



An Ammonium Cation Included Dinuclear Cd(II) Complex and A Face-Shared Octahedral Dinuclear Cd(II) Complex with N₂O Donor Tridentate Schiff base Ligand

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One face-shared octahedral Cd(II) complex and one ammonium cation included Cd(II) complex have been examined with the N₂O donor monoanionic Schiff-base ligand 4-methyl-2,6-bis(((phenylmethyl)imino)methyl)phenol (HL) having a central phenoxide unit. The configuration of the cadmium coordination geometries is responsible for varying modes of ligand binding and structures. The gas phase geometry of complex **1** has been optimized by density functional theory. In CH₃OH, the reaction between HL and Cd(NO₃)₂·4H₂O in the presence of triethylamine produces a *tris*-L clipped face-shared octahedral dinuclear complex [Cd₂(μ-L)₃](OH) (**1**). Use of Cd(NO₃)₂·4H₂O and NH₄SCN in CH₃OH in the absence of triethylamine leads to the synthesis of [Cd₂(μ-L)₂(μ_{1,1}-NCS)(μ-NH₄⁺)(NCS)₂] (**2**), which contains a NH₄⁺ cation at its center. Changes in co-ligands have an ability to regulate the synthesis of these two Cd(II) complexes, effectively allowing self-assembly to be directed. Three types of bridges of Cd(OPh)₃Cd and Cd(OPh)₂(μ_{1,1}-NCS)(μ-NH₄⁺)Cd in **1** and **2** are responsible for the Cd...Cd separations of 3.324 and 3.432 Å, respectively.

Keywords: *Tris*(μ-phenoxido) bridging, Thiocyanato bridging, Ammonium cation, Cd(II) complex, Crystal structure, DFT.

INTRODUCTION

For a long time, cadmium was considered a highly poisonous element and frequently associated with the physiologically dangerous elements like lead and mercury [1,2]. The marine diatom *Thalassiosira weissflogii* [3-6] has cadmium in its carbonic anhydrase and this finding eliminates the myth that cadmium is immune to the effects of living organisms.

Due to the lack of any CFSE in a *d*¹⁰ electronic arrangement, Cd(II) does not show any preference for any specific geometrical conformation. Thus, the varieties of geometries and coordination numbers (from 4 to 9) of Cd(II) are mostly governed by the ligands' steric needs [7-17]. Because of the filled *d*¹⁰ electronic arrangement, improvements in the fluorescence intensity of the chemosensors can be detected with Cd(II) ions. The excited state is typically not deactivated in the filled *d*¹⁰ electronic arrangement by any electron or transfer of energy pathways [18-24]. The investigations of molecular sensing characteristics reveal that the Cd(II) complexes are able to be used as fluorescence sensors to identify anions [25], cations [26], nitroaniline [27], Fe³⁺ and nitroaromatic compounds [28].

An essential field of study in this regard is the synthesis and characterization of novel Cd(II) complexes. In current study, one N₂O donor tridentate Schiff base ligand, 4-methyl-2,6-bis(((phenylmethyl)imino)methyl)phenol (HL) *via* the Schiff-base condensation between 4-methyl-2,6-diformylphenol and benzylamine. 4-Methyl-2,6-diformyl-phenol derivatives have two imine moieties (–HC=N–R) was synthesized, which offer synthetic versatility *via* modified R group (Fig. 1). When the ligand coordinates with Cd(NO₃)₂·4H₂O in the presence of triethylamine, it generates a triple phenoxide bridge face-shared octahedral dinuclear complex *via* ligand coordination only. On the other hand, using ammonium thiocyanate in place of triethylamine, a dinuclear Cd(II) complex containing two phenoxides, one thiocyanate and one ammonium cation bridge is produced. By using FT-IR and X-ray single crystal structural analysis, the solid-state structures of the synthesized cadmium(II) complexes are determined. The UV-vis, electrospray ionization mass spectrometry (ESI-MS) and ¹H NMR spectra have been employed to determine the solution phase structures of the synthesized Cd(II) complexes.

