Coordination geometries and crystal structures of cadmium(II) complexes with a new amino alcohol (NN′O) ligand

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Coordination geometries and crystal structures of cadmium(II) complexes with a new amino alcohol (NN′O) ligand

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The new ligand 2-(2-(2-hydroxyethylamino)ethylamino)cyclohexanol, (HEAC), was prepared under microwave conditions through ring opening of cyclohexene oxide with 2-(2-amino-ethylamino)ethanol. Its cadmium(II) complexes $[Cd_2(HEAC)_2(\mu\text{-}Cl)_2Cl_2]$ (**1**) and $[Cd(HEAC)_2][CdI_4]$ (**2**) were identified by elemental analysis, FT-IR, Raman, ^{1}H NMR spectroscopies, and single-crystal X-ray diffraction. HEAC formed 1:1 M:L complexes with cadmium chloride and cadmium iodide. Complex **1** crystallized as a dimer with two asymmetrically bound bridging Cl$^-$ and a terminally coordinated Cl$^-$ on each metal. The geometry around the cadmiums in **1** with four five-membered chelate rings and four Cl$^-$ ligands is distorted octahedral for each Cd(II). The cyclohexanol OH of each ligand forms intramolecular hydrogen bonds. In **2**, the coordination numbers for cadmium in $[Cd(HEAC)_2]^{2+}$ and $[CdI_4]^{2-}$ moieties are six and four, respectively. In $[Cd(HEAC)_2]^{2+}$ each ligand coordinates through two N- and one O-donors, leading to a distorted octahedral geometry. The geometry of $[CdI_4]^{2-}$ in **2** is slightly distorted tetrahedral. The protonation equilibrium constants of the two secondary amino groups in HEAC, determined by pH-potentiometry, were 6.26 and 9.26, respectively, at 25°C. Stability constants for this ligand with Ni(II), Cu(II), and Zn(II) (1:1 M:L), determined by glass-electrode potentiometry, were 7.13, 10.50, and 5.42, respectively.

Keywords: Amino alcohol; Cadmium; X-ray structure; Dimer; Stability constant

1. Introduction

β-Amino alcohols are important sub-units commonly found in natural products, biologically active molecules, ligands, and chiral auxiliaries [1–4] and play important roles controlling a range of asymmetric transformations by forming five-membered metal chelates. This can occur through both amino and hydroxyl groups [5].

Our research interests lie in the study of d^{10} metal ion complexes [6–12]. In this study, a new amino alcohol, 2-(2-(2-hydroxyethylamino)ethylamino)cyclohexanol (HEAC) (scheme 1), was synthesized through ring opening of cyclohexene oxide with 2-(2-amino-ethylamino)ethanol. This ligand, potentially tetradentate asymmetric ligand

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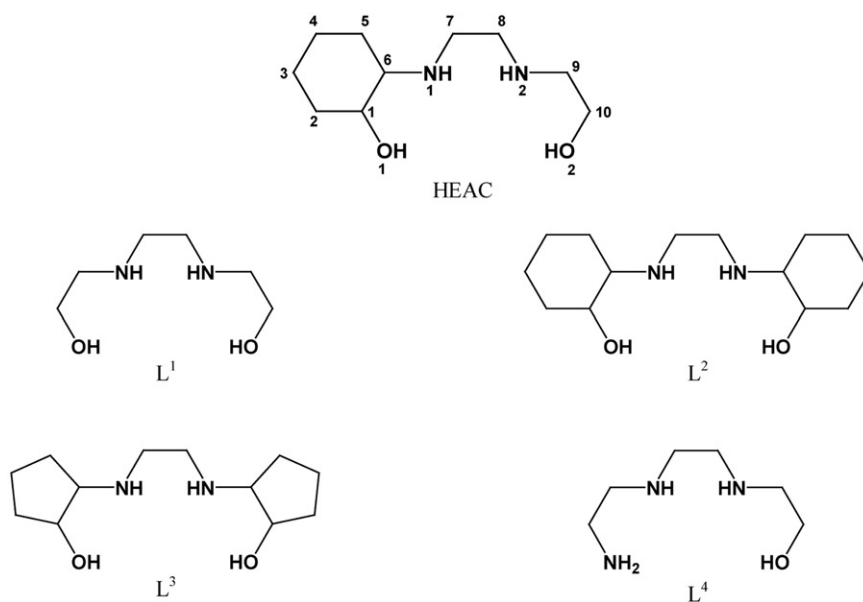
Scheme 1.   The HEAC ligand and its analogs.

which also contains an aliphatic cyclohexane ring, provides different types of donors, two aliphatic secondary amines and two hydroxyl groups.

In this work, cadmium chloride $[Cd_2(HEAC)_2(\mu\text{-}Cl)_2Cl_2]$ (**1**) and cadmium iodide $[Cd(HEAC)_2][CdI_4]$ (**2**) with different coordination geometries were synthesized and their spectroscopic characteristics (IR, ^1H NMR, and Raman) and crystal structures determined. A search of the CSD for cadmium structures forming 1 : 2 M : L complexes with NN′O chelate donor aliphatic ligands reveals that the coordination in **2** is unique.

Protonation equilibria of the ligand and its metal ion selectivity were obtained for Ni(II), Cu(II), and Zn(II) by pH-potentiometry. Selectivity is defined as the difference in $\log K$ for the ligand with the metal ion of interest relative to that for a competing metal ion, where $\log K$ is the formation constant [13].

