

Complexation to Cadmium(II) of a Tetradentate Ligand Resulting from the Condensation of 2-Pyridinecarbaldehyde with *N*-(2-Aminoethyl)propane-1,3-diamine

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The reaction of 2-pyridinecarbaldehyde with *N*-(2-aminoethyl)propane-1,3-diamine in a 2 : 1 molar ratio under microwave irradiation gave 2-(2-(pyridin-2-yl)-tetrahydropyrimidin-1(2*H*)-yl)-*N*-(pyridin-2-ylmethylene)ethanamine (L) as a mixture with the isomer 3-(2-(pyridin-2-yl)imidazolidin-1-yl)-*N*-(pyridin-2-ylmethylene)propan-1-amine (L^{*}). The molecules were characterized by elemental analyses and spectroscopic methods. Percentages of L and L^{*} were evaluated through integration of selected ¹H NMR signals. The cadmium iodide complex of L, [Cd(L)I₂]·H₂O (**1**), was prepared and identified by elemental analysis, FT-IR, Raman, and ¹H NMR spectroscopy, and single-crystal X-ray diffraction. In the crystal structure of **1** the cadmium atom with four coordinated nitrogen atoms and two iodide ions has a distorted octahedral geometry. A water molecule is also incorporated in the crystal network. Several hydrogen bonds including N–H···O, C–H···O, C–H···I, and O–H···I interactions are present in the crystal structure of **1**.

Key words: Hydropyrimidine, Cadmium Complex, Spectroscopic Characterization, X-Ray Crystal Structure, Microwave Irradiation

Introduction

The multifunctionalized hexahydropyrimidine scaffold is one of the most commonly encountered heterocycles in medicinal chemistry. It exhibits diverse pharmacological properties, such as antiviral, antitumor, antibacterial and antiinflammatory activities [1, 2]. Hexahydropyrimidine derivatives are also used as valuable reagents in organic synthesis [3, 4]. Their basic structural framework is present in a number of alkaloids, such as tetraponerines, verbamethine and verbametrine [5, 6]. The 1,3-N,N-heterocycles show ring-chain tautomerism [7, 8] like that of their 1,3-O,N- and 1,3-S,N-heterocycle analogs. The relative tendency for ring-chain tautomerism in a series of 1,3-X,N-heterocycles (X = O, NR, NAr, S) was estimated [9].

In this work the preparation under microwave irradiation and the characterization of 2-(2-(pyridin-

2-yl)-tetrahydropyrimidin-1(2*H*)-yl)-*N*-(pyridin-2-ylmethylene)ethanamine (L, Fig. 1) and the preparation of its cadmium(II) complex are described.

Results and Discussion

Pyridine-2-carbaldehyde reacts with *N*-(2-aminoethyl)propane-1,3-diamine in a 2 : 1 molar ratio to form the tetradentate ligand, L. Previously, the synthesis of L in a boiling solvent was reported [10] while we report this synthesis with a similar yield using microwave radiation. Possible products from the 2 : 1 condensation reaction are shown in Fig. 1. The bis-Schiff base was not observed here [10, 11], but two dissymmetric isomers (L and L^{*}) containing three heterocyclic rings were obtained. A *ca.* 62% content L^{*} was estimated through integration of selected ¹H NMR signals. A search of the CSD database [12] revealed that only one complex of L has been reported previously [10].