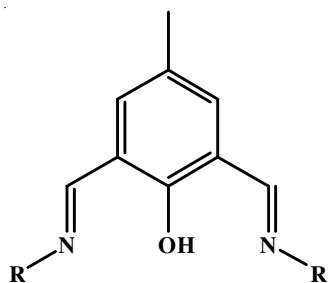


Fig. 1. Various ligands can be synthesized by modifying R group

EXPERIMENTAL

Ammonium thiocyanate from SRL (India), cadmium(II) nitrate tetrahydrate, benzylamine from Loba Chemie (India), paraformaldehyde, *p*-cresol, hexamine, triethylamine procured from Merck India Ltd. All other substances, including solvents, were of reagent grade and utilized as such without additional purification. After adapting a modified version of a published process, 2,6-diformyl-4-methylphenol was synthesized [29]. All the syntheses were carried out in the atmospheric air.

Physical measurements: The elemental analyses (CHN) were performed with a Perkin-Elmer model 2400 elemental analyzer and mass spectra were recorded in a Bruker MicroTOF-II mass spectrometer in ESI ionization mode. The FTIR spectra were recorded on a Nexus 670 model equipped with a Centaurus 10 × (Microscope) having a spectral range from 4000 to 400 cm⁻¹ with an MCT-B detector. The electronic spectra were obtained using a Unico (model 4802) UV-Visible-NIR spectrophotometer with a quartz cuvette holder of 1 cm × 1 cm dimension. The ¹H NMR spectra were recorded on 500 MHz (BRUKER) spectrometer in DMSO-*d*₆ as an internal standard. The chemical shifts (δ) are given in ppm and *J* values are given in Hz. The single crystal X-ray analyses were carried out using Bruker D8 Quest diffractometer. Complex **1** has been optimized and calculated for the UV-Vis spectrum using the density functional theory as implemented in Gaussian 16 quantum chemical software package [30]. In this calculation, B3LYP has been used as the functional and mixed type of basis sets 6-31** for carbon, hydrogen, nitrogen and oxygen and LANL2DZ for cadmium. The optimized structure is a minimum on the given surface and it has been confirmed with the presence of no imaginary frequency.

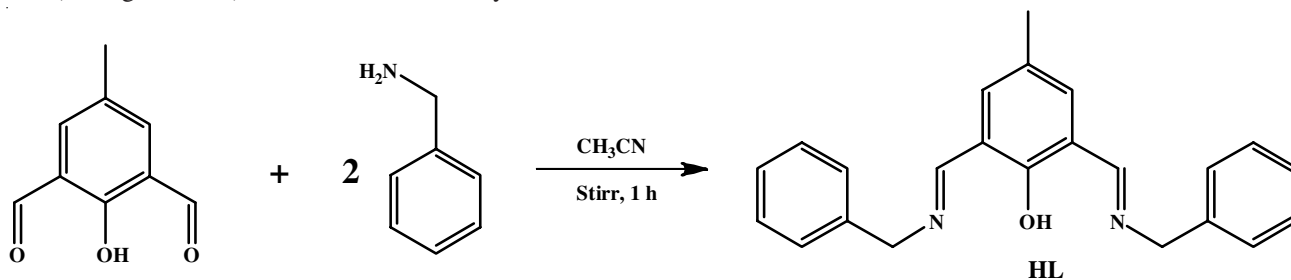
Syntheses

4-Methyl-2,6-bis(((phenylmethyl)imino)methyl)phenol (HL) ligand: In 60 mL of acetonitrile, 4-methyl-2,6-diformylphenol (3.280 g, 20 mmol) was dissolved followed by the addition