2. Experimental

2.1. *Instrumentation and reagents*

The microwave-assisted synthesis of HEAC was carried out using a Microwave Laboratory Systems MicroSYNTH, Milestone s.r.l. Mass spectra were recorded with a VG 70-S Micromass spectrometer operating at 70 eV. Elemental analyses of carbon, hydrogen, and nitrogen in each sample were determined with a Thermo Finnigan Flash Elemental Analyzer 1112 EA. Infrared spectra of samples were carried out with KBr pellets from 4000 to $400\,cm^{-1}$ using an FT-IR 8400-Shimadzu spectrometer. Raman spectra were obtained using a Nicolet Model 910 Fourier-transform spectrometer.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Aspect 3000 instrument operating at 300 MHz; chemical shifts are given in parts per million, with values referenced to a TMS internal standard. Melting points were determined using a Barnsted Electrothermal 9200 electrically heated apparatus. The absorption spectra were recorded in DMF using a Shimadzu model 2550 UV-Vis spectrophotometer (190–900 nm). The protonation equilibria of HEAC were determined by pH-potentiometry, using a stirred and temperature-controlled glass cell fitted with a pH electrode, and an autotitrator, all under computer control. In-house software was employed for data analysis of the formation constants. All starting chemicals and solvents were of reagent or analytical reagent grade and used as received.

2.2. Syntheses

2.2.1. Synthesis of HEAC. A mixture of 0.29 g (3 mmol) of cyclohexene oxide and 0.31 g (3 mmol) 2-(2-amino-ethylamino)ethanol was reacted in a microwave reactor (MicroSYNTH Milestone s.r.l.) for 30 min at 550 W under solvent free conditions. The mixture was then recrystallized from boiling ethyl acetate to yield a white crystalline solid. Yield (0.30 g) 50%; m.p. 132°C. Anal. Calcd for $C_{10}H_{22}N_2O_2$ (%): C, 59.37; H, 10.96; N, 13.85. Found: C, 59.51; H, 10.82; N, 13.75. IR (cm^{-1}, KBr): 3267 s (ν OH), 3097 m (ν NH), 2930 s (ν CH), 2824 s (ν CH$_2$), 1449 w (δ_{as} CH$_2$), 1348 m (δ_s CH$_2$), 1230 w (νCO), 1124 s (ν C^{6}N), 1077 s (ν C^{7}N). Raman (cm^{-1}): 1451 s (δ_{as} CH$_2$), 1234 s (ν CO), 1125 w (ν C^{6}N), 1080 s (ν C^{7}N). UV-Vis (H$_2$O, λ_{max} (nm)): 300. MS (70 eV): m/z 41, 43, 61, 70, 85, 98, 114, 130, 154, 184, 202. ^{1}H NMR (300 MHz, DMSO): 4.82 (1H, O^{1}H), 4.78 (1H, O^{2}H), 2.11 (2H, N^{1}H, N^{2}H), 3.6 (2H, C^{10}H$_2$), 3.3 (1H, C^{1}H), 2.7 (6H, C^{7}H$_2$, C^{8}H$_2$, & C^{9}H$_2$), 2.4 (1H, C^{6}H), 2.0 (2H, C^{2}H$_2$), 1.7 (2H, C^{5}H$_2$), 1–1.2 (4H, C^{4}H$_2$, and C^{3}H$_2$). ^{13}C NMR (dept 135, 300 MHz, DMSO): $\delta = 72.8$ (C^1), 61.4 (C^6), 60.1 (C^{10}), 49.8 (C^9), 47.7 (C^7), 44.6 (C^8), 33.5 (C^2), 28.9 (C^5), 24.0 (C^3), 23.7 (C^4).

2.2.2. Synthesis of [Cd$_2$(HEAC)$_2$(μ-Cl)$_2$Cl$_2$] (1). A solution of 0.20 g (1 mmol) of HEAC, dissolved in methanol (15 mL), was added to a stirring solution of 0.23 g (1 mmol) of CdCl$_2$ · 2.5H$_2$O in the same solvent (25 mL). The reaction mixture was then stirred at 60°C for 6 h. Colorless crystals suitable for X-ray diffraction studies were obtained by slow evaporation of the solution and collected by filtration. Yield (0.27 g) 68%; m.p. 222°C. Anal. Calcd for $C_{20}H_{44}Cd_2Cl_4N_4O_4$ (%): C, 31.15; H, 5.75; N, 7.26. Found: C, 30.93; H, 5.70; N, 7.11. IR (cm^{-1}, KBr): 3355 s (ν OH), 3224 s (ν NH), 2931 s (ν CH), 2862 m (ν CH$_2$), 1450 w (δ_{as} CH$_2$), 1380 m (δ_s CH$_2$), 1200 w (ν CO), 1110 m (ν C^{6}N), 1056 m (ν C^{7}N). Raman (cm^{-1}): 2979 w (ν CH), 2869 w (ν CH$_2$), 1308 m (ν CO), 1130 m (ν CN), 550 m (ν CdN), 415 w (ν CdO), 311 w (ν CdCl$_{terminal}$), 249 w (ν CdCl$_{bridging}$). ^{1}H NMR (300 MHz, DMSO): 6.5 (1H, O^{1}H), 4.8 (1H, O^{2}H), 3.5 (2H, N^{1}H, N^{2}H), 2.8–2.9 (7H, C^{6}H, C^{7}H$_2$, C^{8}H$_2$, & C^{9}H$_2$), 1.9–2.0 (3H, C^{1}H, C^{10}H$_2$), 1.6 (2H, C^{2}H$_2$), 1.1 (6H, C^{3}H$_2$, C^{4}H$_2$, and C^{5}H$_2$).

