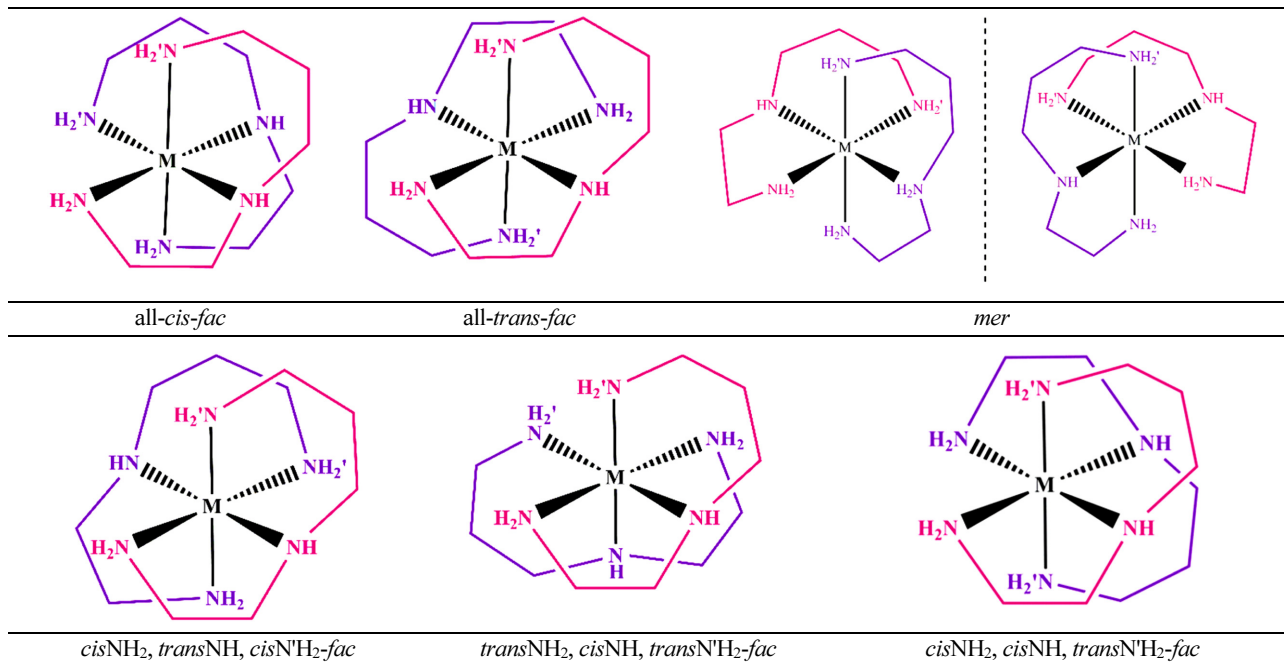
A Structural Survey on Complexes of aepn

Each tridentate ligand can be coordinated to metal in facial or meridional forms. In the *mer* form there are two 90° angles, one 180° but three 90° angles in *fac* form. Base on this principle, percentage of *mer* form in complexes of aepn is 91%. All complexes of aepn with *fac* form are including [Re(aepn)(CO)₃][PF₆],⁷ [Co(aepn)L][ClO₄] (L: (*S*)-aspartato-*O,O',N*),⁸ [Co(aepn)(py)₂Cl][ZnCl₄]⁹ and [Cd(aepn)(CN)₃].^{5,10} Only one complex of aepn, [Co(aepn)(CN)₃],⁵ with both *fac* and *mer* forms have been deposited in CSD (updated to Aug 2012).¹¹ In **1** and **2**, two angles of each aepn are deviating from 90° due to the chelating bite angle, while the third one is about 160°, to incline to the *mer* form.