of benzylamine (4.36 mL, 40 mmol) and finally the resultant reaction mixture was stirred for 1 h. Filtration of the reaction mixture gave orange solid which was isolated, washed with water and dried (**Scheme-I**). The obtained Schiff base, HL was recrystallized from CH₃CN [31,32]. Yield: 2.736 g, 80%. Anal. calcd. (found) % for C₂₃H₂₂N₂O (*m.w.* 342.17): C, 80.67 (80.34); H, 6.48 (6.31); N, 8.18 (7.95). Selected FTIR bands (KBr, cm⁻¹): 3028 (br), 2837 (br), 1635 (vs), 1602 (vs), 1454 (vs), 1365 (m), 1253 (m), 1064 (m), 740 (m), 694 (s). UV-vis spectra [λ_{\max} , nm (ϵ , l mol⁻¹ cm⁻¹)] (DMF solution): 350 (18110), 270 (26005). ¹H NMR (DMSO-*d*₆) δ ppm: 14.33 (s, 1H, Ar-OH); 8.76 (s, 2H, -CH=N); 7.58 (s, 2H, Ar-H); 7.37 to 7.28 (m, 10H, benzylic Ar-H); 4.80 (s, 4H, -CH₂-Ar); 2.271 (s, 3H, -CH₃). ESI-MS [*m/z*]: calculated for C₂₃H₂₃N₂O ([HL+H⁺]): 343.1810; found: 343.1733.

[Cd₂(μ-L)₃](OH) (1): Cd(NO₃)₂·4H₂O (0.616 g, 2.00 mmol) dissolved in methanol (15 mL) was added dropwise while stirring to a yellow methanol solution (15 mL) of ligand HL (0.342 g, 1.00 mmol) at the ambient temperature in the air. The resultant yellow solution was stirred for 5 min and a solution of triethylamine (NEt₃, 0.202 g, 2.0 mmol) in methanol (10 mL) was added dropwise. The yellow solution that initially formed changed to a yellow precipitate in about 5 min. For an additional hour, the reaction mixture was stirred. Filtration of the reaction mixture gave a yellow solid, which was isolated, washed with water and dried. From DMF solution, yellow single crystals appropriate for an X-ray study were produced over the course of 8 days. Yield: 0.316 g, 74%. Anal. calcd. (found) % for C₆₉H₆₄Cd₂N₆O₄ (*m.w.* 1266.11): C, 65.46 (65.30); H, 5.10 (5.14); N, 6.64 (6.72). Selected FTIR bands (KBr, cm⁻¹): 3444 (br), 3027 (br), 1631 (vs), 1540 (vs), 1450 (s), 1404 (s), 1354 (s), 1228 (m), 1092 (s), 1064 (s), 726 (m), 694 (m). UV-vis spectra [λ_{\max} , nm (ϵ , l mol⁻¹ cm⁻¹)] (DMF solution): 400 (18670), 270 (27360). ESI-MS [*m/z*]: calculated for [C₆₉H₆₃N₆O₃Cd₂]⁺ ([Cd₂(μ-L)₃]⁺), 1249.3053; found: 1249.2764.

[Cd₂(μ-L)₂(μ_{1,1}-NCS)(μ-NH₄⁺)(NCS)₂] (2): Following the same procedure as for compound **1**, but substituting NH₄SCN (0.228 g, 3.0 mmol) for NEt₃, orange compound **2** was synthesized. Using DMF solution, the orange single crystals appropriate for X-ray examination were produced over the course of seven days. Yield: 0.399 g, 72%. Anal. calcd. (found) % for C₄₉H₄₆Cd₂N₈O₂S₃ (*m.w.* 1099.96): C, 53.50 (53.05); H, 4.22 (4.08); N, 10.19 (10.10). Selected FTIR bands (KBr, cm⁻¹): 3442 (br), 2918 (br), 2100 (vs), 2059 (vs), 1805 (m), 1632 (vs), 1540 (vs), 1493 (m), 1449 (s), 1401 (s), 1347 (s), 1321 (m), 1232 (m), 1058 (s), 989 (m), 750 (m), 698 (s). UV-vis spectra [λ_{\max} , nm (ϵ , l mol⁻¹ cm⁻¹)] (DMF solution): 400 (17149), 270 (25958).



