

Crystal Structure and Characterization of a New Eight Coordinated Cadmium Complex

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ABSTRACT. In this work, a new cadmium complex $[\text{Cd}(\text{L})(\text{CH}_3\text{COO})_2]\cdot 2\text{H}_2\text{O}$ (**1**) with the ligand L, *N,N'*-bis(2-pyridinecarboxalidene)-1,2-cyclohexanediamine was prepared and identified by elemental analysis, FT-IR, Raman, ^1H NMR spectroscopy and single-crystal X-ray diffraction. The cadmium atom in the crystal structure of **1** has distorted triangular dodecahedral geometry by coordination of the four nitrogen atoms of L and four oxygen atoms of the two acetate ions. Two water molecules are also incorporated in the crystal network. The O–H...O hydrogen bonds present in the crystal structure of **1**. In this work, three structural surveys including coordination numbers of the cadmium atom, coordination modes of L and resonance in pyridine-2-ylmethanimine-based compounds are presented.

Key words: Triangulated dodecahedral geometry, Cadmium complex, Spectral characterization, X-ray crystal structure

INTRODUCTION

Schiff bases are an important class of ligands that coordinate to metal ions via the azomethine nitrogen and have been studied extensively for their important properties, e.g. their ability to reversibly bind oxygen,¹ transfer of an amino group,² photochromic properties,³ catalytic activity in the hydrogenation of olefins.⁴ Also many Schiff base complexes show catalytic activity in various reactions at high temperature and in the presence of moisture.^{5,6} Schiff bases show strong complexing ability towards some toxic metals⁷ and diverse biological activities, such as antibacterial and antitumor.^{8,9}

In this work the preparation and characterization of the cadmium(II) complex, $[\text{Cd}(\text{L})(\text{CH}_3\text{COO})_2]\cdot 2\text{H}_2\text{O}$ (**1**) with

N,N'-bis(2-pyridinecarboxalidene)-1,2-cyclohexanediamine (L, Scheme 1) is described.

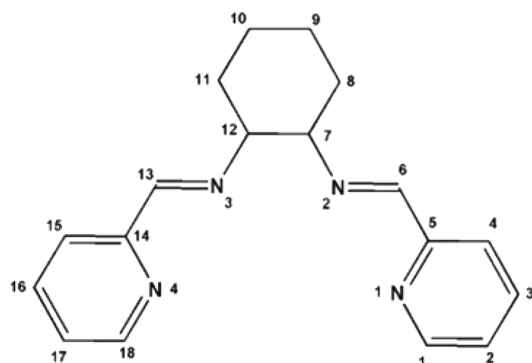
The coordination geometry of the cadmium atom and the nature of the ligands afford the coordination numbers of the cadmium atom in range of 2–10.¹⁰ In this paper we endeavor to introduce coordination aspects of the tetradentate ligand with cadmium atom.

EXPERIMENTAL

All chemicals and solvents were reagent or analytical grade and used as received. The ligand L was prepared according to the literature.¹¹ The carbon, hydrogen, and nitrogen contents were determined in a Thermo Finnigan Flash Elemental Analyzer 1112 EA. The infrared spectrum as KBr pellet was 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. Melting point was determined using a Barnsted Electrothermal 9200 electrically heated apparatus. ^1H NMR spectrum was recorded on a Bruker Aspect 3000 instrument operating at 250 MHz; chemical shifts are given in parts per million, with values in reference to an internal standard of TMS.

Synthesis of $[\text{Cd}(\text{L})(\text{CH}_3\text{COO})_2]\cdot 2\text{H}_2\text{O}$, (**1**)

$\text{Cd}(\text{CH}_3\text{COO})_2\cdot 2\text{H}_2\text{O}$ (1 mmol, 0.26 g) was dissolved in EtOH (10 mL) and added with stirring to a solution of L (1 mmol, 0.29 g) in EtOH (10 mL). The reaction mixture was



Scheme 1. The structure of L, this numbering scheme used for the ^1H NMR spectrum assignments.