EXPERIMENTAL

All chemicals and solvents were reagent or analytical grade and used as received. A conventional three-electrode system voltammetry was employed, with a PGSTAT101 and glassy carbon working electrode. The carbon, hydrogen, and nitrogen contents were determined in a Thermo Finnigan Flash Elemental Analyzer 1112 EA. The infrared spectra as KBr pellets were recorded in the range of 400–4000 cm⁻¹ using a FT-IR 8400-Shimadzu spectrometer. Raman spectra were obtained using a Nicolet Model 910 Fourier-transform spectrometer. The melting points

Table 1. Six possible diastereomers for coordination of two aepr in octahedral geometry. The meridional conformation has a nonsuperimposable mirror image



Scheme 1. The structure of aepr.

were determined using a Barnsted Electrothermal 9200 electrically heated apparatus.

Synthesis of [Cd(aepr)₂]₂ (1)

CdI₂ (1 mmol, 0.37 g) was dissolved in EtOH (15 mL) and added with stirring to a solution of L (2 mmol, 0.23 g) in EtOH (5 mL). After 3 h, a white precipitate was formed, filtered and recrystallized from DMF. Colorless crystals suitable for X-ray diffraction were obtained after several days. Yield: 0.46 g, 76%. m.p. 220 °C; Anal calcd for C₁₀H₃₀CdI₂N₆ (600.61): C, 20.00; H, 5.03; N, 13.99%. Found: C, 20.06; H, 4.98; N, 14.02%; IR (KBr): 3366 m (ν_{as} NH₂), 3248 s (ν_s NH₂), 3148 m (ν NH), 2924 and 2854 m (ν CH₂), 1581 m (δ NH₂), 1430 w (δ_{as} CH₂), 1389 w (δ_s CH₂), 1281 and 1149 m (ν CN), 478 w (ν CdN) cm⁻¹. Raman: 2870 m (ν CH₂), 1557 w (δ NH₂), 1405 s (δ_{as} CH₂), 1256 w and 1108 s (ν CN), 432 m (ν CdN) cm⁻¹.

Synthesis of [Cd(aepr)₂]₂Cl₂·H₂O (2)

The procedure for synthesis of 2 was similar to 1 except that CdI₂ was replaced by CdCl₂·2.5H₂O and DMF by

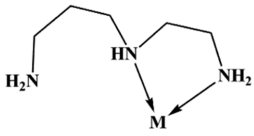
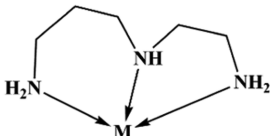
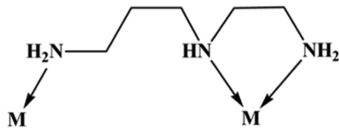
H₂O/EtOH (1:1). Yield: 0.34 g, 77%. m.p. 190 °C; Anal calcd for C₁₀H₃₂CdN₆Cl₂O (435.72); C, 27.57; H, 7.40; N, 19.29%. Found: C, 27.38; H, 6.99; N, 19.33%; IR (KBr): 3456 m (ν_{as} H₂O), 3382 m (ν_s H₂O and/or ν_{as} NH₂), 3279 s (ν_s NH₂), 3194 m (ν NH), 2922 and 2870 m (ν CH₂), 1597 m (δ NH₂ and/or δ H₂O), 1450 w (δ_{as} CH₂), 1389 w (δ_s CH₂), 1288 and 1149 m (ν CN), 633 m (ρ_r H₂O), 538 w (ρ_w H₂O), 501 w (ν CdN) cm⁻¹. Raman: 2947 w and 2825 m (ν CH₂), 1561 m (δ NH₂), 1391 s (δ_s CH₂), 1232 w and 1107 s (ν CN), 695 m (ρ_r H₂O), 557 m (ν CdN and/or ρ_w H₂O), 223 w (ρ_t H₂O) cm⁻¹.

Crystal Structure Determination and Refinement

Suitable crystals of **1** and **2** were placed on Xcalibur Eos Gemini Ultra and Oxford Gemini Ultra diffractometers, respectively, and kept at 150.0 K during data collection. Using OLEX-II,¹² the structures were solved with the SHELXS¹³ structure solution program using Direct Methods and refined with the SHELXL¹³ refinement package using least squares minimization.