Scheme-I: Synthetic route for the synthesis of HL

Crystal data collection and refinement for 2: Under an optical microscope, single crystals with the right diameters were selected and they were put on a glass fiber to collect data. A Bruker D8 Quest diffractometer was used to obtain the crystal data of complex **2** and the CMOS detector was operated in shutter-less mode. The device had Triumph™ X-ray source optics and a graphite monochromatized MoK α X-ray source ($\lambda = 0.71073 \text{ \AA}$). APEX II software was used to manage data gathering, initial indexing and cell refining [33–35]. SAINT+ software was used to perform frame integration including Lorentz polarization corrections and final cell parameter computations [36]. The SADABS programme was used to adjust the data for absorption [37]. Analysis of redundant frames was used to track the decline in reflection intensity. In order to solve the structure, direct approaches and difference Fourier techniques were used. Anisotropic refinement was performed on all non-hydrogen atoms. Using idealized geometries (the riding model), all H atoms were placed in their calculated locations and given constant isotropic displacement values. The OLEX2 crystallographic software's SHELXL-2014 package [38–41] was used to refine the structure using a number of full-matrix least-squares/difference Fourier cycles. The carbon atom of bridging thiocyanate in complex **2** was found to be disordered and was split on two positions. A summary of the crystallographic data for complex **2** is summarized in Table-1.

TABLE-1
CRYSTALLOGRAPHIC DATA FOR COMPLEX 2

Formula	C ₄₅ H ₄₆ Cd ₂ N ₈ O ₂ S ₃
Formula weight	1099.96
Space group	<i>Pbcn</i>
Crystal system	Orthorhombic
a (Å)	17.2121(9)
b (Å)	22.8081(11)
c (Å)	12.6331(6)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å ³)	4959.4(4)
Z	4
Crystal colour	orange
Crystal size/mm	0.27 × 0.16 × 0.03
2 θ range for data collection (°)	4.380 to 50.000
Index ranges	–20 ≤ h ≤ 20, –27 ≤ k ≤ 27, –15 ≤ l ≤ 15
T/K	298(2)
Density (g cm ^{–3})	1.468
μ (mm ^{–1})	1.030
F(000)	2208
Reflections collected	207791
Independent reflections	4375
R _{int}	0.0589
R _{sigma}	0.0135
Data/restraints/parameters	4375/0/296
Goodness of fit on F ²	1.234
R1(F _o), wR2(F _o) (I ≥ 2 σ (I))	R1 = 0.0775, wR2 = 0.2250
R1(F _o ²), wR2(F _o ²) (all data)	R1 = 0.0976, wR2 = 0.2609
Largest diffraction peak/hole/e Å ^{–3}	1.258/-1.121
CCDC 2284608 contains the supplementary crystallographic data for the complex 2 .	

