Design and structural studies of diimine/CdX₂ (X = Cl, I) complexes based on 2,2-dimethyl-1,3-diaminopropane ligand

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Highlights
- Synthesis of a novel diimine ligand.
- Two diimine Cd(II) complexes have synthesized.
- Crystal structure of Cd(II) complex has been investigated.

Abstract
Two related diimine Cd(II) complexes, [CdLCl₂]₁ and [CdLI₂]₂, derived from ligand, (N₁Z,N₃Z)-N₁,N₃-bis(2-chlorobenzylidene)-2,2-dimethylpropane-1,3-diamine, L were reported. The synthesized and isolated ligand and its Cd(II) complexes were characterized by elemental analyses, IR, ¹H- and ¹³C NMR and UV/Vis spectroscopy, ESI-MS spectrometry, and TGA/DTG studies. Both the complexes were synthesized under similar synthetic procedures and structure of complex 2 was additionally determined by single crystal X-ray diffraction studies. The diimine ligand was coordinated to Cd(II) ion through two nitrogen atoms, and possessed distorted tetrahedral geometry. TGA and DTG studies of the complexes were carried out at 20–800 °C, and showed that the complexes were thermally stable and decomposed into three steps.

1. Introduction
The synthesis of new ligands is the most important step in the development of coordination chemistry with unique properties and novel reactivity [1]. In recent years, diimine ligands and their metal complexes have attracted considerable attention due to their ease of synthesis, multidenticity, combination of donor atoms (coordination usually through the imine nitrogen, and other atoms like oxygen, sulfur or nitrogen), stability and extensive applications in various fields viz., catalysis, biological modeling, design of molecular ferromagnets, liquid crystals, medical imaging and optical materials [2–7]. One of the most important methods in preparing the diimine complexes is the syntheses and isolation of their ligands. Divalent metal ions viz., Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, and VO²⁺ are commonly used in complexation because the ligands lose two protons and coordinate as divalent anions [8]. Recently, metal complexes containing cations with a stable d¹⁰ electronic configuration have received a lot of attention in various fields viz., inorganic chemistry, biochemistry and environmental chemistry [9–11]. Among complexes with cations...
containing stable d^{10} electronic configuration, the coordination chemistry of cadmium is important both in biological and non-biological areas. Furthermore, cadmium(II) has recently been found to serve as the catalytic centre in a newly discovered carbonic anhydrase, and has been reported to enhance the catalytic activity in several metalloenzymes [12]. Moreover, it has been reported that various metal ions with d^{10} electronic configuration viz., Cd(II), Zn(II) etc., with chromophore ligand has been investigated as potential luminescent materials [13]. In addition, the coordination sphere of Cd(II) is very flexible with possible coordination numbers ranging from four to eight, corresponding to different geometries viz., Cd(II) is very flexible with possible coordination numbers ranging from four to eight, corresponding to different geometries viz., octahedron, pentagonal-bipyramid, bicapped triangular prism, and tedoctahedron [14]. Herein we report the syntheses and physicochemical studies of two novel Cd(II) complexes derived from a bidentate diimine ligand, (N’Z,N’Z)-N,N’-dimethylpropane-1,3-diamine. The structure of complex Z has been additionally determined on the basis of single crystal X-ray diffraction studies.

2. Experimental

2.2-Dimethyl-1,3-diaminopropane, 2-chlorobenzaldehyde, cadmium chloride, and cadmium iodide were purchased from Aldrich. All other reagents and solvents were of high purity and used as purchased without any further purification.