Crystallographic data for the structures reported here have been deposited with CCDC (Deposition No. CCDC-913890 (**1**) and 913894 (**2**)). These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, E-mail: deposit@ccdc.cam.ac.uk.

Table 2. Different types of coordination modes of aepn collected by ConQuest.²⁸

Coordination modes of aepn			
			
Name	One-chelate form	Two-chelate form	Helicated form
Number of deposited structures	2	71	1
Coordinated metals	Co, ²⁹ Ni ²⁹	Cr, ¹⁴ Co, ¹⁵ Ni, ¹⁶ Cu, ¹⁷ Zn, ¹⁰ Cd, ² Re ⁷	Cd ³

RESULTS AND DISCUSSION

A study using CSD data showed that complexes of Cr,¹⁴ Co,¹⁵ Ni,¹⁶ Cu,¹⁷ Zn,¹⁰ Cd² and Re⁷ with aepn have been reported previously. All coordination modes of aepn are presented in Table 2. Among these modes, Two-chelate form which was observed in **1** and **2** is most frequent.

Reaction between aepn and ethanolic solution of cadmium(II) iodide and chloride in a molar ratio of 1:2 (M:L) give **1** and **2**, respectively. These complexes are air-stable and soluble in DMSO and DMF.

Spectroscopic Characterization

In the IR spectra of **1**, **2** and aepn, the bands above 3100 cm⁻¹ were assigned to vibrations of the ν_{as} (NH₂), ν_s (NH₂) and ν (NH).¹⁸ Also the NH₂ bending vibration appears near 1600 cm⁻¹ in these compounds. Presence of

the water molecule in **2** affects the IR and Raman spectra in the three regions including 3456 and 3382 cm⁻¹ respectively for asymmetric and symmetric OH stretches, 1597 cm⁻¹ for H₂O bending and 200–600 cm⁻¹ for “librational modes”. These modes are due to rotational oscillations of the water molecules restricted by interactions with neighboring atoms and they are classified into three types (wagging (ρ_w), twisting (ρ_t) and rocking (ρ_r)) depending upon the direction of the principal axis of rotation.¹⁹ In the IR and Raman spectra of **2**, vibrations such as ν_s (H₂O), δ (H₂O) and ρ_w (H₂O) overlapped with vibrations due to the ν_{as} (NH₂), δ (NH₂) and ν (CdN) respectively.

Information about the low-frequency vibrations of metal-ligand bonds can be obtained by Raman spectroscopy.²⁰ In the Raman spectrum of **1**, a band at 432 cm⁻¹ was assigned to the Cd–N stretching vibrations. In the Raman spectrum of **2**, similar band was observed at 557 cm⁻¹. These assign-