stirred at 60 °C for 2 h. Colorless crystals suitable for X-ray diffraction were obtained from the solution after standing for few days. Colorless crystals (47%), m.p. 209 °C; Anal. Calc. for $C_{22}H_{30}CdN_4O_6$ (558.90): C, 47.28; H, 5.41; N, 10.02. found: C, 46.93; H, 5.45; N, 9.93%; IR (KBr disk): 3472 (ν_{as} H₂O), 3293 (ν_s H₂O), 3058 (ν CH_{imine} and/or CH_{ar}), 3016 (ν CH_{imine} and/or CH_{ar}), 2932 (ν CH₂), 1659 (ν C=N_{imine} and/or δ H₂O), 1581 (ν C=N_{py}), 1558 (ν_{as} COO), 1475 (ν_s COO and/or ν C=C), 1419 (δ_{as} CH₂), 1342 (δ_s CH₂), 1149 (ν C-N), 779 and 663 (γ py and/or δ OCO), 625 (ρ_r H₂O), 584 (ρ_w H₂O) cm^{-1} . Raman: 3019 (ν CH_{imine} and/or CH_{ar}), 2901 (ν CH₂), 1634 (ν C=N_{imine} and/or δ H₂O), 1511 (ν C=N_{py} and/or C=C), 1391 (δ_{as} CH₂), 1150 (ν C-N), 804 and 649 (γ py and/or ρ_r H₂O), 494 (ν Cd-N), 369 (ν Cd-O), 246 (ρ_t H₂O). ¹H NMR (250 MHz, [D₆]DMSO): δ = 1.6–2.1 (m, 8 H, C⁸H₂–C¹¹H₂); 3.5 (d, 2 H, C⁷H, C¹²H); 4.1 (s, 3 H, CH₃COO⁻); 7.5–8.1 (m, 4 H, C²H, C³H, C¹⁶H, C¹⁷H); 8.4 (s, 2 H, C⁶H, C¹³H); 8.9–8.6 (d, 2 H, C⁴H, C¹⁵H); 8.7–8.8 (d, 2 H, C¹H, C¹⁸H).

Crystal Structure Determination and Refinement

A suitable crystal of **1** was placed on an Oxford Diffraction Gemini Ultra diffractometer and kept at 150.0 K during data collection. Using Olex-II,¹² the structure was determined with the Shelxs¹³ structure solution program using Direct Methods and refined with the Shelxl¹³ refinement package using least-squares minimization.

CCDC 870105 for [Cd(L)(CH₃COO)₂].2H₂O (**1**) contain 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.

RESULTS AND DISCUSSION

Synthesis and Spectroscopic Characterization

A study using CSD data for complexes of L showed that complex **1** is the first example of a complex with a CdN₄O₄ environment in which N₄ and O₄ belong to a tetradentate ligand and two acetate groups, respectively.

This study also showed that complexes of Mn,¹⁴ Pr, Sm,¹⁵ Cu,¹⁶ Gd, Ce, Yb, Nd, Er,¹⁷ Pt,¹⁸ Mo,¹⁹ Ag,²⁰ and Pd²¹ with L were reported previously. All coordination modes of L are presented in Table 1. Among these modes, the three chelate form which was observed in **1** is most frequent.

Reaction between L and aqueous solution of cadmium (II) acetate in a molar ratio of 1:1 gave **1** which was characterized by IR, Raman, ¹H NMR spectroscopy and X-ray crystallography. This complex is air-stable and soluble in DMSO and DMF.

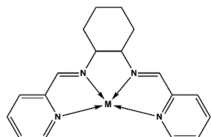
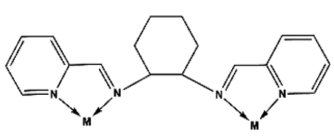
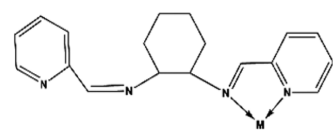
In the IR spectra of **1** and L, there are two bands near 1650 and 1600 cm^{-1} which were assigned to the vibrations of the ν (C=N_{imine}) and ν (C=N_{py}) respectively. The ν (C=N_{imine}) in the IR spectrum of **1** shifted 16 cm^{-1} to higher energy indicating coordination through the nitrogen atom.