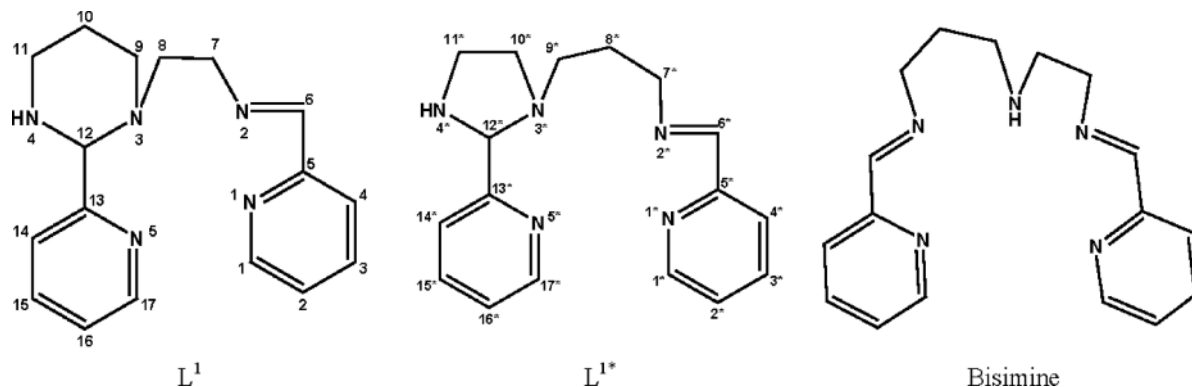


Fig. 1. Possible products from the 2 : 1 condensation reaction of pyridine-2-carbaldehyde with *N*-(2-aminoethyl)propane-1,3-diamine.

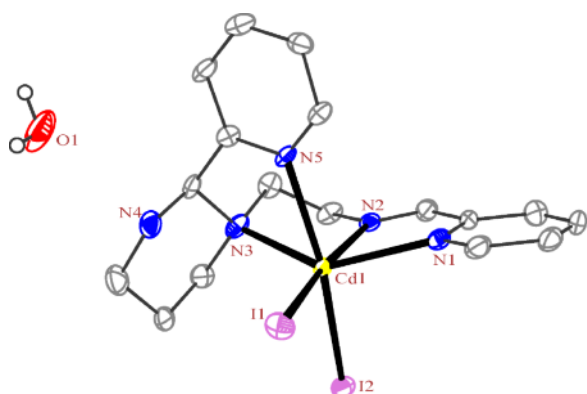


Fig. 2 (color online). ORTEP-III diagram of the molecular structure of [Cd(L)I₂]·H₂O (**1**). The displacement ellipsoids are drawn at the 40% probability level. The hydrogen atoms of the ligand were omitted for clarity.

The reaction between **L** and cadmium(II) iodide in a molar ratio of 1 : 1 in ethanol provided colorless crystals of **1**. This complex was characterized by IR, Raman, and ¹H NMR spectroscopy, and X-ray crystallography. It is air-stable and soluble in DMSO and DMF.

In the IR spectra of **1** and **L** there are two bands near 1650 and 1600 cm⁻¹ which were assigned to ν (C=N_{imine}) and ν (C=N_{py}), respectively. ν (C=N_{imine}) is shifted by 13 cm⁻¹ to higher energy indicating coordination through this nitrogen atom.

The presence of the water molecule in **1** affects the IR and Raman spectra in three regions including 3200–3550 cm⁻¹ for asymmetric and symmetric OH stretches, 1600–1630 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 [13, 14]. δ (H₂O) overlaps with ν (C=N_{imine}).

In the Raman spectrum of **1**, two bands at 446 and 340 cm⁻¹ were assigned to the Cd–N stretching vibrations, consistent with the values reported in the literature [15, 16] and in agreement with the results of the X-ray diffraction. The terminal Cd–I stretching vibration was assigned to the weak band at 128 cm⁻¹ [17, 18].

The numbering schemes used for the ¹H NMR and ¹³C NMR spectra of the free ligand are given in Fig. 1. In the ¹H NMR spectrum of **L**, the signal at 8.20 ppm was assigned to the C⁶H proton which is shifted by 0.82 ppm to lower field upon coordination. Evaluation of **L/L*** with the ratio of 38 : 62 is based on the relative integrations resulting from the distinguishable signals at δ = 4.10 (C¹²H, int = 0.71) for **L** and 4.18 ppm (C^{12*}H, int = 1.17) for **L***. The same result was reported previously with integration of different signals [10].

The crystal structure of [Cd(L)I₂]·H₂O (**1**) has been determined by single-crystal X-ray diffraction analysis. Diagrams of the molecular structure and unit cell were created using the programs ORTEP-III [19], MERCURY [20] and DIAMOND [21]. Crystallographic data are listed in Table 1, selected bond lengths and angles in Table 2 and hydrogen bond geometries in Table 3.