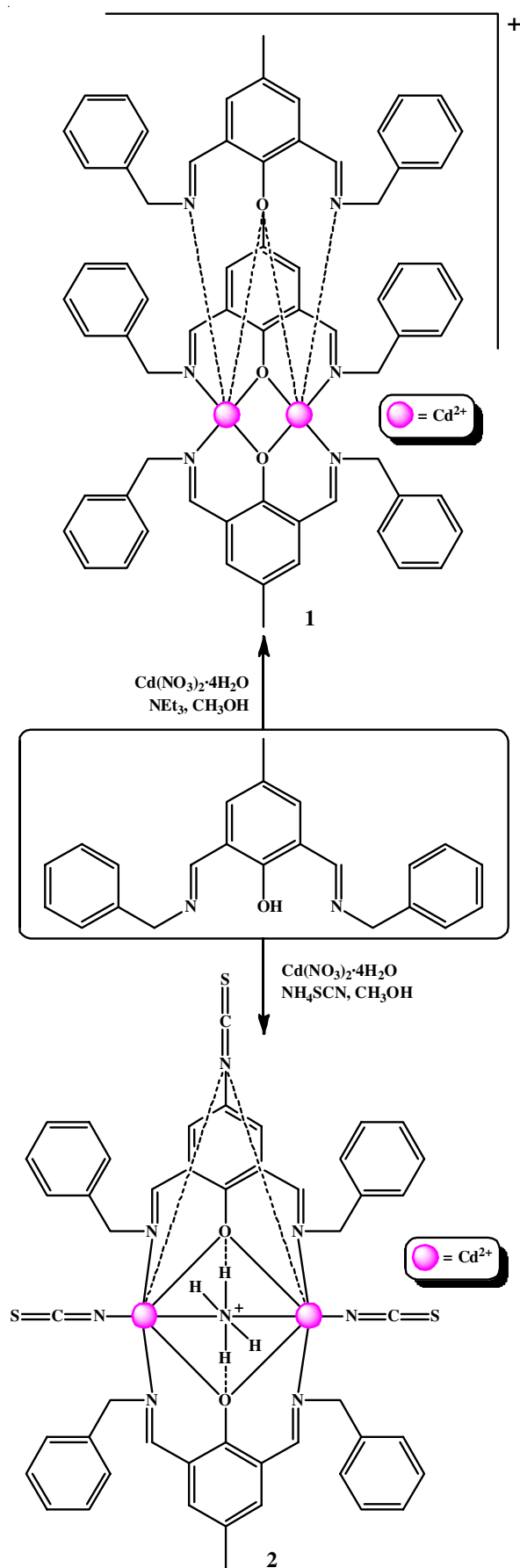
RESULTS AND DISCUSSION

In this work, Schiff base 4-methyl-2,6-bis(((phenylmethyl)imino)methyl)phenol (HL) had been synthesized (**Scheme-I**) in accordance with a literature-based approach [31,32]. **Scheme-II** represents the systematic mechanism about the reaction of Schiff base with cadmium(II) nitrate. While Cd(NO₃)₂·4H₂O reacted with HL in MeOH and in the presence of triethylamine (NEt₃), [Cd₂(μ -L)₃](OH) (**1**, **Scheme-II**) was obtained. A triple phenoxide bridge face-shared octahedral compound readily separates as yellow solid with a yield of ~74% from the reaction mixture. The other reaction in a similar approach was investigated by using NH₄SCN in place of NEt₃ where the process of thiocyanato-bridge formation is preferred against phenoxido-bridge. In absence of triethylamine, NH₄⁺ and thiocyanato-bridge complex [Cd₂(μ -L)₂(μ ,1,1'-NCS)(μ -NH₄⁺)(NCS)₂] (**2**, **Scheme-II**) was produced with ~72% yield as an orange solid from the reaction mixture.

The ¹H NMR spectrum of Schiff base ligand (HL) detected a phenolic proton as a singlet at δ 14.331 ppm. The two imine protons (–CH=N) appeared as a singlet at δ 8.762 ppm. Two aromatic (imine group containing) protons were observed as a singlet at δ 7.584 ppm. Ten benzylic aromatic protons were spotted in the vicinity of δ 7.373–7.285 ppm. The four methylene protons (–CH=N–CH₂–Ar) were seen as a singlet at δ 4.805 ppm, whereas the methyl protons were obtained as a singlet at δ 2.271 ppm.

FT-IR spectral studies: In all two cadmium(II) complexes, the characteristic bands of the cadmium-bound L[–] show the most prominent features. For complexes **1** and **2**, the ν (C=N) stretching frequencies were appeared between 1631 and 1632 cm^{–1}, whereas the free ligand exhibits ν (C=N) stretching at a frequency of 1635 cm^{–1}. In the both complexes, the free ligands' ν (C=N) stretching frequency is moved to a lower value (Fig. 2). These reductions in stretching frequency result from the nitrogen atoms' coordination with the Cd(II) centers, which reduces the double bond characteristics of the C=N bonds [42–45]. For complex **1** stretching vibration of the one non-coordinated hydroxide group was detected at 3444 cm^{–1}. Two consecutive high peaks at 2100 and 2059 cm^{–1} are seen in the infrared spectrum of complex **2**, which correspond to the existence of the terminal (N-bonded) and end-on bridged thiocyanate, respectively [46,47]. This vibration of NH₄⁺, which is typically seen in materials when the ammonium ion is tightly hydrogen bound [49–52], is of sufficient energy to be attributed to the ν_4 (δ {H–N–H}) + ν_6 (lattice torsion) combination vibration [48, 49]. Other frequencies from the NH₄⁺ cation can be seen in a broad band with centers at 1493 cm^{–1} (ν_4) and 3442 cm^{–1} (ν_3 ; ν_{as} {N–H}, including combination bands) [49–52]. The IR spectra of ligand HL as well as two complexes exhibit bands in the 3057–2830 cm^{–1} range that are caused by different C(Ar)–H and C(sp³)–H bond stretching vibrations [53].

