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An ionic Cd/Hg mixed-metal complex with an aminoalcohol ligand

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Abstract: A cadmium–mercury mixed-metal complex of *cis*-2-((2-((2-hydroxyethyl)amino)ethyl)amino)cyclohexan-1-ol (HEAC), [Cd(HEAC)₂][HgI₄] (**1**), was prepared and identified by elemental analysis, FT-IR, ¹H NMR spectroscopy, and single-crystal X-ray diffraction. The X-ray analysis revealed an ionic structure for **1** in which the cadmium and mercury atoms have CdN₄O₂ and HgI₄ environments, with distorted octahedral and tetrahedral geometries, respectively. The packing of the components in the crystal of **1** is supported by O–H⋯I hydrogen bonds, and these interactions lead to the formation of an R₄²(22) motif.

Keywords: β-amino alcohol; Cd/Hg mixed-metal complex; diastereomer; X-ray crystal structure.

1 Introduction

β-Amino alcohols exhibit a broad spectrum of biological activities [1–4] and industrial uses [5–9]. Functionalized amino alcohols contain several coordination sites, which may interact with a metal center in different manners. An example of such ligands is *cis*-2-((2-((2-hydroxyethyl)amino)ethyl)amino)cyclohexan-1-ol (HEAC), which (based on data from the Cambridge Structural Database (CSD) [10]) can act as an N₂ and an N₂O donor, with the latter being the most commonly observed [11, 12].

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Complexes containing both cadmium and mercury atoms are relatively rare and only 27 structures have been reported. The Cd/Hg mixture can form a variety of compounds including clathrate [ML_nM'(CN)₄·2G] [13, 14], heterometallic host–guest cages [15], heteronuclear complexes of cyanometallates [16], coordination polymers [17–21], heterobimetallic RHg/Cd species [22], and non-centrosymmetric materials [23]. Cadmium–mercury thiocyanate exhibits good second-order nonlinear optical effects, a wide transparency wavelength region [18, 23, 24], and piezoelectric properties [23]. [CdHgI₂(SCN)₄]_n presents high two-photon absorption (2 PA) cross-sections (σ) [25].

To extend the chemistry of this class of compounds, this work details the preparation, characterization (elemental analysis, FT-IR, ¹H NMR spectroscopy), and crystal structure of [Cd(HEAC)₂][HgI₄].

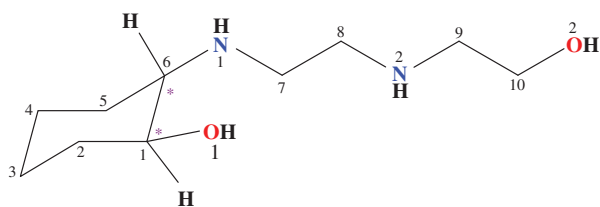
2 Results and discussion

The reaction between HEAC and a solution of a CdI₂/HgI₂ mixture in ethanol afforded crystals of **1**, which are air-stable and soluble in DMF and DMSO.

2.1 Spectroscopic studies

The frequencies of the IR bands for the free ligand are different from those of the corresponding complexes, providing significant indications that the HEAC is bound to the acceptor. In the FT-IR spectrum of **1**, a broad peak at 3419 cm⁻¹ can be assigned to the O–H frequency, which is increased by 152 cm⁻¹ compared to the free ligand [11]. A similar shift (133 cm⁻¹) was observed for the N–H frequency, confirming coordination through these donor groups. Bands in the range of 2800–3000 cm⁻¹, which can be assigned to the asymmetric and symmetric stretching vibrations of the C–H bonds, confirm the presence of the aliphatic moieties in the structure of **1**.

In the ¹H NMR spectrum of **1** (see Scheme 1 for numbering), the peaks corresponding to the hydrogen atoms of the two alcohol groups of HEAC are observed at the



Scheme 1: Structure of the HEAC ligand.

lowest magnetic field. The proton on the cyclohexane alcohol group is shifted downfield by approximately 1.41 ppm with respect to the free ligand, revealing the coordination through this moiety. A similar downfield shift by 0.3 ppm was also observed for the protons of the amine groups.