2.1. Physical measurements

Table 1

<table>
<thead>
<tr>
<th>Crystal data and structure refinement for diiodo-(N’Z,N’Z)-N,N’-bis(2-chlorobenzylidene)-2,2-dimethylpropane-1,3-diamine (CdII)</th>
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<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
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<td><strong>Crystal size</strong></td>
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<td><strong>Theta range for data collection</strong></td>
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<td><strong>Index ranges</strong></td>
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<td><strong>Reflections collected</strong></td>
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<td><strong>Independent reflections</strong></td>
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<td><strong>Completeness to theta = 25.03°</strong></td>
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<td><strong>Absorption correction</strong></td>
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<td><strong>Max. and min. transmission</strong></td>
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<td><strong>Refinement method</strong></td>
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<td><strong>Goodness-of-fit on F²</strong></td>
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<td><strong>Final R indices</strong></td>
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<td><strong>R indices (all data)</strong></td>
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<td><strong>Largest diff. peak and hole</strong></td>
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as a KBr pellet using Perkin Elmer 621 spectrophotometer. Far-IR (400–10 cm⁻¹) spectra were recorded on VERTEX80 FT-IR spectrophotometer. ¹H- and ¹³C NMR spectra of ligand and its Cd(II) complexes were recorded in CDCl₃ using JEOL 400 spectrometer. ESI-MS spectrometry was performed using Agilent technologies Ion trap LC/MS 6320 mass spectrometer with electrospray positive ionization mode. Electronic spectra of the complexes were obtained in dichloromethane on Pharmacia LKB-Biochem, UV/Vis spectrophotometer at room temperature. Thermal behavior of the synthesized compounds was studied by using SDTQ-600 (TA Instrument) in helium atmosphere (100 ml min⁻¹) at heating rate of 20 °C/min. in the temperature range 20–800 °C.

2.2. Synthesis of ligand, (N’Z,N’Z)-N,N’-bis(2-chlorobenzylidene)-2,2-dimethylpropane-1,3-diamine, L

A methanolic solution (10 ml) of 2,2-dimethyl-1,3-diaminopropane (0.102 mg, 1 mmol) was added dropwise to the methanolic solution (10 ml) of 2-chlorobenzaldehyde (0.280 mg, 2 mmol). The reaction mixture was stirred for 5 h resulting into a yellow colored solution, which was allowed to evaporate at room temperature. After three days, light yellow colored microcrystalline product was isolated.

Yield 65%. Color: Yellow, Mp. 112 °C; Molecular formula C_{19}H_{20}N_{2}Cl_2; Anal Calc. C, 65.71; H, 5.80; N, 8.06%; Found: C, 65.67; H, 5.77; N, 7.95% ¹H NMR (CDCl₃); δ (ppm) 8.70 (s ~CH=N), 7.28–7.45 (m Ar–H), 3.58 (s ~CH₂), 1.06 (s ~CH₃). ¹³C NMR (CDCl₃); δ (ppm) 158 (–CH=N), 133.5 (~C–Cl), IR, 1638 cm⁻¹ (υ(CH=N)).

2.3. Synthesis of complexes, [CdLX₂][X = Cl⁻, I⁻] [CdCl₂L] 1 and [CdI₂L] 2

A methanol solution (10 ml) of CdX₂ (1 mmol) (0.183 mg, 1 mmol for CdCl₂; 0.366 mg, 1 mmol for CdI₂) was added dropwise into 10 ml methanol solution of ligand (0.347 mg, 1 mmol). The resulting reaction mixture was stirred for 10 h, and then filtered off, and the filtrate was left undisturbed. After five days, yellow colored X-ray diffraction quality crystals separated out for complex Z. Unfortunately, all our efforts failed to get suitable X-ray diffraction quality crystal for complex I.

Complex 1: Yield 55%, Color: Yellow, Mp. 210 °C; Molecular formula C_{19}H_{20}N_{2}CdCl_4; Anal Calc. C, 43.00; H, 3.79; N, 5.28%; Found: C, 42.95; H, 3.74; N, 5.23% ¹H NMR (CDCl₃); δ (ppm) 8.72 (s ~CH=N), 7.29–8.10 (m Ar–H), 13³C NMR (CDCl₃); δ (ppm) 189.9 (~CH=N), IR, 1635 cm⁻¹ (υ(CH=N)), 465 cm⁻¹ (υ(C≡N)).

Complex 2: Yield 62%, Color: Yellow, Mp. 195 °C; Molecular formula C_{19}H_{20}N_{2}CdI₂; Anal Calc. C, 31.98; H, 2.82; N, 3.92%; Found: C, 31.95; H, 2.75; N, 3.87% ¹H NMR (CDCl₃); δ (ppm) 8.75 (s ~CH=N), 7.30–7.52 (m Ar–H), 13³C NMR (CDCl₃); δ (ppm) 185.5 (~CH=N), IR, 1630 cm⁻¹ (υ(CH=N)), 445 cm⁻¹ (υ(C≡N)).