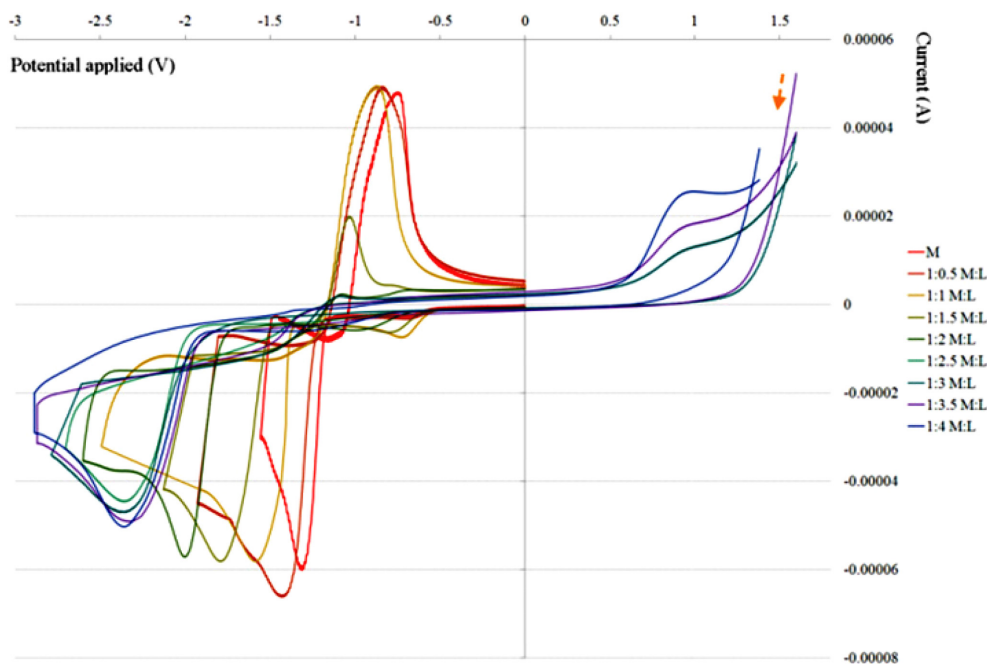


Figure 1. The current-potential curves of DMSO solution of 0.01 M Cd²⁺ containing 0.1 M TBAP in the absence and presence of increasing concentrations of aepn. After each addition, reaction mixture was stirred at 60 °C for 1 h.

ments are in consistent with values reported in the literature.⁴

Cyclic Voltammetry Experiments

The experiments of cyclic voltammetry were investigated in DMSO solution containing 0.10 M TBAP (tetrabutylammonium perchlorate) and 0.01 M reagents using Ag/AgCl as reference electrode at room temperature, in potentials range of +1.5 to -2.9 V with a scan rate of 50 mV s⁻¹ and starting voltage -2.9 V. The cyclic voltammogram of aepn shows an irreversible anodic wave near +0.9 V which can be attributed to the oxidation of the groups present in the aepn (Fig. 1).

The cyclic voltammogram of Cd²⁺ solution displays two reduction waves at the negative potential region, -1.309 V and -1.705 V which are corresponding to Cd(II)/Cd(I) and Cd(I)/Cd(0) process, respectively.²¹⁻²³ Addition to these waves, there is one oxidation wave at -0.746 V (Fig. 1) which appears with measuring in the opposite directions thus it is not corresponding to Cd(I)/Cd(II) process. Fig. 1 shows the current-potential curves of 0.01 M solutions of Cd²⁺ (using the cadmium chloride salt) either with or without

increasing concentrations of aepn. The waves corresponding to the Cd(I)/Cd(0) process were deleted for clarity. With increasing concentration of aepn, the cathodic wave is shifted slightly to more negative values, whereas that of the oxidation slightly is disappeared. These observations demonstrate that the electrochemical behavior of Cd²⁺ solution is strongly affected by aepn. The potentials shift, indicating the formation of a cadmium complex with aepn. The cathodic wave have no more shift upon the 2.5:1 (L:M) ratio which suggests that the cadmium ion and aepn reach a state of coordination equilibrium. Also one anodic wave near +0.9 V (Fig. 1) corresponding to the oxidation of the free aepn appears after this ratio and increases with accentuating of L:M ratio. These results demonstrate that maximum of eight coordination site of Cd²⁺ ion in DMSO solution can be occupied by 2.5 molecules of aepn.

The acid dissociation constants of the three amino groups of aepn and stability constants for this ligand with Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) have been previously reported.²⁴ As expected, the values of formation constant for 1:2 (M:L) complexes considerably are higher than those of 1:1 (M:L). In 1:1 (M:L) reaction condition which of the species,

Table 3. Crystal data and structure refinement for **1** and **2**.