In the crystal structure of **1** (Fig. 2) the cadmium atom has a distorted octahedral coordination environ-

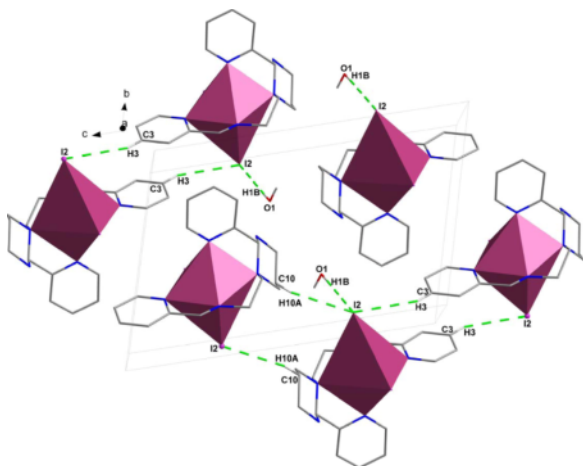


Fig. 3 (color online). Packing of complexes **1** in the crystal showing the hydrogen bonds in the *bc* plane. Only the hydrogen atoms involved in hydrogen bonding are shown. Each CdN_4I_2 unit is shown as an octahedron.

ment. Four sites are occupied by four nitrogen atoms of the ligand **L** with the Cd–N bond lengths in the range of 2.305(7)–2.500(8) Å. The two other sites are occupied by two iodide ions with bond lengths of 2.768 (1)–2.929(9) Å. The average Cd–I bond lengths in two similar structures [22, 23] is 2.802 Å. The water molecule does not coordinate to the cadmium atom and is trapped in the crystal network by hydrogen bonding. Tetradentate **L** forms three five-membered chelate rings, and only one of them is planar (r. m. s. 0.061 Å for the N1 atom). The ligand has one chiral center (C12), and a new one (N3) is formed after coordination [24], however the crystals contain a racemic mixture of *R,R* and *S,S* isomers in alternate layers.

In the network of **1** (Fig. 3), there are intermolecular hydrogen bonds including N–H···O, C–H···O, C–H···I and O–H···I (Table 3). In these hydrogen bonds, iodide atoms act as proton acceptors whereas nitrogen and carbon atoms participate as proton donors. The oxygen atom of the water molecule acts as both proton donor and acceptor.

Conclusion

In this work, pyridine-2-carbaldehyde was reacted with *N*-(2-aminoethyl)propane-1,3-diamine in a microwave reactor to produce **L/L*** in a 38 : 62 ratio. The complex $[\text{Cd}(\text{L})\text{I}_2]\cdot\text{H}_2\text{O}$ (**1**) was synthesized in

Table 1. Crystal data and parameters pertinent to data collection and structure refinement of $[\text{Cd}(\text{L})\text{I}_2]\cdot\text{H}_2\text{O}$ (**1**).

Empirical formula	$\text{C}_{17}\text{H}_{23}\text{CdI}_2\text{N}_5\text{O}$
Formula weight, g mol^{-1}	679.60
Crystal size, mm^3	$0.03 \times 0.02 \times 0.01$
Temperature, K	150
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
<i>a</i> , Å	7.4595(9)
<i>b</i> , Å	10.2503(12)
<i>c</i> , Å	15.285(2)
α , deg	103.126(11)
β , deg	98.827(10)
γ , deg	100.105(10)
Volume, Å ³	1097.5(2)
<i>Z</i>	2
Calculated density, g cm^{-3}	2.05
Absorption coefficient, mm^{-1}	3.8
<i>F</i> (000), e	644
θ range for data collection, deg	3.1–29.6
<i>h</i> , <i>k</i> , <i>l</i> ranges	$-9 \leq h \leq 9$, $-13 \leq k \leq 12$, $-21 \leq l \leq 20$
Reflections collected / independent / <i>R</i> _{int}	8268 / 5146 / 0.0589
Data / ref. parameters	5146 / 238
Goodness-of-fit on <i>F</i> ²	1.053
<i>R</i> 1 / <i>wR</i> 2 [<i>I</i> > 2σ(<i>I</i>)]	0.0593 / 0.1367
<i>R</i> 1 / <i>wR</i> 2 (all data)	0.0818 / 0.1522
Largest diff. peak / hole, e Å ⁻³	1.95 / –2.14

Table 2. Selected bond lengths (Å) and angles (deg) for $[\text{Cd}(\text{L})\text{I}_2]\cdot\text{H}_2\text{O}$ (**1**) with estimated standard deviations in parentheses.