2.4. X-ray crystallography of complex Z

Crystals suitable for X-ray structural analysis were obtained for the desired complex without solvent of crystallization in the lattice. Suitable block like section was cut from larger colorless crystal and Epoxy mounted on glass fibers. Data was collected at room temperature employing enhanced Mo radiation, λ = 0.71073 Å, and using Xcalibur/Oxford Diffractometer equipped with Eos CCD detector. Crystalys Pro software was used for data collection, absorption correction and data reduction [15]. 6 cr update scans, 408 frames collected after optimization, exposure time 38.46 s, 1° frame width, 45 mm detector distance. ‘multi-scan’ absorption corrections were applied with Min and Max transmission factors of 0.685 and 1.000, respectively. Cell parameters were retrieved using all observed reflections. The structures were initially solved using
Olex2 [16]. Subsequent re-solution and refinement were done using SHELXTL program package [17]. The complex was solved by direct methods as triclinic P̅1 and refined by least squares on \( F^2 \) to R1 = 0.0267 \( [I > 2\sigma(I)] \) with \( \theta = 2.97^\circ \) to 25.03\(^\circ\) and \( S = 1.033 \). Largest diff. peak and hole were 0.958 and –0.767 e Å\(^{-3}\). All nonhydrogen atoms were refined anisotropically with the hydrogen atoms placed constrained and assigned isotropic thermal parameters of 1.2 times that of the riding atoms. Molecular graphics and publication material were compiled using SHELXTL [17].

3. Results and discussion

A new bidentate diimine ligand, L has been easily prepared from the reaction of 2-chlorobenzaldehyde and 2,2-dimethyl-1,3-diaminopropane. Complexes of this ligand, L are synthesized by the reaction of \( \text{CdX}_2 \) [X = Cl, I] with ligand, L in 1:1 M ratio (Scheme 1). The complexes are soluble in common organic solvents such as \( \text{CHCl}_3 \), ethanol, methanol, tetrahydrofuran, and insoluble in water. The analytical and spectral data are completely consistent with the proposed formulation.

3.1. X-ray crystal structure of complex 2

The molecular structure with atom labeling of complex 2 is shown in Fig. 1. There is no significant interaction between the discrete molecules in the structure. No halogen-centroid of rings contacts, and no hydrogen bonding between molecules could be reported (Fig. 2). Related crystallographic data is presented in Table 1. Selected bond distances and angles of complex 2 are presented in Table 2. The aromatic rings in the ligand, L are rather parallel to each other with dihedral angle of 5.56(1)\(^\circ\) in the case of the Cd1 complex, and 3.19(1)\(^\circ\) in the case of the Cd2 complex.

3.2. Spectroscopic studies

The binding mode of the ligand to cadmium ion in complexes has been studied by comparing the IR spectrum of the ligand with that of cadmium complexes. Important bands with their

![Fig. 1. ORTEP diagram showing the molecular structure of the complex 2.](image-url)
assignments are listed in Table 3 (Fig. 3). A characteristic \( \nu(C=\text{H}) \) stretching band, observed at 1638 cm\(^{-1} \) in free ligand, is shifted to lower frequency, and appears at 1635 cm\(^{-1} \) for complex 1 and 1630 cm\(^{-1} \) for complex 2, indicating the coordination of azomethine nitrogen to Cd(II) ion [24–26], which is further confirmed by the appearance of a band at 158 cm\(^{-1} \) assigned to \( \nu(C=\text{N}) \) vibration, supporting the coordination of azomethine nitrogen to Cd(II) ion [21]. The downward shifting of vibration frequency of azomethine nitrogen can be safely attributed to the \( \pi \) back bonding of metal to the ligand, which also depends on coordinated anions [27]. It seems with increasing of softness and polarizability of coordinated halides from Cl\(^{-} \) to I\(^{-} \), the \( \pi \) back donation and therefore, the red shift of azomethine frequency is smoothly increased. The stretching vibrations due to C–H groups of aromatic, alkenic, aliphatic and iminic carbons appearing at 3065 cm\(^{-1} \), 1441 cm\(^{-1} \), 2952 cm\(^{-1} \) and 2850 cm\(^{-1} \), respectively in the free ligand are nearly unchanged after coordination in Cd(II) complexes [28].