Mass spectral studies: The mass spectra of ligand HL and complex **1** exhibited molecular ion peaks at m/z 343.1733 [M+H]⁺ and 1249.2764 [M]⁺, respectively (Fig. 3). These peaks are associated with [H₂L]⁺ and [Cd₂(μ -L)₃]⁺, respectively, due to the fact that the theoretical and observed isotope distribution



Scheme-II: Schematic representation for the preparation of complexes

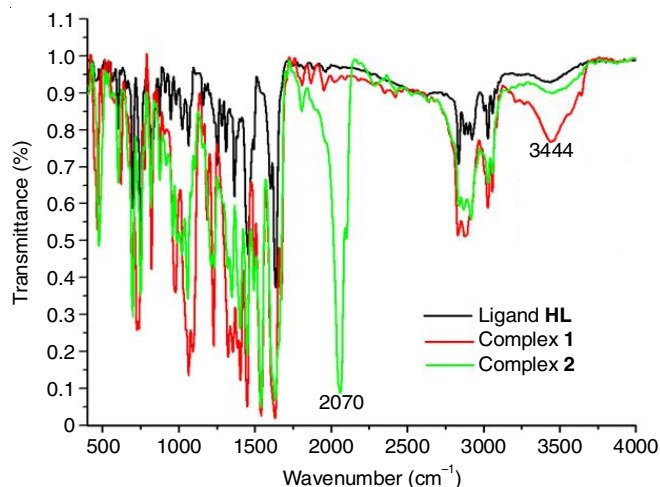


Fig. 2. FT-IR spectra in the region of diagnostic bands of HL, 1 and 2

patterns correspond extremely well. Since complex 2 doesn't have any cation binding sites, it does not exhibit a molecular ion peak.

Electronic spectral studies: The absorption spectrum of HL exhibits a narrow band with maxima at 270 nm and a broad band with maxima at 350 nm at room temperature in DMF (intra-ligand charge transitions). In order to study the HL's ability to bond towards Cd(II), the UV-vis spectra of complex 1 and 2 were also measured in the DMF. The maximum absorbance of HL, which is at 350 nm, reduces (Fig. 4). In addition, a new absorption band with a maximum at 400 nm observed, which can be attributed to the bonding between HL and Cd(II). As a result of Cd(II) being coordinated to the N₂O binding sites, shifts in the UV-vis spectra have taken place [32]. The Cd(II) complexes have d^{10} electronic arrangements; therefore, no band is present that corresponds to $d-d$ electronic transitions. The calculated electronic transitions of complex 1 occur at 378 nm (HOMO to LUMO, *i.e.* from MO number 283 to 284) and at 262 nm (MO number 280 to 289) (Fig. 5).

Description of the structures: By slowly evaporating a solution of dimethylformamide of complex 2, single crystals appropriate for X-ray structural analyses were produced. Table-1 presents a summary of the crystallographic information, while Table-2 lists selected interatomic angles and distances.

[Cd₂(μ-L)₃](OH) (1): The DFT optimized structure of 1 is shown in Fig. 6, together with the atom labeling scheme used. The complex consists of one cation [Cd₂(μ-L)₃]⁺ and one non-coordinated hydroxide anion. Three imine nitrogen atoms from the three ligands and three phenoxide oxygen atoms from the three ligands together bond to Cd(II) and fulfill its hexa coordination. Three phenoxide O atoms in three deprotonated ligand molecules bridge the two Cd(II) centers. The Schiff base ligand is behaving as a two bidentate chelating ligand. The environment around Cd1 center is similar to that of the Cd2 center. The [Cd1 O1 O2 O3 N1 N2 N3] and [Cd2 O1 O2 O3 N4 N5 N6] octahedra in 1 are face-shared with each other to form [Cd₂(μ-L)₃]⁺ dimer (Fig. 7).

