

A Spectral and Structural Study of the New Cadmium Salt $[(H_2L)_2][Cd_2I_6][(NO_3)_2]$

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The reaction between 2-(piperazin-1-yl)ethanol and cyclohexene oxide under microwave irradiation gave 2-(4-(2-hydroxyethyl)piperazin-1-yl)cyclohexanol (L). The new cadmium salt $[(H_2L)_2][Cd_2I_6][(NO_3)_2]$ (**1**) was prepared from the reaction of cadmium iodide with L and identified by elemental analysis, FT-IR and Raman spectroscopy, and single-crystal X-ray diffraction. In the crystal structure of **1**, there is a $[Cd_2I_6]^{2-}$ dianion with distorted tetrahedral geometry for each cadmium atom. The piperazine and cyclohexane rings in **1** have a chair conformation. In the crystal there are several intermolecular hydrogen bonds including N–H...O, O–H...O, O–H...I, C–H...O, and C–H...I interactions.

Key words: Cadmium Complex, Iodide Bridge, Piperazine Moiety, Amino Alcohol, X-Ray Crystal Structure

Introduction

2-Amino alcohols are characteristic structural features of many natural products [1]. They are used in the synthesis of biologically active natural products, pharmaceuticals and pesticides [2–4]. Moreover, they play an important role as auxiliaries to control a range of asymmetric transformations by forming a 5-membered chelate in the presence of a metal ion [2].

In this work, the new potentially tetradentate ligand, 2-(4-(2-hydroxyethyl)piperazin-1-yl)cyclohexanol (L, Fig. 1) as well as the cadmium salt $[(H_2L)_2][Cd_2I_6][(NO_3)_2]$ (**1**) were prepared, and their spectral and structural properties were investigated.

Results and Discussion

The reaction of 2-(piperazin-1-yl)ethanol and cyclohexene oxide under microwave irradiation afforded L which is a potentially tetradentate asymmetric ligand with two different types of donor centers: two nitrogen atoms of the piperazine ring and two oxygen atoms of the two hydroxyl groups. Reaction of L with

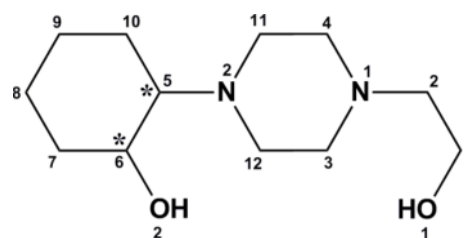


Fig. 1. Structure of 2-(4-(2-hydroxyethyl)piperazin-1-yl)-cyclohexanol, L.

an ethanolic solution of cadmium(II) iodide and neutralization with HNO_3 in a molar ratio of 1 : 1 gave $[(H_2L)_2][Cd_2I_6][(NO_3)_2]$, **1**, which was characterized by elemental analysis, IR and Raman spectroscopy and single-crystal X-ray diffraction. This compound is air-stable and soluble in ethanol, water, DMF, and DMSO.

In the IR spectrum of **1**, the $\nu(NH)$ band at 3016 cm^{-1} appears at lower frequency than that of an amine group typically of alkylammonium ions [5]. Four bands in the IR spectrum at 1381, 1280, 1072, and 910 cm^{-1} can be assigned to vibrations of the nitrate groups (ν_4 , ν_1 , ν_2 and ν_6) [6]. The lines in the Raman spectrum were observed in similar regions. The free

Table 1. Crystal data and structure refinement for [(H₂L)₂][Cd₂I₆][(NO₃)₂] (**1**).

Empirical formula	C ₁₂ H ₂₆ CdI ₃ N ₃ O ₅
Formula weight, g mol ⁻¹	785.46
Crystal size, mm ³	0.18 × 0.13 × 0.07
Temperature, K	150
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	
<i>a</i> , Å	12.2894(6)
<i>b</i> , Å	14.2810(6)
<i>c</i> , Å	12.7047(6)
β , deg	97.850(5)
Volume, Å ³	2208.83(18)
<i>Z</i>	4
Calculated density, g cm ⁻³	2.36
Absorption coefficient, mm ⁻¹	5.2
<i>F</i> (000), e	1464
θ range for data collection, deg	2.9–29.3
<i>h</i> , <i>k</i> , <i>l</i> ranges	–8 ≤ <i>h</i> ≤ 16, –17 ≤ <i>k</i> ≤ 18, –17 ≤ <i>l</i> ≤ 13
Reflections collected / independent / <i>R</i> _{int}	11 861 / 5156 / 0.025
Data / ref. parameters	5156 / 218
Goodness-of-fit on <i>F</i> ²	1.059
<i>R</i> 1 / <i>wR</i> 2 (<i>I</i> > 2σ(<i>I</i>))	0.0358 / 0.0858
<i>R</i> 1 / <i>wR</i> 2 (all data)	0.0479 / 0.0928
Largest diff. peak / hole, e Å ⁻³	2.17 / –1.50