	1	2
Empirical formula	C ₁₀ H ₃₀ CdI ₂ N ₆	C ₁₀ H ₃₂ CdCl ₂ N ₆ O
Formula weight (g mol ⁻¹)	600.61	435.72
Temperature (K)	150.0	150.0
Crystal system	Monoclinic	Monoclinic
Space group	<i>P2₁/c</i>	<i>P2₁/c</i>
Unit cell dimensions (Å, °)		
<i>a</i>	9.9722(5)	14.1054(6)
<i>b</i>	15.5603(9)	9.5134(4)
<i>c</i>	12.6360(5)	13.9766(6)
β	101.715(5)	101.871(4)
Volume (Å ³), <i>Z</i>	1919.89(17), 4	1835.43(13), 4
Calculated density (mg mm ⁻³)	2.071	1.577
Absorption coefficient (mm ⁻¹)	4.352	1.49
<i>F</i> (000)	1136	896
Crystal size (mm ³)	0.15 × 0.03 × 0.01	0.22 × 0.16 × 0.04
2 θ range for data collection (°)	6.38–58.74	5.96–58.84
<i>h</i> , <i>k</i> , <i>l</i> ranges	-13:7, -18:20, -15:17	-18:19, -11:12, -19:18
Reflections collected	7929	8910
Independent reflections	4292	4297
<i>R</i> _{int}	0.0658	0.0238
Data / restraints / parameters	4292 / 1 / 197	4297 / 0 / 184
Goodness-of-fit on <i>F</i> ²	1.050	1.053
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0424, <i>wR</i> ₂ = 0.0859	<i>R</i> ₁ = 0.0359, <i>wR</i> ₂ = 0.0888
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0617, <i>wR</i> ₂ = 0.1005	<i>R</i> ₁ = 0.0456, <i>wR</i> ₂ = 0.0976
Largest diff. peak and hole (e.Å ⁻³)	1.35 and -1.09	2.83 and -0.94

Table 4. Selected bond lengths (Å) and angles (°) for **1** and **2**

1		2	
Bond lengths (Å)			
Cd(1)–N(1)	2.356(5)	Cd(1)–N(1)	2.369(3)
Cd(1)–N(2)	2.410(6)	Cd(1)–N(2)	2.372(4)
Cd(1)–N(3)	2.346(5)	Cd(1)–N(3)	2.355(3)
Cd(1)–N(4)	2.355(5)	Cd(1)–N(4)	2.389(3)
Cd(1)–N(5)	2.401(6)	Cd(1)–N(5)	2.362(3)
Cd(1)–N(6)	2.361(5)	Cd(1)–N(6)	2.335(3)
Angles (°)			
N(1)–Cd(1)–N(2)	80.25(19)	N(1)–Cd(1)–N(2)	77.51(14)
N(1)–Cd(1)–N(4)	92.51(19)	N(1)–Cd(1)–N(4)	91.22(10)
N(1)–Cd(1)–N(5)	108.13(19)	N(1)–Cd(1)–N(5)	96.03(10)
N(1)–Cd(1)–N(6)	89.68(19)	N(1)–Cd(1)–N(6)	94.87(10)
N(5)–Cd(1)–N(6)	75.2(2)	N(5)–Cd(1)–N(6)	86.81(10)
N(5)–Cd(1)–N(4)	80.3(2)	N(5)–Cd(1)–N(4)	76.35(10)

[Cd(aepn)]²⁺ and/or [Cd(aepn)₂]²⁺, are formed in solution? The cyclic voltammetry experiments can answer to this question. The formation of [Cd(aepn)]²⁺ ion is confirmed, although [Cd(aepn)₂]²⁺ ion is more stable than [Cd(aepn)]²⁺, owing to the position of one reduction wave (Cd(II)/Cd(I)) in the curve of 1:1 (M:L) ratio as illustrated in Fig. 1. The crystal structure of 1:1 (M:L) ratio, [Cd₂(aepn)₂Cl₄], has been reported previously.²