2.2.3. Synthesis of [Cd(HEAC)$_2$][CdI$_4$] (2). A solution of 0.20 g (1 mmol) of HEAC dissolved in ethanol (15 mL) was added to a stirred solution of 0.33 g (1 mmol) of CdI$_2$ in the same solvent (25 mL). The reaction mixture was then stirred at 60°C for 6 h. The white precipitate was collected and washed with dichloroethane. The product was

dissolved in a mixture of ethanol-water (1 : 1, 10 mL) and colorless crystals of the complex suitable for X-ray studies were obtained by slow evaporation. Yield (0.35 g) 71%; m.p. 219°C. Anal. Calcd for $C_{20}H_{44}Cd_2I_4N_4O_4$ (%): C, 21.13; H, 3.90; N, 4.93. Found: C, 21.54; H, 3.84; N, 4.64. IR (cm^{-1}, KBr): 3417 s (ν OH), 3232 m (ν NH), 2931 s (ν CH), 2862 m (ν CH$_2$), 1450 m (δ_{as} CH$_2$), 1357 w (δ_s CH$_2$), 1204 w (ν CO), 1095 m (ν C^{6}N), 1056 m (ν C^{7}N). Raman (cm^{-1}): 1281 w (ν CO), 1153 w (ν CN), 585 w (ν CdN), 491 w (ν CdO), 155 w (ν CdI). ^{1}H NMR (300 MHz, DMSO): 6.6 (1H, O^{1}H), 5.0 (1H, O^{2}H), 3.5 (2H, N^{1}H, N^{2}H), 2.9 (4H, C^{7}H, C^{8}H$_2$), 2.6 (3H, C^{6}H, C^{9}H$_2$), 1.9 (3H, C^{1}H, C^{10}H$_2$), 1.6 (2H, C^{2}H$_2$), 1.1 (6H, C^{3}H$_2$, C^{4}H$_2$, and C^{5}H$_2$).

2.3. *Crystal structure determinations*

Intensity data were collected on a Bruker APEX II CCD area detector diffractometer with graphite-monochromated Mo-Kα radiation (50 kV, 30 mA) using the APEX2 [14] data collection software. The collection method involved ω-scans of width 0.5° and 512 × 512 bit data frames. Data reduction was carried out using SAINT + [15] and face indexed absorption corrections made using XPREP [15]. The crystal structures were solved by direct methods using SHELXTL [16]. Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full-matrix least-squares calculations based on F^2 using SHELXTL. Hydrogen atoms were first located in the difference map then positioned geometrically and allowed to ride on their respective parent atoms. HEAC in the structure of **2** were disordered, and as a consequence, we refined with equal occupancies over two positions using a combination of SIMU, DELU, and SAME constraints. Diagrams and publication material were generated using SHELXTL, PLATON [17], ORTEP-3 [18], and Mercury (Version 2.3) [19]. Crystallographic data and details of the data collection and structure refinement are listed in table 1. Selected bond lengths (Å) and angles (°) are listed in table 2.

3. Results and discussion

3.1. *Synthesis and spectroscopic characterization*

HEAC was synthesized by the reaction of 2-(2-aminoethylamino)ethanol with cyclohexene oxide. Reactions between HEAC and an ethanolic solution of cadmium(II) chloride or cadmium(II) iodide in a 1 : 1 molar ratio yielded colorless crystals of **1** and **2**, respectively (scheme 2). The complexes are air-stable and soluble in DMF and DMSO. IR and Raman spectral assignments for the ligand and the complexes are listed in section 2. The frequencies of the IR bands for the free ligand are different from those of the corresponding complexes, providing indications of bonding sites of HEAC. The ν(O–H) in IR spectra of **1** and **2** shifted 88 and 150 cm^{-1}, respectively, to higher frequency compared to the free ligand. The shift of ν(N–H) was similar to ν(O–H) (127 and 135 cm^{-1} in **1** and **2**, respectively). The ν(C–N) and ν(C–O) of free ligand were shifted to lower energy after coordination, indicating coordination through nitrogen and oxygen.