Bond lengths		Angles	
Cd(1)–N(1)	2.443(8)	N(1)–Cd(1)–N(2)	69.3(2)
Cd(1)–N(2)	2.305(7)	N(2)–Cd(1)–N(3)	72.3(3)
Cd(1)–N(3)	2.500(8)	N(3)–Cd(1)–N(5)	68.9(2)
Cd(1)–N(5)	2.429(7)	N(1)–Cd(1)–I(1)	101.0(2)
Cd(1)–I(1)	2.768(1)	N(2)–Cd(1)–I(1)	170.3(2)
Cd(1)–I(2)	2.929(9)	N(3)–Cd(1)–I(1)	116.7(2)
		N(5)–Cd(1)–I(1)	91.1(2)
		I(1)–Cd(1)–I(2)	98.22(3)

a reaction between cadmium iodide and the ligand **L**, (2-(2-(pyridin-2-yl)-tetrahydropyrimidin-1(2*H*)-yl)-*N*-(pyridin-2-ylmethylene)ethanamine). Spectral (IR, Raman, ¹H NMR) and structural properties were investigated for this complex. Structural analysis of **1** has exhibited a distorted octahedral geometry. Hydrogen bonds such as N–H···O, C–H···O, C–H···I, and O–H···I are present in the crystal network of **1**. Synthesis of new complexes with **L** is ongoing in our research group.

D–H...A	<i>d</i> (D–H)	<i>d</i> (H...A)	<(DHA)	<i>d</i> (D...A)	Symmetry code
N(4)–H(4A)...O(1)	0.860	2.66	96.6	2.89(1)	<i>x</i> , <i>y</i> , <i>z</i>
O(1)–H(1B)...I(2)	0.85	2.7459	164.6	3.75(1)	<i>x</i> , 1 + <i>y</i> , <i>z</i>
C(3)–H(3)...I(2)	0.93	3.1211	146.7	3.93(1)	1 – <i>x</i> , – <i>y</i> , 2 – <i>z</i>
C(6)–H(6)...I(2)	0.93	3.0350	158.2	3.914(9)	1 + <i>x</i> , <i>y</i> , <i>z</i>
C(8)–H(8B)...O(1)	0.970	2.51	152.3	3.40(2)	1 – <i>x</i> , 1 – <i>y</i> , 1 – <i>z</i>
C(10)–H(10A)...I(2)	0.969	3.1192	150.1	3.989(8)	– <i>x</i> , – <i>y</i> , 1 – <i>z</i>
C(15)–H(15)...I(2)	0.93	3.0768	151.5	3.92(1)	1 + <i>x</i> , 1 + <i>y</i> , <i>z</i>

Table 3. Hydrogen bond geometries (Å, deg) for [Cd(L)I₂]·H₂O (**1**).

Experimental Section

Materials and instrumentation

All chemicals and solvents were reagent or analytical grade and used as received. The carbon, hydrogen, and nitrogen contents were determined in a Thermo Finnigan Flash Elemental Analyzer 1112 EA. The infrared spectra of KBr pellets were recorded in the range of 400–4000 cm^{−1} using a FT-IR 8400 Shimadzu spectrometer. The Raman spectrum was obtained using a Nicolet Model 910 Fourier-transform spectrometer. The melting point was determined using a Barnsted Electrothermal 9200 electrically heated apparatus. The microwave-assisted reaction was carried out using a Microwave Laboratory Systems MicroSYNTH reactor from Milestone s. r. l. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Aspect 3000 instrument operating at 250 and 63 MHz, respectively; chemical shifts are given in parts per million, with values relative to TMS as internal standard.

2-(2-(Pyridin-2-yl)-tetrahydropyrimidin-1(2H)-yl)-*N*-(pyridin-2-ylmethylene)ethanamine, **L**