2.2 Crystal and molecular structure of $[\text{Cd}(\text{HEAC})_2][\text{HgI}_4]$

The crystal structure determination revealed that compound **1** consists of one $[\text{Cd}(\text{HEAC})_2]^{2+}$ cation and one $[\text{HgI}_4]^{2-}$ anion (Fig. 1). The cadmium atom has a distorted octahedral environment (Fig. 1) as a result of the *mer* coordination of the two N_2O -donor HEAC ligands. A search in the CSD [10] for cadmium complexes containing two N_2O -donor amino alcohol ligands revealed that there are two such analogues of **1** [12, 26]. The averages of the four Cd–N (2.313(8) Å) and two Cd–O bond lengths (2.520(6) Å) are comparable with the average taken from these analogues (2.306 and 2.477 Å, respectively). Each ligand forms two five-membered nonplanar chelate rings. Because of the nonresolvable disorder of some of the ring-carbon and nitrogen atoms in the crystal, the five- and six-membered

rings appear to be essentially flat (Fig. 1), which, however, is an artifact peculiar to this crystal structure determination.

The HEAC ligand used is a racemic mixture containing two chiral carbon atoms (C1 and C6; Scheme 1) [11]. Upon coordination, two new chiral centers (N1, N2; Scheme 1) are formed. All together, the $[\text{Cd}(\text{HEAC})_2]^{2+}$ unit has eight chiral centers [27, 28].

The tetracoordinate geometry of a mercury atom in the $[\text{HgI}_4]^{2-}$ unit could adopt either a tetrahedral or a square-planar configuration. To determine the geometry of such structures, the formula devised by Hakimi et al. [29] was applied, in which the angular structural parameter (τ_{sq}) is represented as the index of tetragonality $\tau_{\text{sq}} = (\theta_{\text{max}} - \theta_{\text{min}})/90$, where θ_{max} and θ_{min} are the maximum and minimum bond angles, respectively. An ideal square-planar conformation will have $\theta_{\text{max}} = 180^\circ$ and $\theta_{\text{min}} = 90^\circ$, and therefore $\tau_{\text{sq}} = 1$; but an ideal tetrahedron will have $\theta_{\text{max}} = 109.28^\circ$, $\theta_{\text{min}} = 109.28^\circ$, and therefore $\tau_{\text{sq}} = 0$. The τ_{sq} value is calculated to be 0.18 for Hg1, thus indicating a distorted tetrahedral geometry (Fig. 2) [29]. Among the four Hg–I bonds, the one that participates in two separate hydrogen bonding interactions has a significantly longer bond length than the others that only participate in one or none of the interactions of this nature.

Of particular interest from a coordination chemistry perspective is that the asymmetric HEAC ligand may form several diastereomers when coordinated to a metal. There are six possible arrangements of a pair of HEAC ligands acting as tridentate chelators around an octahedral metal ion (Scheme 2). Among the different possible isomers for ML_2 [L: 2-((2-aminoethyl)amino)ethanol-based ligands] complexes, examples for *mer* [30, 31], *fac*-(*trans*-O, *cis*-N', *cis*-N) [32–34], *fac*-(*all-trans*) [35, 36], and *fac*-(*all-cis*) [37] configuration have been reported. Complex **1** is the *mer*-diastereomer.