Information about metal-ligand vibration frequencies can be obtained by Raman spectroscopy. The Cd–I stretching vibration was assigned to a band at 155 cm^{-1},

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

	1	**2**
Empirical formula	$C_{20}H_{44}Cd_2Cl_4N_4O_4$	$C_{20}H_{40}Cd_2I_4N_4O_4$
Formula weight (g mol^{-1})	771.19	1132.96
Temperature (K)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
Space group	*C2/c*	*Pbca*
Unit cell dimensions (Å, °)		
a	15.2783(7)	15.5796(12)
b	15.3805(7)	15.4470(11)
c	12.9264(5)	27.790(2)
β	95.821(2)	90
Volume (Å^3), Z	3021.9(2), 4	6687.9(9), 8
Calculated density (Mg m^{-3})	1.695	2.250
Absorption coefficient (mm^{-1})	1.792	4.993
$F(000)$	1552	4224
Crystal size (mm^3)	$0.41 \times 0.08 \times 0.05$	$0.36 \times 0.21 \times 0.12$
θ range for data collection (°)	1.88–28.00	1.47–26.00
Limiting indices	$-20 \leq h \leq 12$;	$-19 \leq h \leq 11$;
	$-20 \leq k \leq 20$;	$-12 \leq k \leq 19$;
	$-17 \leq l \leq 16$	$-34 \leq l \leq 27$
Reflections collected	15,560	18,182
Independent reflections	3647 [$R(\text{int}) = 0.0603$]	6412 [$R(\text{int}) = 0.0320$]
Completeness to θ (°)	28.00	26.00
Absorption correction	Integration	Integration
Max. and min. transmission	0.9157 and 0.5270	0.5856 and 0.2665
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3647/3/164	6412/238/483
Goodness-of-fit on F^2	0.890	1.014
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0280$, $wR_2 = 0.0409$	$R_1 = 0.0357$, $wR_2 = 0.0715$
R indices (all data)	$R_1 = 0.0462$, $wR_2 = 0.0442$	$R_1 = 0.0593$, $wR_2 = 0.0772$
Largest difference peak and hole (e Å^{-3})	0.526 and -0.558	1.204 and -1.662

consistent with values reported in the literature (100–200 cm^{-1}) for CdI_2 [20]. The bridging Cd–Cl stretching frequency appeared around 250 cm^{-1}, which was lower than the terminal Cd–Cl stretching frequency observed at 311 cm^{-1}.

Numbering used for the ^{1}H NMR and ^{13}C NMR spectra of the free ligand is given in scheme 1. In HEAC, signals at 4.82, 4.78, and 2.11 ppm, which were absent in the presence of D_2O, were assigned to the O^1H, O^2H, and NH (including N^1H and N^2H) protons, respectively. After coordination, O^1H signal shifts by 1.73 ppm (in **1**) and 1.84 ppm (in **2**) to lower magnetic field than the free ligand. Similar shifts were observed for N^1H and N^2H signals (1.45 ppm) in both complexes. The very small shift of O^2H indicates that this oxygen does not participate in coordination.

The logarithms of the protonation constants for HEAC and formation constants of the ligand with various metal ions were compared to L^1, L^2, L^3, and L^4 in table 3 (included in scheme 1) [21]. The protonation constants for HEAC and L^1 were similar as expected. Two protonation constants, pK_1 9.29 and pK_2 6.65, were identified by potentiometric titration of HEAC, due to proton addition to the secondary amines. The formation constants of 1:1 and 1:2 (M:L) complexes were determined for Ni(II), Cu(II), and Zn(II) *via* titration of acidic solution of metal salts and HEAC with base. The HEAC and similar ligands including L^1, L^2, and L^3 (table 3) show higher tendency

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

1		2	
Cd(1)–N(1)	2.345(2)	Cd(2)–I(1)	2.8099(6)
Cd(1)–N(2)	2.337(2)	Cd(2)–I(2)	2.7790(7)
Cd(1)–O(1)	2.3776(18)	Cd(2)–I(3)	2.7898(7)
Cd(1)#1–Cl(1)	2.5134(7)	Cd(2)–I(4)	2.7591(7)
Cd(1)–Cl(1)	2.8186(6)	Cd(1)–N(1)	2.345(13)
Cd(1)–Cl(2)	2.5748(7)	Cd(1)–N(2)	2.370(15)
		Cd(1)–O(1)	2.540(4)
N(2)–Cd(1)–N(1)	77.04(7)	I(2)–Cd(2)–I(1)	115.44(2)
N(2)–Cd(1)–O(1)	147.48(7)	I(3)–Cd(2)–I(1)	102.11(2)
O(1)–Cd(1)–Cl(1)#1	94.97(5)	I(4)–Cd(2)–I(3)	116.61(2)
N(2)–Cd(1)–Cl(2)	92.85(5)	N(2)–Cd(1)–N(1)	72.8(4)
Cl(1)#1–Cd(1)–Cl(1)	84.25(2)	N(2)–Cd(1)–N(4)	127.4(8)
Cd(1)#1–Cl(1)–Cd(1)	95.75(2)	N(1)–Cd(1)–O(1)	68.6(3)
		N(1)–Cd(1)–O(3)	82.9
		O(3)–Cd(1)–O(1)	94.4(3)