A mixture of 1.07 g (10 mmol) pyridine-2-carbaldehyde and 0.58 g (5 mmol) *N*-(2-aminoethyl)propane-1,3-diamine was irradiated inside a microwave oven for 15 min with a power up to 700 W. After microwave irradiation a brown oily liquid was obtained. Then 10 mL ethylacetate was added, and excess precursors and solvent were removed using a rotary evaporator. A viscous brown oil was obtained. Several attempts to crystallize the compound were unsuccessful. Yield: 1.42 g, 96%. – C₁₇H₂₁N₅ (295.38): calcd. C 69.12, H 7.17, N 23.71; found C 68.11, H 6.85, N 24.23. – IR (KBr disk): ν = 3282 (NH), 3055 (CH_{imine} and/or CH_{ar}), 3009 (CH_{imine} and/or CH_{ar}), 2935 (CH₂), 1647 (C=N_{imine}), 1589 (C=N_{py}), 1524 (C=C), δ_{as} = 1435 (CH₂), δ_s = 1358 (CH₂), ν = 1149 (C–N), γ = 775 and 663 (py) cm^{−1}. – ¹H NMR (250 MHz, CDCl₃): δ = 2.3–3.5 (m, 22 H, C⁷H–C¹¹H, N⁴H, C^{7*}H–C^{11*}H, N^{4*}H); 4.1 (s, 1 H, C¹²H); 4.2 (s, 1 H, C^{12*}H); 7.1–7.8 (m, 12 H, C¹H–C³H, C¹⁵H–C¹⁷H, C^{1*}H–C^{3*}H, C^{15*}H–C^{17*}H); 8.2 (s, C⁶H, 2 H, C^{6*}H); 8.5–8.6 (m, 4 H, C⁴H, C¹⁴H, C^{4*}H, C^{14*}H). – ¹³C{¹H} NMR (63 MHz, CDCl₃): δ = 26.1 (C⁸); 29.5

(C¹⁰); 44.5–44.7 (C¹¹, C^{11*}); 50.1–57.8 (C^{7*}–C^{10*}, C⁷, C⁹); 81.5–83.6 (C¹², C^{12*}); 120.2–162.2 (C¹–C⁶, C¹³–C¹⁷, C^{1*}–C^{6*}, C^{13*}–C^{17*}).

[Cd(L)I₂]·H₂O (**1**)

CdI₂ (1 mmol, 0.36 g) was dissolved in EtOH (5 mL) and added with stirring to the solution of L/L* (1 mmol, 0.29 g) in EtOH (5 mL). The reaction mixture was stirred at 60 °C for 3 h. The solvent was removed using a rotary evaporator, and a dark-brown thick oil was obtained. Then 15 mL H₂O was added to this oil and the mixture stirred for 1 h and filtered. Colorless crystals suitable for X-ray diffraction were obtained from the filtrate after standing for 6 days. Yield: 0.20 g, 31 % (based on weight of CdI₂), 79 % (based on weight of L); m. p.: 180 °C. – C₁₇H₂₃CdI₂N₅O (679.60): calcd. C 30.04, H 3.41, N 10.30; found C 29.72, H 3.40, N 9.93. – IR (KBr disk): ν_{as} = 3520 (H₂O), ν_s = 3448 (H₂O), ν = 3248 (NH), 3070 (CH_{imine} and/or CH_{ar}), 3030 (CH_{imine} and/or CH_{ar}), 2974 (CH₂), 1660 (C=N_{imine} and/or δ H₂O), 1597 (ν C=N_{py}), 1470 (C=C), δ_{as} = 1443 (CH₂), δ_s = 1385 (CH₂), ν = 1157 (C–N), γ = 771 and 665 (py), ρ_r = 633 (H₂O), ρ_w = 588 (H₂O) cm^{−1}. – Raman: ν = 3088 (CH_{imine} and/or CH_{ar}), 2983 (CH₂), ν = 1696 (C=N_{imine} and/or δ H₂O), ν = 1573 (C=N_{py}), δ_{as} = 1437 (CH₂), ν = 1132 (C–N), γ = 833 and 709 (py), ρ_w = 557 (H₂O), ν = 446 and 340 (Cd–N), ρ_t = 233 (H₂O), ν = 128 (Cd–I). – ¹H NMR (250 MHz, [D₆]DMSO): δ = 2.3–4.0 (m, 11 H, C⁷H–C¹¹H, N⁴H); 4.7 (s, 1 H, C¹²H); 7.4–8.3 (m, 6 H, C¹H–C³H, C¹⁵H–C¹⁷H); 8.5–8.8 (m, 2 H, C⁴H, C¹⁴H); 9.0 (s, 1 H, C⁶H).

X-Ray structure determination of **1**

A suitable single crystal of **1** was placed on a Xcalibur Eos Gemini Ultra diffractometer and kept at 150.0 K during data collection. Using the program package OLEX-II [25]. The structure was solved with the SHELXS [26–28] structure solution program using Direct Methods and refined with the SHELXL [26–28] refinement package using least-squares minimization. Crystallographic data and details of the data collection and structure refinement are listed in Table 1.

CCDC 870101 for [Cd(L)I₂]·H₂O (**1**) 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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