Table 5. Dimensions of the hydrogen bonds (Å and °) in **1** and **2**

	D–H...A	d(D–H)	d(H...A)	<(DHA)	d(D...A)	Symmetry code on A atom
1	N(1)–H(1A)···I(2)	0.900	2.8885	161.3	3.752(5)	1 – x, 1 – y, 1 – z
	N(1)–H(1B)···I(2)	0.900	3.0507	157.2	3.896(6)	x, y, z
	N(3)–H(3AA)···I(1)	0.899	2.8982	148.2	3.693(6)	x, 0.5 – y, 0.5 + z
	N(3)–H(3AB)···I(1)	0.899	3.0199	131.9	3.681(5)	2 – x, 0.5 + y, 1.5 – z
	N(5)–H(5)···I(1)	0.911	3.0321	156.6	3.885(5)	2 – x, 0.5 + y, 1.5 – z
	N(6)–H(6A)···I(1)	0.900	2.8984	163.4	3.770(5)	x, 0.5 – y, 0.5 + z
	N(6)–H(6B)···I(2)	0.900	2.8278	161.8	3.693(5)	x, y, z
	C(3)–H(3A)···I(2)	0.969	3.1505	173.9	4.115(8)	1 – x, 0.5 + y, 1.5 – z
2	N(1)–H(1A)···Cl(1)	0.900	2.6206	159.4	3.477(3)	–1 + x, 0.5 – y, –0.5 + z
	N(1)–H(1B)···Cl(2)	0.900	2.4777	162.7	3.348(3)	1 – x, –0.5 + y, 1.5 – z
	N(2)–H(2)···Cl(2)	0.910	2.5121	154.8	3.357(3)	1 – x, 1 – y, 1 – z
	N(3)–H(3A)···Cl(1)	0.900	2.5050	171.6	3.398(3)	x, y, z
	N(4)–H(4A)···Cl(1)	0.900	2.5733	154.9	3.410(3)	x, y, z
	N(4)–H(4B)···Cl(2)	0.900	2.5051	168.7	3.392(3)	1 – x, –0.5 + y, 1.5 – z
	N(5)–H(5)···Cl(1)	0.909	2.5056	173.0	3.410(3)	1 – x, –y, 1 – z
	N(6)–H(6A)···Cl(2)	0.900	2.6809	164.3	3.556(3)	1 – x, 1 – y, 1 – z
	N(3)–H(3B)···O(1)	0.900	2.430	142.7	3.193(5)	1 – x, –0.5 + y, 0.5 – z
	N(6)–H(6B)···O(1)	0.899	2.159	167.3	3.043(4)	1 – x, –0.5 + y, 0.5 – z
	O(1)–H(1E)···Cl(1)	0.850	2.430	161.7	3.248(4)	1 – x, 1 – y, 1 – z
	O(1)–H(1F)···Cl(1)	0.849	2.3801	153.97	3.165(4)	x, 0.5 – y, –0.5 + z
	C(3)–H(3C)···O(1)	0.971	2.685	121.0	3.293(8)	1 – x, 1 – y, 1 – z

Description of the Crystal Structures

The diagrams of the molecular structures and unit cells were created using ORTEP-III²⁵ and Diamond (*version 3.2g*)²⁶ softwares. Table 3 contains crystallographic data and details of the data collection and structure refinement.

Selected bond lengths (Å) and angles (°) and dimensions of the hydrogen bonds (Å and °) for complexes are listed in Tables 4 and 5, respectively.

In the crystal structure of **1** and **2** (Fig. 2), cadmium atom with coordination number six has a distorted octahedral geometry. Four sites of this geometry are occupied by nitrogen atoms of the NH₂ groups with the Cd–N bond lengths in the range of 2.346(5)–2.361(6) and 2.335(3)–2.389(3) Å for **1** and **2**, respectively. The two other sites are occupied by nitrogen atoms of the NH groups with the Cd–N bond lengths in the range of 2.401(6)–2.410(6) and 2.363(3)–2.373(3) Å for **1** and **2**, respectively. To estimate the bond lengths averages for different types of the Cd–N bond a study was carried out using CSD data and the results are listed in Table 6. Based on this study, the Cd–N_{imine} distance is shorter than the other types of the Cd–N bonds while the Cd–NR₃ distance is among the longest. Similar results were also observed in **1** and **2** for distances average.