Symmetry transformations used to generate equivalent atoms: #1: $-x, -y+1, -z+1$.
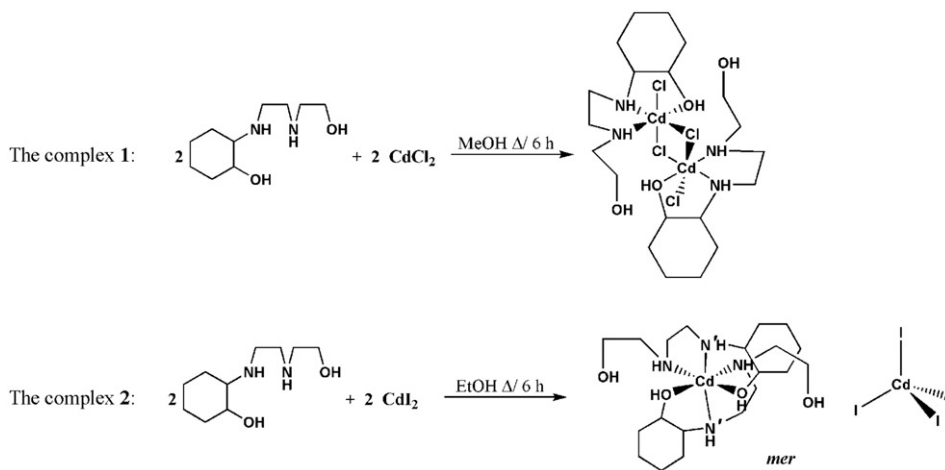
Scheme 2. Synthesis of **1** and **2**.

Table 3. Hydrogen-bond and H···H interaction geometries (Å and °) in **1** and **2**.

M	Complex	log K				
		HEAC	L^1	L^2	L^3	L^4
H$^+$	H + L ↔ HL	9.26	9.24	9.75	–	–
	H + HL ↔ H$_2$L	6.26	6.26	9.07	–	–
	H + H$_2$L ↔ H$_3$L	–	–	6.58	–	–
Ni^{2+}	M + L ↔ ML	7.13	6.67	14.0	7.75	3.70
	M + L$_2$ ↔ ML$_2$	10.53	10.9	–	–	–
Cu^{2+}	M + L ↔ ML	10.50	9.68	20.06	11.29	6.75
	M + L$_2$ ↔ ML$_2$	14.15	15.6	–	–	–
Zn^{2+}	M + L ↔ ML	5.42	4.79	11.95	–	–
	M + L$_2$ ↔ ML$_2$	–	9.1	–	–	–

to coordinate with Cu(II) compared to Ni(II) and Zn(II). This trend in selectivity, Cu(II) > Ni(II) > Zn(II), is consistent with the Irving–Williams series. The nature of metal–donor interaction in amino alcohol complexes is not only dependent on the Lewis acidity of the metal center and the nucleophilicity of the donor atom, but influenced by the morphology of the ligand. For example, if an ethylene bridge between two donors in L^1 or two cyclohexyl bridges in HEAC and L^2 is replaced by a cyclohexyl bridge, the selectivity of the ligand remains unchanged, but the formation constant for each increases. However, the formation constants for each metal ion decrease when the ethylene bridge is replaced with a cyclopentyl bridge as in L^3. Replacement of the donors has a major effect on formation constants as reported for L^4 in table 3.

3.2. *Description of the structures of the complexes*

X-ray single-crystal structures were obtained for **1** and **2**. The ORTEP diagrams of **1** and **2** are shown in figure 1. HEAC shows a tendency to form 1 : 1 M : L complexes with cadmium chloride and iodide, previously observed with a similar ligand (bis(2-hydroxyethyl)ethane-1,2-diamine) [22]. The crystal structure for **1** reveals the presence of a dimer with four five-membered chelate rings and four Cl^- ligands providing a distorted octahedral geometry around each Cd(II). There are terminal and asymmetrically-bound bridging Cl^- ligands in the structure of **1**. All Cl^- ligands and cadmiums are co-planar (r.m.s. deviation 0.043 Å for Cd1). Cd–Cl bond lengths of the bridging Cl^- and difference between the bond lengths in the structure of **1** are similar to those in reported complexes of the type $Cd_2(L)_2(\mu\text{-Cl})_2Cl_2]$, where L is an "NN′O-donor" as indicated by a search of the February 2012 edition of the CSD [23]. The results of the search are given in table 4. However, the Cd–Cl bond length with the terminal Cl^- is longer than the average found in analogous structures deposited in the CSD (2.49(7) Å). The hydroxyl of the cyclohexyl ring is coordinated to cadmium ion while the other hydroxyl is clearly not. Complex **1** has a center of inversion near the center of Cl2/Cd1/Cl1/Cd1/Cl1/Cl2 plane and C_i symmetry. In **1**, the molecules are stabilized *via* O–H⋯O, O–H⋯Cl, and N–H⋯Cl hydrogen bonds (table 5 and figure 2). Comparing these hydrogen-bond lengths with the values reported [24] reveal that the O(1)–H(1H)⋯O(2) intramolecular hydrogen bond is strong while the intermolecular hydrogen bonds are relatively weak. The O(2)–H(2H)⋯Cl(2) hydrogen bonds form a hydrogen bonded chain down the *c*-axis (figure 2), while the other hydrogen bonds lead to a 3-D network.