The far-infrared spectra of complexes 1 and 2 were obtained in the region 10–400 cm\(^{-1} \) in order to identify frequencies due to \( \nu(Cd=\text{O}) \) and \( \nu(Cd=\text{N}) \) bands. The FT-IR spectra showed \( \nu(Cd=\text{O}) \) and \( \nu(Cd=\text{N}) \) vibration absorption frequencies at 295 cm\(^{-1} \) and 138 cm\(^{-1} \) for complex 1 and 2, respectively [27].

\( ^1H \) NMR spectrum of free ligand, L shows a significant azomethine proton (s \(-\text{CH}N\)) signal at 8.70 ppm, while the chemical shifts for \(-\text{CH}_2 \) (s 4H), \(-\text{CH}_3 \) (s 6H), and aromatic protons (m Ar–H) appear at 3.58, 1.06, and 7.25–7.45 ppm, respectively (Fig. 15). These values undergo deshielding upon coordination to Cd(II) ion, and appear at ca. 8.72 for azomethine proton, (s \(-\text{CH}N\)), while \(-\text{CH}_2 \) (s 4H), \(-\text{CH}_3 \) (s 6H) and aromatic protons (m Ar–H) appear at ca. 3.59 ppm, 1.10 ppm and 7.29–813 ppm, respectively (Fig. 4).

The \( ^{13}C \) NMR spectral findings further ascertain the \( ^1H \) NMR spectral data, and show characteristic sets of signals belonging to aliphatic and aromatic carbons.

The \( ^{13}C \) NMR spectrum of ligand, L shows sharp resonance signals at 24.8, 70.5 and 37.2 ppm corresponding to \(-\text{CH}_2 \), \(-\text{CH}_3 \) and quaternary carbon, respectively, and the azomethine carbon appear at 158 ppm, while the \( ^{13}C \) NMR signals for aromatic carbon appear at 127.0–133.5 ppm (Fig. 2S). These values undergo downfield shift upon coordination to Cd(II) ion, and appear at 189.9 ppm and 185.5 ppm, attributed to \(-\text{CH}N\) carbon for complex 1 and 2, respectively, while the signals for \(-\text{CH}_2 \), quaternary carbon and \(-\text{CH}_3 \) carbon appear at 24.7 and 24.89 ppm, 37.20 and 36.9 ppm, and 70.5 and 71.1 ppm for complex 1 and 2, respectively (Fig. 5). The remaining aromatic signals were found at their expected positions.

The structure of the ligand, L and its cadmium(II) complexes was further supported by mass spectrometry under positive ion ESI condition. The ESI-MS spectra of the ligand, and its Cd(II) complexes show the presence of the molecular ion peak as sodium adduct [M+Na]\(^+ \). The ESI-MS spectra showed molecular ion peaks [M+Na]\(^+ \), m/z at 348.28, 531.60, 714.49 corresponding to their free ligand, L and its complexes 1 and 2, while their corresponding calculated m/z being 347.28, 530.60, 713.49, respectively (Fig. 3S).

Electronic spectra of ligand, L and its Cd(II) complexes have been recorded in dichloromethane. The bands, observed at 350–380 nm due to the azomethine (CH=\text{N}) group, assigned to the n-p transition, are shifted to lower frequencies in Cd(II) complexes, indicating the involvement of imine nitrogen to Cd(II) ion. Furthermore, the spectra of the complexes show intense bands at 300–350 nm attributed to L–M charge transfer bands [29,30].

### 3.3. Thermal analyses

To examine the solid state thermal properties and stability of the complexes, 1 and 2, thermogravimetric (TG) analysis was...