Two aepn in **1** and **2**, which act as tridentate forming two

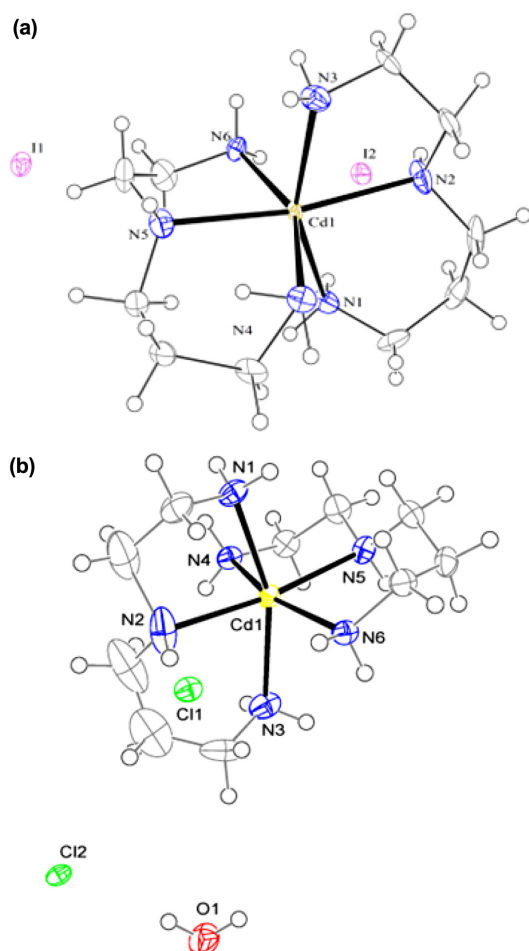
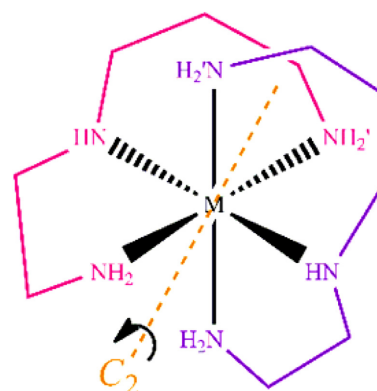


Figure 2. The ORTEP-III diagrams of the molecular structure of **1** (a) and **2** (b). The ellipsoid is drawn at the 40% probability level.

five- and two six-membered chelate rings with the cadmium atom and neither are planar. The dihedral angle between the two N1/N2/N3/Cd1 and N4/N5/N6/Cd1 plans in **1** and **2** is 89.65° and 89.55° , respectively that confirm the *mer* form. *mer*-[Cd(aepn)₂]²⁺ has a nonsuperimposable mirror image (Table 1) which is observed in the crystal structure of **1** and **2**. If the distortion in the [Cd(aepn)₂]²⁺ cation is disregarded, it has a C₂ axis and C₂ symmetry (Scheme 2) and must be optically active but the unit cells of **1** and **2** contain racemic mixture and are non-optically active. The



Scheme 2. Showing C₂ symmetry in complexes of **1** and **2**.

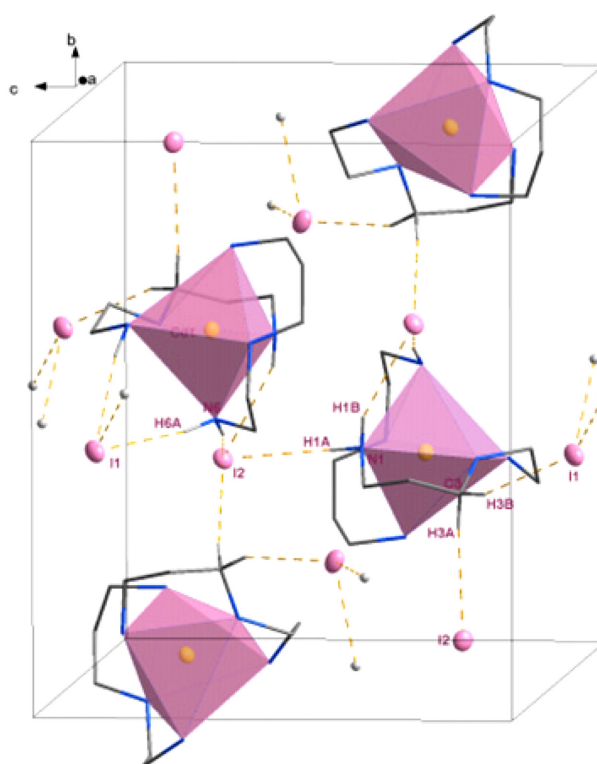


Figure 3. Packing of **1**, showing the hydrogen bonds. Only the hydrogen atoms involved in hydrogen bonding are shown. Each CdN₆ unit is shown as an octahedron.