Single-crystal X-ray analysis of **2** reveals two cadmiums in the structure with different coordination numbers, six for Cd1 and four for Cd2 (figure 1b). Cd1 is coordinated to four nitrogen atoms and two oxygen atoms of two HEAC forming four five-membered chelate rings. Bond angles listed in table 2 show that geometry around Cd1 is distorted octahedral. Of particular interest from the coordination chemistry perspective is that several diastereomers are possible in complexation of the asymmetrical HEAC. Six possible arrangements of the pair of ligands around the octahedral metal ion exist (scheme 3) for octahedral coordination of two HEAC ligands as tridentate chelates. The mean planes through the metal and the chelate rings of each ligand are 84.37°, confirming *mer* diastereomer for **2**. Geometry around Cd2 with four I^- ligands have bond angles in the range 102.11(2)–116.61(2)°, indicating a slightly
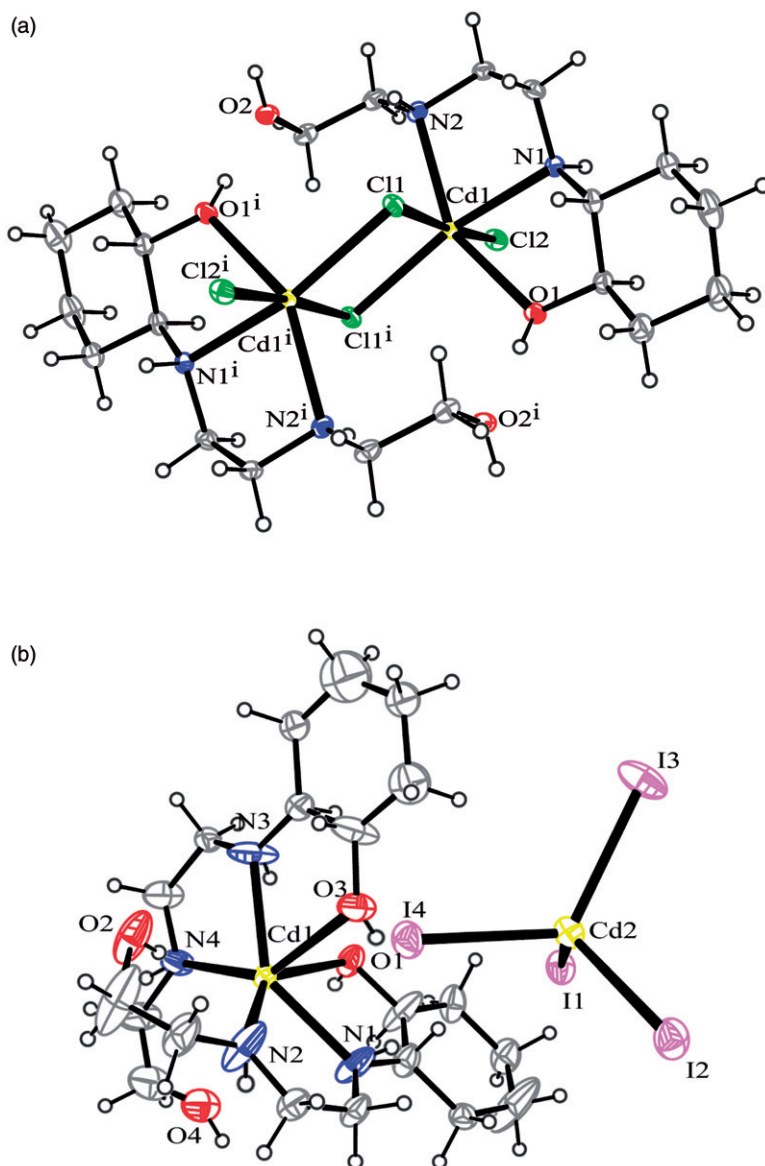
Figure 1. ORTEP diagrams for molecular structures of **1** (a) and **2** (b). The analog atoms in dicadmium complex **1** are indicated with superscript "i" in the atom labels, which is not implied to C and H for clarity of the image. The ligand in **2** is conformationally disordered over two positions. For the purpose of clarity, only one is shown here. Ellipsoids are drawn at the 30% probability level.

distorted tetrahedron. The CdI_4^{2-} has four interactions with adjacent molecules and is a hydrogen-bond link between neighboring complexes (figure 3).

A search of the CSD (updated to February 2012) for all compounds that have CdI_4^{2-} in the crystal structure (polymeric structures omitted) reveals that 40 such compounds have been deposited. Of these, only 4 complexes have a $[CdL_x][CdI_4]$ structure (similar

Table 4. Cd–Cl bond lengths to bridging Cl⁻ ligands, and difference between the bond lengths, in some representative compounds of the type [(μ-Cl)$_2$(Cd(L)Cl)$_2$)].

	Cd–Cl$_{bridging}$			Cd–Cl$_{terminal}$	
L	d_1	d_2	δd		Ref.
2-(2-(2-Hydroxyethylamino)ethylamino)cyclohexanol	2.513	2.819	0.306	2.575	This work
Bis(2-hydroxyethyl)ethane-1,2-diamine	2.478	2.935	0.457	2.549	[22]
Dipyridin-2-ylmethanediol	2.582	2.656	0.074	2.490	[25]
8-((1H-benzo[d]imidazol-2-yl)methoxy)quinoline	2.488	2.929	0.441	2.550	[26]

Table 5. Protonation constants for HEAC, L^1, L^2, L^3, L^4, and their stability constants with M = Ni(II), Cu(II), and Zn(II).