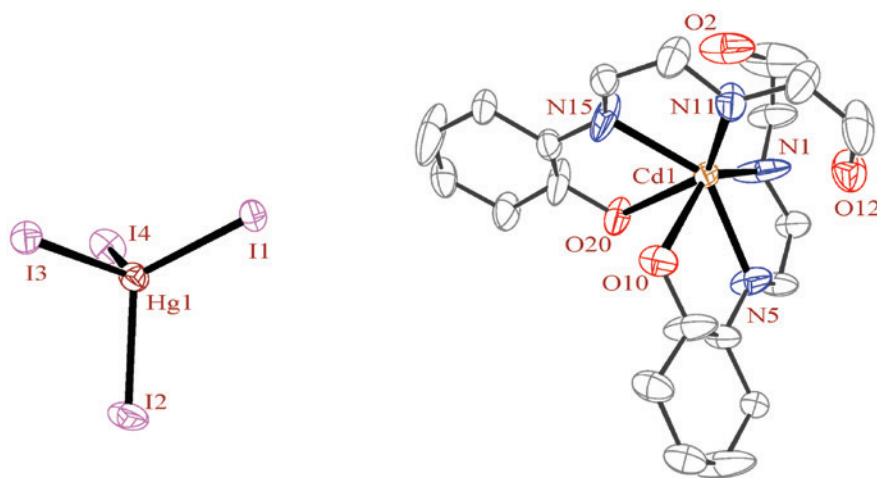


Fig. 1: ORTEP-III diagram of the molecular structure of complex **1**. The displacements ellipsoids are drawn at the 35% probability level.

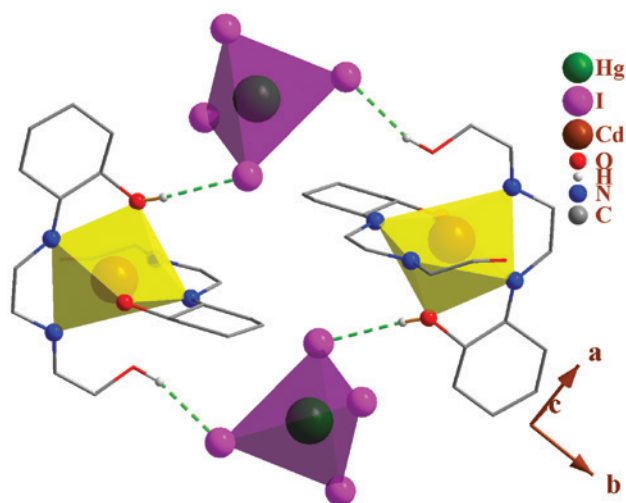


Fig. 2: Packing of **1**, showing the hydrogen bonds. Only the hydrogen atoms involved in hydrogen bonding are shown. HgI_4 and CdN_4O_2 units are shown as a tetrahedron and octahedron, respectively.

Each tridentate ligand can be coordinated to a metal center in facial or meridional forms. In the *mer* form, there are two angles of 90° and one of 180° ; in the *fac* form, there are three angles, all of 90° [38]. In **1**, two of the relevant bond angles of the HEAC ligand deviate slightly from 90° because of the chelating bite angle, whereas the third one is approximately 140° and thus inclines to the *mer* form (135° is exactly halfway between *fac* and *mer*).

In the structural network of the **1** (Fig. 2), the $\text{O}-\text{H}\cdots\text{I}$ hydrogen bonds participate in the formation of one $\text{R}_4^4(22)$ hydrogen bond motif (four acceptors, four donors with degree of 22) [39] between four cationic and anionic units.