Three bands at 1558, 1475 and 663 cm^{-1} which were assigned to the ν_{as} (COO), ν_s (COO) and δ (OCO) respectively, confirmed the presence of acetate ion in **1**. The differences between asymmetric (ν_{as}) and symmetric (ν_s) stretching of the acetate group (Δ) can reveal its coordination type. The Δ value for acetate salt is 164 cm^{-1} . In unidentate complexes, Δ values are much greater than the acetate salt while in bidentate complexes these values are significantly less than the acetate salt.^{22a} The Δ value for **1** is 83 cm^{-1} , thus acetate ion here acts as a bidentate ligand.

The presence of a 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.^{22b,23} We assigned all types of the vibrations for H₂O molecules in the IR and Raman spectra of **1** but vibrations such as δ (H₂O), ν (C=C) and γ (py) overlapped with vibrations due to ν (C=N_{imine}), ν_s (COO) and δ (OCO), respectively.

Information about the low-frequency vibrations of metal-

Table 1. Different types of coordination modes of L collected by CSD

Coordination modes for L			
			
Name	Three-chelate form	Two-chelate form (Helicated form)	One-chelate form
Number of records	21	15	1
Coordinated metals	Mn, Pr, Cu, Sm, Gd, Se, Yb, Nd and Er	Mn, Pt, Cu, Mo, Ag and Pd	Mn

ligand bonds can be obtained by Raman spectroscopy.²⁴ In the Raman spectrum of **1**, two bands at 494 and 369 cm⁻¹ were assigned to the ν (Cd–N)²⁵ and ν (Cd–O)²⁶ respectively. Attention to the Cd–N and Cd–O bond lengths confirms the higher stretching vibration of the Cd–N bond in respect to the Cd–O bond.

The numbering scheme used for the ¹H NMR spectrum of **1** is given in Scheme 1. In the ¹H NMR spectrum of L,¹¹ the signal at 8.3 ppm was assigned to the C⁶H proton. After coordination to **1**, the C⁶H signal is shifted by 0.1 ppm to lower field.

Table 2. Crystal data and structure refinement for [Cd(L)(CH₃COO)₂].2H₂O

Empirical formula	C ₂₂ H ₃₀ CdN ₄ O ₆
Formula weight, g mol ⁻¹	558.90
Crystal size, mm ³	0.11 × 0.08 × 0.03
Temperature, K	150
Crystal system	triclinic
Space group	<i>P</i> -1
Unit cell dimensions	
<i>a</i> , Å	8.5520(3)
<i>b</i> , Å	11.2524(4)
<i>c</i> , Å	13.0219(5)
α , °	87.639(3)
β , °	76.893(3)
γ , °	77.716(3)
Volume, Å ³	1192.49
<i>Z</i>	2
Calculated density, g cm ⁻³	1.56
Absorption coefficient, mm ⁻¹	0.9
<i>F</i> (000), e	572
θ range for data collection (deg)	2.9–29.3
<i>h</i> , <i>k</i> , <i>l</i> ranges	–11 ≤ <i>h</i> ≤ 11, –14 ≤ <i>k</i> ≤ 15, –16 ≤ <i>l</i> ≤ 17
Reflections collected / independent/ <i>R</i> _{int}	9501 / 5539 / 0.0278
Data / ref. parameters	5539 / 306
Goodness-of-fit on <i>F</i> ²	1.061
<i>R</i> 1 / <i>wR</i> 2 (<i>I</i> ≥ 2 σ (<i>I</i>))	0.0490 / 0.1070
<i>R</i> 1 / <i>wR</i> 2 (all data)	0.0612 / 0.1137
Largest diff. peak / hole, e Å ⁻³	1.13 / –0.72