	D–H⋯A	Hydrogen bond (Å)				H⋯H interaction (Å)	
		d(D–H)	d(H⋯A)	<(DHA)	d(D⋯A)		
1	O(2)–H(2H)⋯Cl(2)#2	0.84	2.36	160.9	3.1607(18)	H(3A)⋯H(9B)#5	2.349
	N(1)–H(1N)⋯Cl(2)#3	0.847	2.604	158	3.404(2)	H(7B)⋯H(7B)#4	2.173
	N(2)–H(2N)⋯Cl(1)#4	0.85	2.814	145	3.540(2)		
	O(1)–H(1H)⋯O(2)#1	0.82	1.872	177	2.688(2)		
2	O(1)–H(1A)⋯I(1)#6	0.949	2.8736	132.4	3.583(5)	H(5B)⋯H(8B)#9	2.234
	O(2)–H(2HA)⋯I(3)#7	0.84	3.0404	158.0	3.83(2)	H(7A)⋯H(7A)#9	2.195
	O(3)–H(3HA)⋯I(4)#8	0.95	2.608	179.8	3.56(1)	H(10A)⋯H(13A)#7	2.243
	O(4)–H(4)⋯I(2)#9	0.839	2.7299	155.7	3.512(6)	H(20B)⋯H(3A)#6	2.138
	C(3)–H(3B)⋯O(4)#10	0.99	2.619	162.0	3.58(2)		
	C(13)–H(13A)⋯O(2)#11	0.99	2.47	152.0	3.38(2)		

Symmetry transformations used to generate equivalent atoms: for **1**: #1: $-x$, $-y+1$, $-z+1$; #2: x, $-y+1$, $z+0.5$; #3: $-x+0.5$, $-y+0.5$, $-z+1$; #4: $-x$, y, $-z+1.5$; for **2**: #5: $0.5-x$, $0.5+y$, $1.5-z$; #6: $1.5-x,0.5+y$, $-z$; #7: $1-x$, $0.5+-y$, $1.5-z$; #8: x, y, z; #9: $1-x$, $1-y$, $1-z$; #10: $0.5+x$, $1.5-y$, $1-z$; #11: $1-x$, $-0.5+y$, $1.5-z$.

to **2**) (shown in scheme 4). The geometry around cadmium in cadmium iodide complexes can be manipulated by change in M : L ratio. For example, in scheme 5 with variation in ratio of pyridine N–oxide–O to cadmium iodide, different complexes are obtained.

In the crystal structures of **1** and **2**, there are H⋯H interactions (table 5) with intermolecular distances in the range 2.138–2.349 Å, comparable to weak hydrogen bonds. These interactions have been observed in similar structures with bond lengths in the range 2.348–2.388 Å [22]. In **1** and **2,** each complex has six and eight H⋯H interactions with adjacent complexes, respectively.

4. Conclusion

A new ligand (HEAC) and its complexes **1** and **2** were prepared and identified by elemental analysis, IR, Raman, ^{1}H NMR spectroscopy, and single-crystal X-ray diffraction. The X-ray crystallography and spectral data of **1** show a distorted
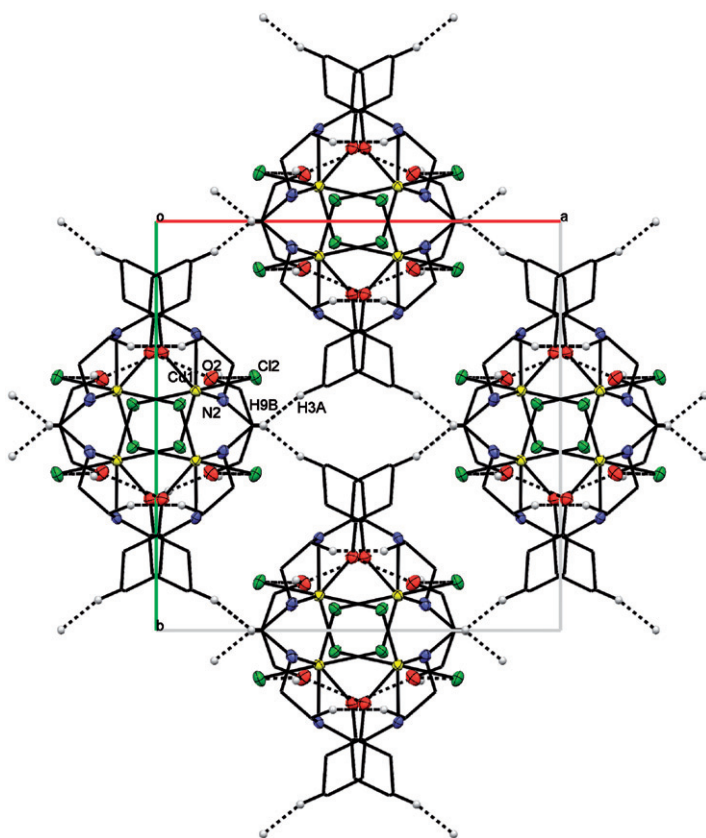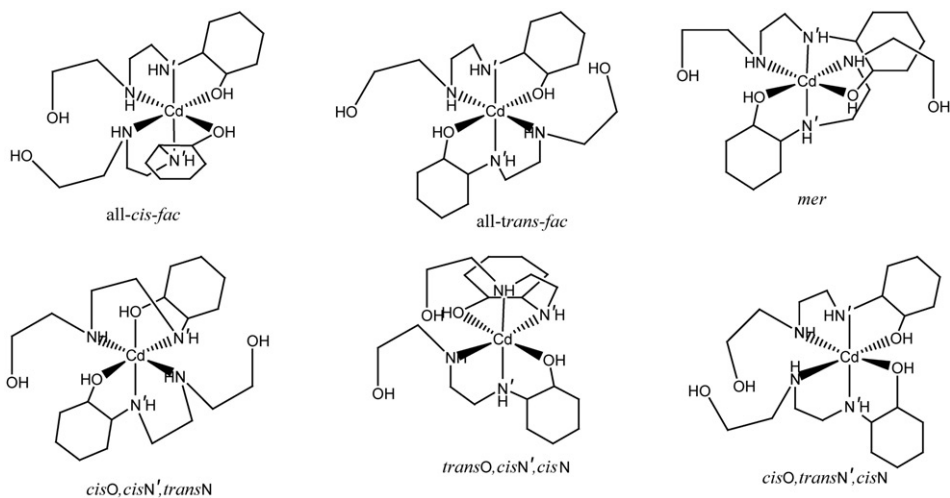
Figure 2. Packing of **1** showing the hydrogen bonds and H⋯H short contacts in the *ab* plane. Only hydrogen atoms involved in hydrogen-bonding are shown.