nitrate ion has *D*_{3*h*} symmetry and three infrared active vibrations, but this symmetry is lowered to *C*_{2*v*} and *C*_s in metal complexes [7] to give up to six infrared-active vibrations. In **1**, the nitrate groups are involved in hydrogen bonds lowering their symmetry. In the Raman spectrum of **1**, the terminal Cd–I stretching vibration has been assigned to the strong band at 125 cm⁻¹ consistent with values reported in the literature [8].

The crystal structure of [(H₂L)₂][Cd₂I₆][(NO₃)₂] (**1**) was determined by single-crystal X-ray diffraction analysis (Table 1 and Experimental Section). Diagrams of the molecular structure and unit cell were

Table 2. Selected bond lengths (Å) and angles (deg) for [(H₂L)₂][Cd₂I₆][(NO₃)₂] (**1**) with estimated standard deviations in parentheses^a.

Bond lengths		Angles	
Cd1–I1	2.7124(5)	I1–Cd1–I2	116.448(19)
Cd1–I2	2.7369(6)	I1–Cd1–I3	105.808(18)
Cd1–I3	2.8682(6)	I1–Cd1–I3 ⁱ	116.788(19)
Cd1–I3 ⁱ	2.8491(6)	I3–Cd1–I3 ⁱ	97.192(16)
N1–H1	0.9100	Cd1–I3–Cd1 ⁱ	82.808(16)
N1–C2	1.508(7)	C3–N1–H1	107.7
N1–C3	1.500(7)	C3–N1–C4	108.6(4)
N1–C4	1.500(6)	C3–N1–C2	113.3(4)
N3–O3	1.246(6)	O3–N3–O4	118.9(5)
N3–O4	1.259(6)	O3–N3–O5	120.1(5)
N3–O5	1.223(6)	O4–N3–O5	120.9(5)

^a Symmetry code: ⁱ –*x*, 1 – *y*, 2 – *z*.

drawn with the use of the programs ORTEP-III [9] and DIAMOND [10]. Selected bond lengths and angles are collected in Table 2 and hydrogen bond geometries in Table 3.

In the crystal structure of **1** (Fig. 2), the cadmium atoms with a coordination number four have distorted tetrahedral geometry with average Cd–I bond lengths of 2.7916 Å which is similar to an average Cd–I bond length of 2.792 Å based on CSD data. The dihedral angle between the Cd1/I3/I3ⁱ/Cd1ⁱ and I1/I2/Cd1/Cd1ⁱ/I2ⁱ/I1ⁱ planes is 86.81°. The [Cd₂I₆]²⁻ unit has a center of inversion which lies in the center of the Cd1/I3/I3ⁱ/Cd1ⁱ plane (*C*_i symmetry).

In the cation of **1**, the piperazine moiety has a chair conformation, and its two nitrogen atoms are protonated and have a distorted tetrahedral geometry. The conformation of the cyclohexane ring is similar to that of the piperazine ring. As an indicator of their relative orientation, the dihedral angle between their mean planes is 83.94°. The cyclohexane ring has two chiral centers at C6 and C5 with the same absolute configu-