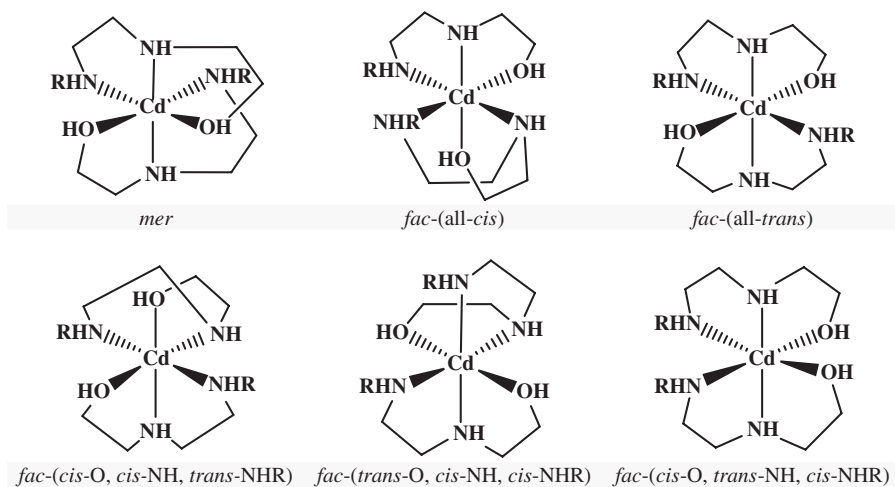
3 Conclusion

In this work, a complex of cadmium and mercury $[\text{Cd}(\text{HEAC})_2][\text{HgI}_4]$ (**1**) was synthesized and its spectral properties (IR, ^1H NMR) and crystal and molecular structure (by single-crystal X-ray diffraction) were investigated. In the ionic complex **1**, the cadmium atom has a distorted octahedral geometry that is formed by two *mer*- N_2O -donor HEAC ligands. The mercury atom has a tetrahedral HgI_4 coordination geometry. Two tridentate HEAC ligands are capable of forming six different diastereomers when reacted with a cadmium atom; the observed conformation in **1** is the *mer*-diastereomer. In the crystal packing of the **1**, the $\text{O}-\text{H}\cdots\text{I}$ hydrogen bonds participate in the formation of one $\text{R}_4^4(22)$ hydrogen bond motif [40, 41].

4 Experimental section

4.1 Materials and measurements

All starting chemicals and solvents were reagent or analytical grade, and used as received. The HEAC ligand has been synthesized according to the literature [11]. The infrared spectra of KBr pellets in the range $4000-400\text{ cm}^{-1}$ were recorded with an FT-IR TENSOR 27 spectrometer. ^1H NMR spectra were recorded on Bruker Aspect 3000 instrument. The carbon, hydrogen, and nitrogen contents were determined by a Thermo Finnigan Flash Elemental



Scheme 2: Six possible arrangements of a pair of HEAC ligands acting as tridentate chelators around a cadmium atom.

Analyzer 1112 EA. The melting points were determined with a Barnsted Electrothermal 9200 electrically heated apparatus.

4.2 Preparation of [Cd(HEAC)₂][HgI₄]

HEAC (0.20 g, 1 mmol), CdI₂ (0.18 g, 0.5 mmol), and HgI₂ (0.23 g, 0.5 mmol) were placed in the large arms of a branched tube (see ref. [42]). Methanol was carefully added to fill both arms. The tube was then sealed; and the ligand-containing arm was immersed in a bath at 60°C, whereas the other arm was maintained at ambient temperature [43]. After 3 days, yellow crystals deposited in the cooler arm were filtered off and dried in air. Yield: 0.42 g, 69%; m. p.: 199°C–201°C. – Anal. calcd for C₂₀H₃₈CdN₄O₄HgI₄ (1219.16): C 19.70, H 3.14, N 4.60; found C 20.06, H 3.16, N 4.68%. – IR (KBr): ν = 3419 s (O–H), 3230 m (N–H), ν_{as} = 2928 s (CH₂ and/or CH), ν_{s} = 2859 m (CH₂), δ_{as} = 1446 (CH₂), δ_{s} = 1354 (CH₂), ν = 1201 (C–O), 1095 (C–N) cm⁻¹. –¹H NMR (300 MHz, [D₆]DMSO, atom numbering as in Scheme 1): δ = 6.21 (s, 1H, HO-1), 5.35 (s, 1H, HO-2), 3.39–3.78 (m, 3H, H₂C-10, HC-1), 2.72–3.01 (m, 6H, H₂C-7, H₂C-8, H₂C-9), 2.57 (m, 1H, HC-6), 2.40 (s, 2H, HN-1, HN-2), 1.90–2.07 (m, 2H, H₂C-2), 1.65 (m, 2H, H₂C-5), 1.30 (m, 4H, H₂C-4, H₂C-3) ppm.

4.3 Crystal structure determination

X-ray diffraction data for **1** were collected at $T = 173$ K using a Rigaku FR-X Ultrahigh Brilliance Microfocus RA generator/confocal optics with XtaLAB P200 diffractometer. MoK α radiation ($\lambda = 0.71075$ Å) was used for all the compounds, and intensity data were collected using ω steps, the accumulating area detector images spanning at least a hemisphere of reciprocal space. All data were corrected for Lorentz polarization effects. A multi-scan absorption correction was applied using CrystalClear [44]. The structure was solved using Dual Space Methods (SHELXT [45]) and refined by full-matrix least-squares against F^2 (SHELXL [46]). Nonhydrogen atoms were refined anisotropically, and hydrogen atoms were either refined geometrically using a riding model or found in the electron density map and kept in a chemically sensible location with geometric restraints. All calculations were performed using the CRYSTALSTRUCTURE interface [47]. Selected crystallographic data are presented in Table 1. Diagrams of the molecular structure and unit cell were created using ORTEP-III [48, 49] and DIAMOND [50]. Selected bond lengths and angles

Table 1: Crystal data and structure refinement for complex **1**.