Scheme 3.   Six possible diastereomers for coordination of ligand pairs around the octahedral metal ion.
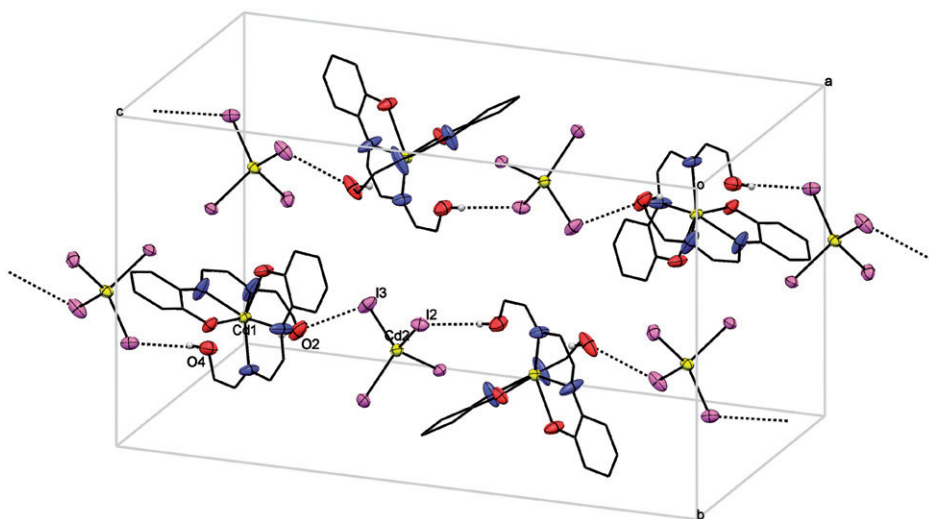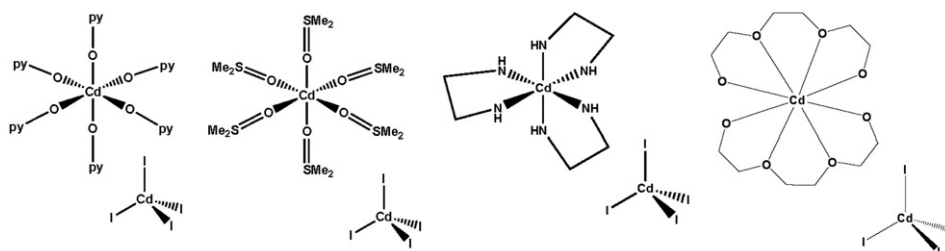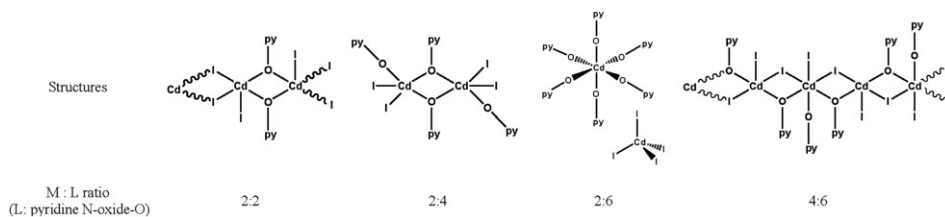
Figure 3. Packing of **2** showing the hydrogen-bonded chain formation along the *c*-axis. Only hydrogen atoms involved in hydrogen-bonding are shown.

Scheme 4. Complexes with a $[CdL_x][CdI_4]$ structure (similar to **2**) that are in CSD.

Scheme 5. Effect of variation in M : L ratio in cadmium iodide complexes (L: pyridine N–oxide–O).

octahedral geometry for cadmium with two Cd(II) ions bridged by two chlorides, resulting in the formation of an asymmetrical binuclear complex. In the crystal structure of **2**, there are two cadmium species, one with distorted octahedral coordination and another with a distorted tetrahedral environment. In

addition to several kinds of hydrogen bonds, there are also H···H interactions. In continuation of our research, we are preparing and characterizing new complexes of the HEAC.

Supplementary material

CCDC 850085 and 869839 for **1** and **2**, respectively, contain the supplementary crystallographic data for this article. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB21EZ, UK; Fax: +44(0)1223-336033; E-mail: deposit@ccdc.cam.ac.uk]. Structure factor table is available from the authors.

Acknowledgments

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