D–H...A	<i>d</i> (D–H)	<i>d</i> (H...A)	< (DHA)	<i>d</i> (D...A)	Symmetry code
N(1)–H(1)...O(4)	0.910	1.851	176.7	2.760(6)	1 – <i>x</i> , 1 – <i>y</i> , 1 – <i>z</i>
N(2)–H(2)...O(3)	0.910	2.006	166.8	2.900(6)	1 – <i>x</i> , 0.5 + <i>y</i> , 0.5 – <i>z</i>
N(2)–H(2)...O(5)	0.910	2.384	129.3	3.044(6)	1 – <i>x</i> , 0.5 + <i>y</i> , 0.5 – <i>z</i>
O(2)–H(2C)...O(1)	0.819	2.128	175.2	2.945(8)	1 – <i>x</i> , 1 – <i>y</i> , 1 – <i>z</i>
O(1)–H(1C)...I(2)	0.820	2.8319	149.3	3.562(5)	– <i>x</i> , 1 – <i>y</i> , 1 – <i>z</i>
C(4)–H(4A)...O(3)	0.969	2.665	110.1	3.133(6)	1 – <i>x</i> , 1 – <i>y</i> , 1 – <i>z</i>
C(5)–H(5)...I(1)	0.980	3.1728	169.9	4.141(6)	1 – <i>x</i> , 0.5 + <i>y</i> , 1.5 – <i>z</i>
C(10)–H(10A)...O(2)	0.97	2.698	129.6	3.40(1)	<i>x</i> , 1.5 – <i>y</i> , –0.5 + <i>z</i>
C(11)–H(11A)...O(5)	0.970	2.648	112.4	3.148(7)	1 – <i>x</i> , 0.5 + <i>y</i> , 0.5 – <i>z</i>
C(10)–H(11B)...O(3)	0.970	2.606	125.8	3.270(7)	1 – <i>x</i> , 1 – <i>y</i> , 1 – <i>z</i>
C(12)–H(12A)...O(4)	0.970	2.522	143.9	3.355(7)	<i>x</i> , <i>y</i> , <i>z</i>
C(12)–H(12B)...O(5)	0.970	2.620	114.6	3.151(7)	<i>x</i> , <i>y</i> , <i>z</i>

Table 3. Hydrogen bond geometries (Å, deg) for [(H₂L)₂][Cd₂I₆][(NO₃)₂] (**1**).

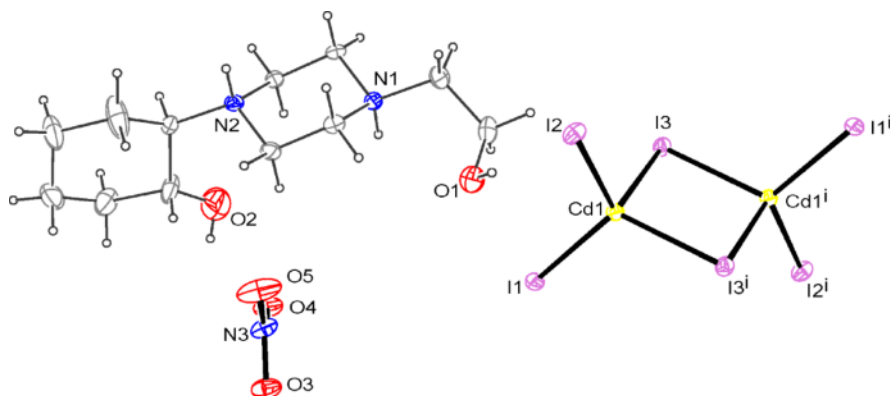


Fig. 2 (color online). ORTEP-III diagram of the crystal structure of $[(H_2L)_2][Cd_2I_6][(NO_3)_2]$ (**1**). The displacement ellipsoids are drawn at the 30% probability level.