Table 4. Hydrogen bond geometries (Å, °) for [Cd(L)(CH₃COO)₂].2H₂O

D–H⋯A	<i>d</i> (D–H)	<i>d</i> (H⋯A)	\angle (DHA)	<i>d</i> (D⋯A)	Symmetry code on A atom
O(5)–H(5A)⋯O(2)	0.851	1.936	163.7	2.763(5)	<i>x</i> , <i>y</i> , <i>z</i>
O(5)–H(5A)⋯O(3)	0.851	2.583	94.7	2.786(6)	<i>x</i> , <i>y</i> , <i>z</i>
O(5)–H(5B)⋯O(2)	0.850	2.687	86.1	2.763(5)	<i>x</i> , <i>y</i> , <i>z</i>
O(5)–H(5B)⋯O(3)	0.850	1.945	170.0	2.786(6)	<i>x</i> , <i>y</i> , <i>z</i>
O(6)–H(6A)⋯O(1)	0.849	1.992	175.8	2.840(5)	1 + <i>x</i> , <i>y</i> , <i>z</i>
O(6)–H(6B)⋯O(4)	0.851	1.922	173.4	2.768(6)	<i>x</i> , <i>y</i> , <i>z</i>

Description of the Crystal Structure

The crystal structure of [Cd(L)(CH₃COO)₂].2H₂O (**1**) has been determined by single-crystal X-ray diffraction analysis. Diagrams of the molecular structure and unit cell were created using Ortep-III,²⁷ Mercury²⁸ and Diamond.²⁹ Crystallographic data and details of the data collection and structure refinement are listed in Table 2. Selected bond lengths and angles for complex are listed in Table 3 and hydrogen bond geometries are presented in Table 4.

In the crystal structure of **1** (Fig. 1), the cadmium atom is coordinated by two imine and two pyridine nitrogen atoms of L and four oxygen atoms of the two acetate ions in distorted triangular dodecahedral geometry (Fig. 2).

The bond length averages of the two Cd–N_{imine} and two Cd–N_{py} bonds are 2.404 and 2.432 Å respectively, which are larger than those of CSD average (2.307 and 2.354 Å for Cd–N_{imine} and Cd–N_{py}, respectively). In the crystal structure of **1**, the cyclohexane ring has a chair conformation and two chiral centers on the C7 and C12 with the same enantiomeric forms. The unit cell of **1** contains two complexes with a racemic mixture of the *R,R* and *S,S* isomers.

In complex **1** the bond length of C6=N_{imine} (1.253(6) Å) is shorter than the C=N_{py} (1.336(5) and 1.340(6) Å for C1=N1 and C5=N1, respectively) and comparable to isolated imine bond lengths in the literature.³⁰ This means that probably there is no resonance or very weak resonance between the pyridine ring and imine group in this structure. The average of all 6-substituted imine bonds in pyridine-2-ylmetha-

Table 3. Selected bond length (Å) and angles (°) for [Cd(L)(CH₃COO)₂].2H₂O with estimated standard deviations in parentheses

Bond lengths		Angles	
Cd(1)–N(1)	2.436(3)	N(1)–Cd(1)–N(2)	67.9(1)
Cd(1)–N(2)	2.398(3)	N(2)–Cd(1)–N(3)	67.6(1)
Cd(1)–N(3)	2.411(3)	N(3)–Cd(1)–N(4)	67.5(1)
Cd(1)–N(4)	2.428(3)	N(1)–Cd(1)–O(1)	91.1(1)
Cd(1)–O(1)	2.455(4)	N(2)–Cd(1)–O(1)	82.3(1)
Cd(1)–O(2)	2.439(4)	N(3)–Cd(1)–O(1)	93.1(1)
Cd(1)–O(3)	2.464(3)	N(4)–Cd(1)–O(1)	88.9(1)
Cd(1)–O(4)	2.469(4)	O(1)–Cd(1)–O(2)	53.0(1)

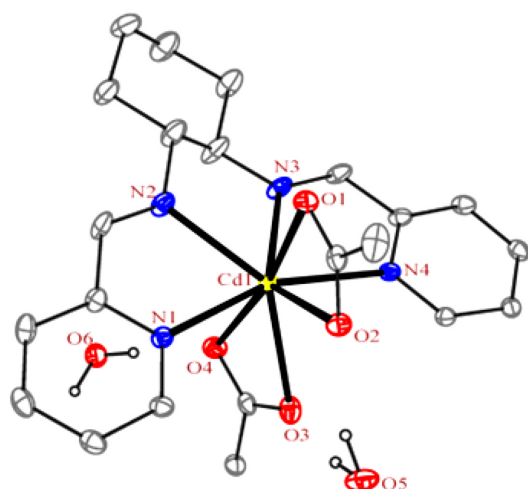


Figure 1. The Ortep-III diagram of the molecular structure of **1**. The displacement ellipsoids are drawn at the 20% probability level. The hydrogen atoms of ligand were omitted for clarity.