Empirical formula	C ₂₀ H ₃₈ CdN ₄ O ₄ ·HgI ₄
Formula weight, g mol ⁻¹	1225.21
Crystal size, mm ³	0.12 × 0.12 × 0.09
Temperature, K	173
Crystal system	Orthorhombic
Space group	<i>Pbca</i>
Unit cell dimensions	
<i>a</i> , Å	15.4891(2)
<i>b</i> , Å	27.5347(5)
<i>c</i> , Å	15.6214(2)
Volume, Å ³	6662.34(17)
<i>Z</i>	8
Calculated density, g cm ⁻³	2.44
Absorption coefficient, mm ⁻¹	9.0
$F(000)$, <i>e</i>	4464.00
θ range for data collection, deg	1.5–29.0
<i>h</i> , <i>k</i> , <i>l</i> ranges	–21 ≤ <i>h</i> ≤ 19, –34 ≤ <i>k</i> ≤ 35, –21 ≤ <i>l</i> ≤ 20
Reflections collected/ independent/ R_{int}	82038/8004/0.031
Data/restraints/parameters	8004/6/31
Goodness-of-fit on F^2	1.208
$R1/wR2$ [$I > 3 \sigma(I)$]	0.0513/0.0997
$R1/wR2$ (all data)	0.0603/0.1019
Largest diff. peak/hole, <i>e</i> Å ⁻³	1.92/–2.23

Table 2: Selected bond lengths (Å) and angles (deg) for complex **1** with estimated standard deviations in parentheses.

Bond lengths		Angles	
Cd1–N1	2.260(8)	N1–Cd1–N5	75.0(3)
Cd1–N5	2.325(8)	N1–Cd1–N11	124.7(4)
Cd1–N11	2.339(8)	N1–Cd1–O10	142.3(2)
Cd1–N15	2.329(8)	N1–Cd1–O20	81.7(5)
Cd1–O10	2.538(6)	N1–Cd1–N15	122.6(4)
Cd1–O20	2.501(4)	N5–Cd1–N11	124.1(4)
Hg1–I1	2.7518(7)	N5–Cd1–N15	143.2(4)
Hg1–I2	2.8029(8)	N5–Cd1–O10	68.6(2)
Hg1–I3	2.8321(7)	N5–Cd1–O20	84.1(4)
Hg1–I4	2.7784(9)	N15–Cd1–N11	75.3(3)
		N15–Cd1–O10	84.1(4)
		N15–Cd1–O20	68.8(3)
		I1–Hg1–I2	117.06(3)
		I1–Hg1–I3	105.49(2)
		I1–Hg1–I4	110.29(3)
		I2–Hg1–I3	101.31(2)
		I2–Hg1–I4	107.23(3)
		I3–Hg1–I4	115.50(3)

are displayed in Table 2 and hydrogen bond geometries in Table 3.

CCDC 1854455 contains the supplementary crystallographic data for this paper. These data can be obtained

Table 3: Hydrogen bond dimensions (Å and deg) in complex 1.

D–H...A	d(D–H)	d(H...A)	d(D...A)	<(DHA)	Symmetry code of atom A
O2–H2...I2	0.980(5)	2.71(7)	148(10)	3.574(13)	0.5+x, y, 1.5–z
O10–H10...I3	0.980(5)	2.83(10)	133(10)	3.571(7)	0.5+x, 1.5–y, 2–z
O12–H12...I4	0.980(5)	2.59(3)	156(5)	3.515(10)	1–x, –0.5+y, 1.5–z
O20–H20...I3	0.98	2.81	166.6	3.766(7)	x, 1.5–y, –0.5+z

free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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