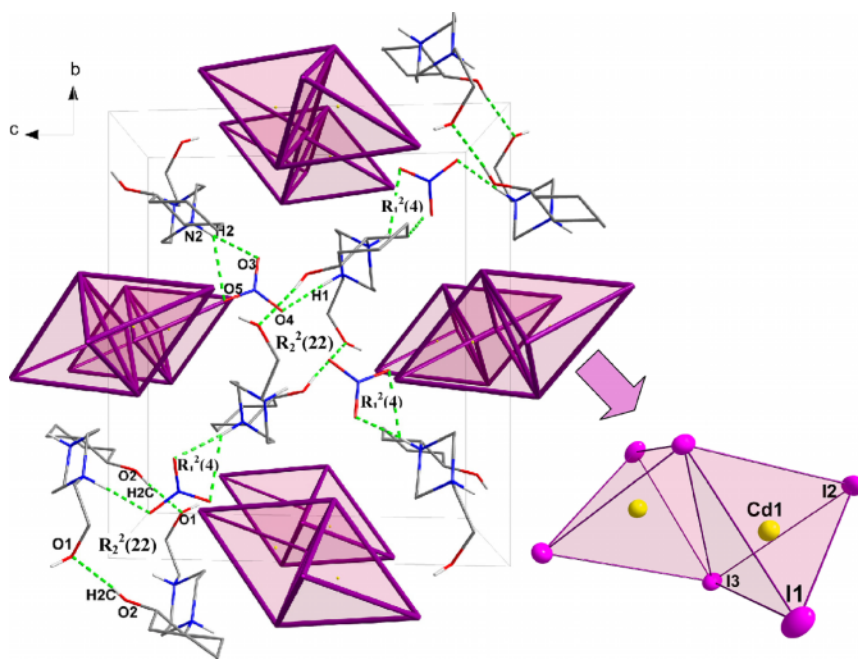


Fig. 3 (color online). Packing of $[(H_2L)_2][Cd_2I_6][(NO_3)_2]$, showing the hydrogen bonds and $R_2^2(22)$, $R_1^2(4)$ motifs. Only the hydrogen atoms of the hydroxyl and ammonium groups are shown. Each CdI_4 moiety is drawn as tetrahedron.

ration. Each unit cell of **1** contains four $[H_2L]^{2+}$ units consisting of a racemic mixture of the *R,R* and *S,S* isomers. The bond lengths and angles of the nitrate anions in **1** (1.224(7)–1.258(6) Å, 119.0(5)–121.0(5)°) show only small deviations from ideal values.

In the crystal structure of **1** there are strong N–H···O, O–H···O, O–H···I, as well as weak C–H···O and C–H···I hydrogen bonds. The iodide ligands act as proton acceptors, and carbon atoms participate in hydrogen bonding as proton donors, whereas the oxygen and nitrogen atoms act as both proton donors and acceptors. Each $[Cd_2I_6]^{2-}$ unit is surrounded by four

$[H_2L]^{2+}$ units *via* two O–H···I and two C–H···I hydrogen bonds, while each $[H_2L]^{2+}$ unit is surrounded by two $[Cd_2I_6]^{2-}$ units *via* O–H···I and C–H···I hydrogen bonds.

Extension of the hydrogen bonds in three directions creates a 3D supramolecular network in the crystal structure of **1**. The two O(2)–H(2C)···O(1) hydrogen bonds participate in the formation of a $R_2^2(22)$ motif [11] between two adjacent $[H_2L]^{2+}$ moieties (Fig. 3) and the N(2)–H(2)···O(3)_{nitrate} and N(2)–H(2)···O(5)_{nitrate} hydrogen bonds form a $R_1^2(4)$ motif between nitrate anions and $[H_2L]^{2+}$ cations (Fig. 3).

Conclusion

In this work 2-(4-(2-hydroxyethyl)piperazin-1-yl)cyclohexanol (L) and $[(H_2L)_2][Cd_2I_6][(NO_3)_2]$ (**1**) were prepared, and their spectral and structural properties were investigated. Crystal structure analysis revealed that the piperazine moiety in **1** has a chair conformation, and its two nitrogen atoms have a distorted tetrahedral geometry. The cadmium atoms with coordination number four have distorted tetrahedral geometries in a $[Cd_2I_6]^{2-}$ moiety with a center of inversion (C_i symmetry). Vibrations of the nitrate group were studied by IR spectroscopy. Hydrogen bonding influences the nitrate geometry and lowers its symmetry from D_{3h} to C_{2v} or C_s . These hydrogen bonds give rise to a 3D supramolecular network.

Experimental Section

Materials and instrumentation

All chemicals and solvents were reagent or analytical grade and used as received. The microwave-assisted reaction for the synthesis of the ligand (L) was carried out using a Microwave Laboratory Systems MicroSYNTH reactor from Milestone s. r. l. The infrared spectra of KBr pellets in the range of $400\text{--}4000\text{ cm}^{-1}$ were recorded with a FT-IR 8400 Shimadzu spectrometer. The Raman spectrum was obtained using a Nicolet Model 910 Fourier-transform spectrometer. The electronic spectrum of L was recorded in H_2O using a Shimadzu model 2550 UV/Vis spectrophotometer ($190\text{--}900\text{ nm}$). 1H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance DPX300 instrument operating at 300 and 100 MHz, respectively; chemical shifts are given in parts per million, with values relative to TMS as internal standard. The carbon, hydrogen and nitrogen contents were determined using a Thermo Finnigan Flash Elemental Analyzer 1112 EA. Melting points were determined with a Barnsted Electrothermal 9200 electrically heated apparatus.