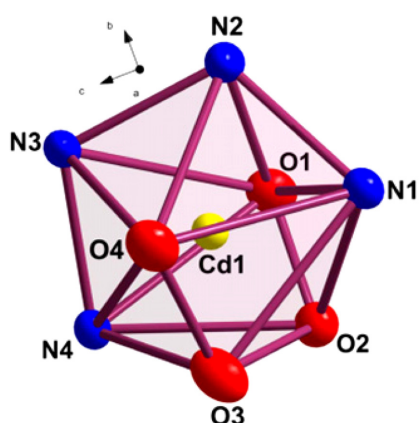
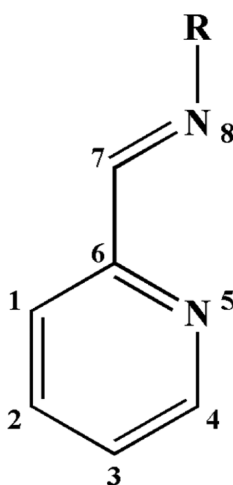


Figure 2. Distorted triangulated dodecahedral geometry around the cadmium atom in **1**.



Scheme 2. The base was used for study of imine bond lengths in CSD.

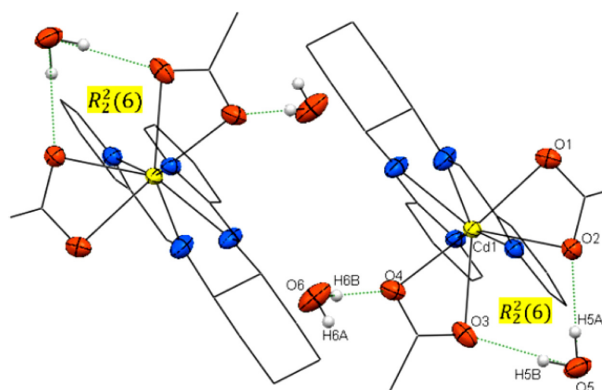


Figure 3. Packing of **1**, showing $R_2^2(6)$ hydrogen bond motifs and $C(sp^3)-H \cdots \pi$, $O-H \cdots O$ hydrogen bonds. Only the hydrogen atoms involved in hydrogen bonds are shown.

nimine-based structures (*Scheme 2*) is 1.264 Å (calculated by Vista³¹) that confirms this result.

In the crystal packing of **1** (*Fig. 3*), two oxygen atoms of each acetate group coordinate to cadmium atom and at the same time form a $R_2^2(6)$ motif^{32,33} by $O(5)-H(5A) \cdots O2$ and $O(5)-H(5B) \cdots O3$ strong hydrogen bonds³⁴ with the water molecule. The other water molecule acts as hydrogen bond bridge and connects two coordinated acetate groups in adjacent complexes by $O(6)-H(6A) \cdots O1$ and $O(6)-H(6B) \cdots O4$ hydrogen bonds. The Cd–O bond lengths (2.439(4)–2.469(4) Å) and O–Cd–O angles (52.5(1), 53.0(1)°) are comparable with analogues in the CSD (2.413 Å, 53.698°).

CONCLUSION

In this work $[Cd(L)(CH_3COO)_2] \cdot 2H_2O$ (**1**) was synthesized from the reaction between cadmium acetate and L, (*N,N'*-bis(2-pyridinecarboxalidene)-1,2-cyclohexanediamine) and its spectral (IR, Raman, ¹H NMR) and structural properties were investigated. Structural analysis of **1** exhibits distorted triangular dodecahedral geometry around the cadmium atom. A study of the CSD structures revealed that the cadmium atom has coordination numbers in range of 2–10. Difference between asymmetric (ν_{as}) and symmetric (ν_s) stretching in the IR spectrum of **1** is 83 cm^{-1} which confirms the acetate ion acts as a bidentate ligand. A survey about complexes of L revealed that this ligand has three coordination modes. The synthesis of new complexes with L is ongoing by our research group.

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