aepn has no chiral center but two new ones (N2, N5) are formed after coordination²⁷ with different enantiomeric

Table 6. Bond distances for different types of the Cd–N bonds. The term “py-b” refers to all pyridine-based compounds and “R” refers to each carbon atom which can be connected to any atoms with single, double or triple bonds

Type						
Cd–N distance (Å)	2.307	2.326	2.341	2.354	2.376	2.457

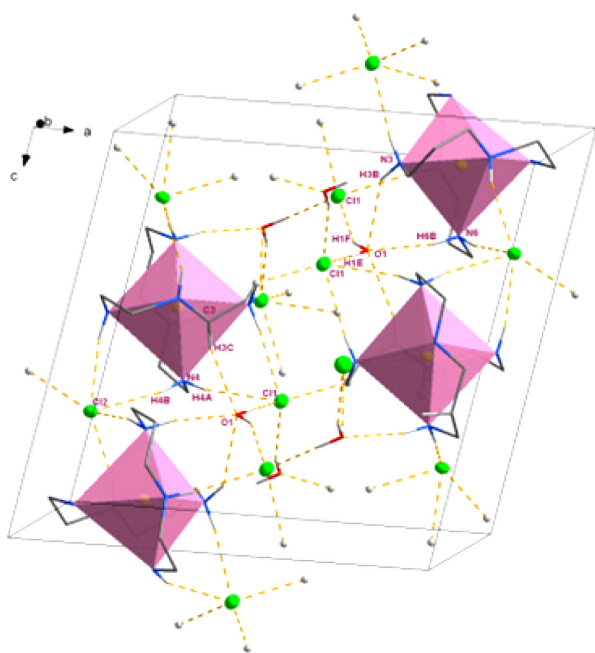


Figure 4. Packing of **2**, showing the hydrogen bonds. Only the hydrogen atoms involved in hydrogen bonding are shown. Each CdN₆ unit is shown as an octahedron.

forms.

In the crystal network of **1** (Fig. 3), there are intermolecular N–H⋯I and C–H⋯I hydrogen bonds (Table 5). In hydrogen bonding, the iodide atoms act as proton acceptors whereas the carbon and nitrogen atoms participate as proton donors. Also the hydrogen bonds including N–H⋯Cl, N–H⋯O, C–H⋯O and O–H⋯Cl stabilized the crystal network of **2** (Fig. 4).

CONCLUSION

Two new complexes, [Cd(aepn)₂]₂ and [Cd(aepn)₂]Cl₂·H₂O, were synthesized in reaction between cadmium(II) iodide and chloride with aepn, *N*-(2-aminoethyl)-1,3-propanediamine, respectively. For these complexes spectral (IR, Raman), electrochemical and structural properties were investigated. Cadmium atom in two complexes has a distorted octahedral geometry by coordination of six nitrogen atoms of two aepn. The complexes have meridional conformation and C₂ symmetry and must be optically active but the unit cells of **1** and **2** contain a racemic mixture and are non-optically active. The aepn has no chiral center but two new ones (N2, N5) are formed after coordination with different enantiomeric forms. A survey on complexes of aepn showed that this ligand has three coordination modes

including One-chelate, Two-chelate and Helicate forms. Among these modes, the Two-chelate mode which was observed in **1** and **2** is most frequent. A study of CSD data showed that the Cd–N_{imine} and Cd–NR₃ distances respectively are shorter and longer than the other types of Cd–N bonds. Similar results were observed in **1** and **2**. The intermolecular N–H⋯I, C–H⋯I hydrogen bonds in **1** and N–H⋯Cl, N–H⋯O, C–H⋯O, O–H⋯Cl in **2** stabilized the crystal network of these complexes.

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