R,S-2-(4-(2-Hydroxyethyl)piperazin-1-yl)cyclohexanol, L

A mixture of 1.30 g (10 mmol) of 2-(piperazin-1-yl)ethanol and 0.98 g (10 mmol) cyclohexene oxide was irradiated inside a microwave oven for 15 min with a power up to 1 kW. After microwave irradiation, an oily liquid was obtained. Excess precursors were removed using a rotary evaporator. A viscous brown oil was obtained. Several attempts to crystallize the compound were unsuccessful. $C_{12}H_{24}N_2O_2$ (228.33): calcd. C 63.12, H 10.59, N 12.27; found C 62.65, H 10.37, N 11.86. – IR (KBr disk): $\nu = 3447$ (OH), 2934 (CH), 2815 (CH_2), $\delta_{as} = 1454$ (CH_2), $\delta_s = 1354$ (CH_2), $\nu = 1294$ (CO), 1157 (C^5N), 1123 ($C^{11}N$, $C^{12}N$) cm^{-1} . – UV/Vis

(H_2O): λ_{max} (nm): 290. – 1H NMR (300 MHz, $CDCl_3$): $\delta = 1.2$ (m, 4 H, C^9H_2 , C^8H_2); 1.6–1.8 (m, 2 H, $C^{10}H_2$); 2.0 (m, 2 H, C^7H_2); 2.5 (m, 9 H, C^5H , $C^{11}H_2$, C^4H_2 , $C^{12}H_2$, C^3H_2); 2.7 (m, 3 H, C^6H , C^2H_2); 3.3 (s, 1 H, C^1OH); 3.6 (t, 2 H, C^1H_2); 3.9 (s, 1 H, C^6OH). – ^{13}C NMR (dept 135, 100 MHz, $CDCl_3$): $\delta = 22.3$ (C^9 , C^8); 24.0 (C^{10}); 25.5 (C^7); 33.1 (C^4 , C^3); 57.7 (C^{11} , C^{12}); 59.3 (C^2); 60.1 (C^1); 68.8 (C^5); 70.1 (C^6).

$[(H_2L)_2][Cd_2I_6][(NO_3)_2]$ (**1**)

A solution of 0.23 g (1 mmol) of L dissolved in ethanol (15 mL) was added with stirring to a solution of 0.36 g (1 mmol) of CdI_2 in ethanol (30 mL). The reaction mixture was stirred at $60^\circ C$ for 3 h, and a colorless precipitate was formed. It was filtered, and the filtrate was cloudy after 2 h. The pH of the cloudy filtrate was adjusted to around 5 by dropwise addition of aqueous 0.1 M HNO_3 until clarity. The mixture was vigorously stirred for 30 min and filtered. The solution was left at room temperature for several days, and colorless crystals suitable for X-ray diffraction were collected. Yield: 0.31 g, 39%; m. p.: $211^\circ C$. – $C_{12}H_{26}CdI_3N_3O_5$ (785.48): calcd. C 18.35, H 3.34, N 5.35; found C 18.12, H 3.29, N 5.14. – IR (KBr disk): $\nu = 3448$ (OH), 3016 (NH), 2939 (CH), 2862 (CH_2), $\delta_{as} = 1442$ (CH_2), $\nu_4 = 1381$ (NO_3^-), $\delta_s = 1344$ (CH_2), $\nu_1 = 1280$ (NO_3^- and/or ν CO), $\nu = 1133$ (CN), $\nu_2 = 1072$ (NO_3^-), $\nu_6 = 910\text{ cm}^{-1}$ (NO_3^-). – Raman: $\nu = 2901$ (CH), $\nu_4 = 1408$ (NO_3^-), $\nu_1 = 1281$ (NO_3^- and/or ν CO), 1156 (CN), $\nu_2 = 1033$ (NO_3^-), $\nu_6 = 893$ (NO_3^-), $\nu = 125\text{ cm}^{-1}$ (Cd-I).

X-Ray structure determination

A suitable single crystal of $[(H_2L)_2][Cd_2I_6][(NO_3)_2]$ was placed on a Xcalibur Eos Gemini Ultra diffractometer and kept at 150 K during data collection. Using the program package OLEX-II [12], the structure was solved with the program SHELXS [13–15] using Direct Methods and refined with SHELXL [13–15] using least-squares minimization. Crystallographic data and details of the data collection and structure refinement are listed in Table 1. Selected bond lengths and angles are reported in Table 2, and hydrogen bond geometries are presented in Table 3.

CCDC 899816 for $[(H_2L)_2][Cd_2I_6][(NO_3)_2]$ contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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