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**Table 2**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>( \nu(C=\text{H}) ) ( [\text{cm}^{-1}] )</th>
<th>( \nu(C=\text{CH}) ) ( [\text{cm}^{-1}] )</th>
<th>( \nu(C=\text{NH}) ) ( [\text{cm}^{-1}] )</th>
<th>( \nu(C=\text{N}) ) ( [\text{cm}^{-1}] )</th>
<th>( \nu(C=\text{O}) ) ( [\text{cm}^{-1}] )</th>
<th>( \nu(C=\text{N}) ) ( [\text{cm}^{-1}] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
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<td>2952</td>
<td>2850</td>
<td>1638</td>
<td>3065</td>
<td>1376</td>
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<tr>
<td>[CdLCl]_2</td>
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<td>2857</td>
<td>1635</td>
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<tr>
<td>[CdL_2]_2</td>
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<td>2951</td>
<td>2855</td>
<td>1630</td>
<td>3068</td>
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**Table 3**

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<tr>
<th>Compounds</th>
<th>( \nu(\text{C=O}) ) ( [\text{cm}^{-1}] )</th>
<th>( \nu(\text{C=NH}) ) ( [\text{cm}^{-1}] )</th>
<th>( \nu(\text{C=CH}) ) ( [\text{cm}^{-1}] )</th>
<th>( \nu(\text{C=CH}) ) ( [\text{cm}^{-1}] )</th>
<th>( \nu(\text{C=CH}) ) ( [\text{cm}^{-1}] )</th>
<th>( \nu(\text{C=CH}) ) ( [\text{cm}^{-1}] )</th>
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<tr>
<td>L</td>
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<td>445</td>
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carried out under helium atmosphere with a heating rate of 20 °C min⁻¹ at temperature 25–800 °C (Figs. 6 and 7). The complex 1 is stable up to 215 °C and then begins to decompose continuously. The weight loss of 3.39% between 215 °C and 250 °C is attributed to the loss of one molecule of water (surface moisture). The weight loss of about 37% in the range 250–460 °C is ascribed to the loss of two molecules of water (surface moisture) and the release of chloro phenyl groups from the breakage of imine linkage. Further heating at 461–710 °C leads to the complete decomposition of ligand and halides (ca. 37%), leaving a final residue of CdO. TGA data is further supported by DTG curve.

Complex 2 is stable up to 150 °C (Fig. 7). The weight loss found as ca. 8% at temperature 150 °C, which is in the agreement of loss of three molecules of water (surface moisture). Further increase in temperature at 151–390 °C leads to the release of chloro-phenyl groups (ca. 35%) due to the breakage at the imine linkage. Further heating at 391–520 °C leads to the complete decomposition of ligand and halides (ca. 49%), leaving a final residue of CdO. TGA data is further supported by DTG curve.

4. Conclusion

In this work, we have synthesized two cadmium(II) complexes based on a new bi-dentate N₂-Schiff base chelating ligand. The experimental data suggest that the bidentate ligand coordinate to cadmium(II) ion through azomethine nitrogen atoms in 1:1 molar ratio, and results mononuclear complexes of the type, CdLX₂ where X = Cl⁻, I⁻ and L = (N¹Z,N³Z)-N¹,N³-bis(2-Chlorobenzylidene)-2,2-dimethylpropane-1,3-diamine. The complexes so formed are neutral and stable at room temperature. Both the ligand and its Cd(II) complexes have been characterized by various physicochemical and spectroscopic studies. The crystal structure analysis of complex, [CdLI₂] by using X-ray crystallography confirmed that complexes have distorted tetrahedral geometry, and shows there is no significant interaction between the discrete molecules in the structure. No halogen-centroid of rings contacts and no hydrogen bonding between molecules could be reported. IR and ¹H NMR spectra are complementary to the molecular structures determined by X-ray crystallography.
Fig. 5. $^{13}$C NMR spectrum of complex 1.

Fig. 6. TGA/DTG curve of complex 1.

Fig. 7. TGA/DTG curve of complex 2.
Acknowledgements

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Appendix A. Supplementary material

Crystallographic data for the complex 2 have been deposited at the Cambridge Crystallographic Data Center (CCDC 951033). Copies of this information may be obtained from the director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Tel.: +44 1223 762910; fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or on the web www: http://www.ccdc.cam.ac.uk/deposit. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2014.01.001.

References