There may not be any interaction between two Cd(II) centers given their large distance (3.324 Å) from one another. Average bond lengths for the Cd-N (imine) and Cd-O (phenoxido) atoms

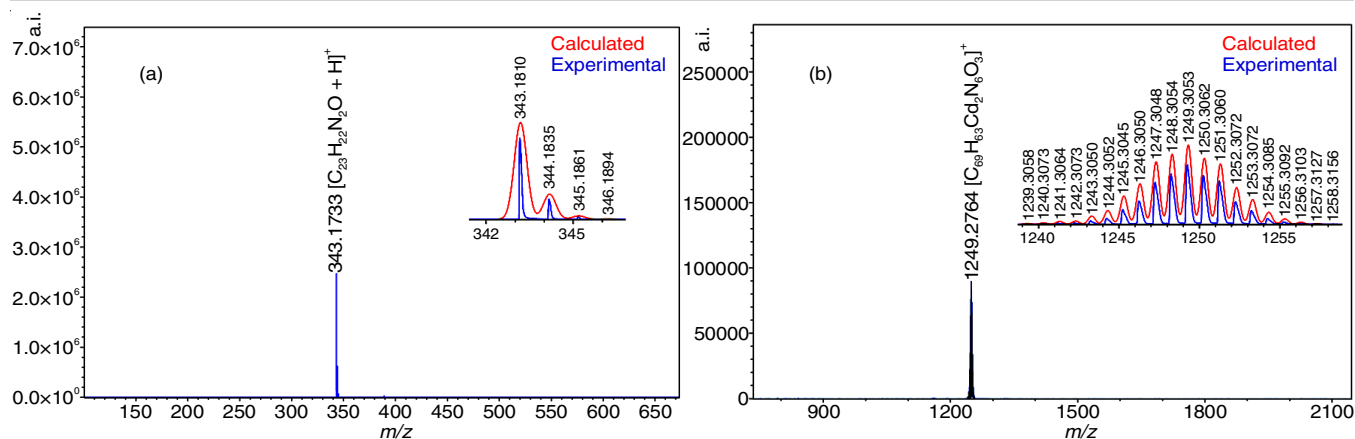


Fig. 3. ESI-MS spectra of (a) HL and (b) complex 1

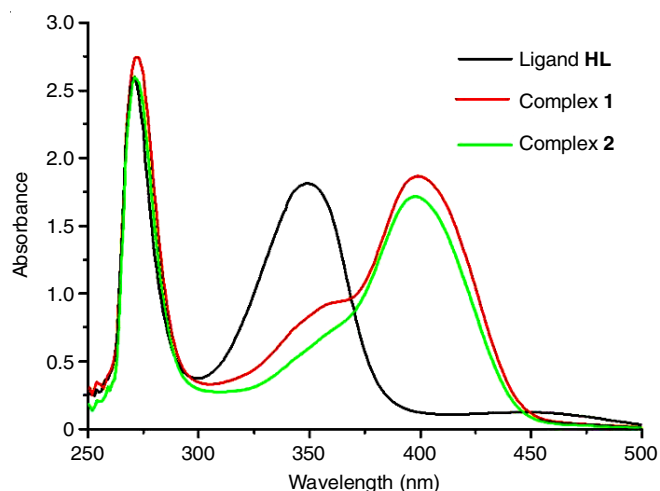


Fig. 4. UV-Vis absorption spectra of HL, 1 and 2

in the octahedral coordination environment are 2.394 Å and 2.318 Å, respectively. These values are comparable to those of other related Cd(II) compounds [43,54-57]. Each hexacoordinated Cd(II) takes a deformed octahedral shape with axial angles that vary from 149.34° to 149.53°, which differs in comparison to the desired 180° value. Compared to the optimum value of 90°, the angles surrounding the Cd(II) in the square base deviate significantly [N1-Cd1-N3 100.27°, N1-Cd1-O3 77.90°, O2-Cd1-N3 110.00° and O2-Cd1-O3 74.28°]. The non-coplanar arrangement of the three ligands around the two Cd(II) ions is caused by the pendant benzyl groups of the ligands. The N-benzyl groups are not included in the optimum mean planes of three ligands, which are angled [44].

[Cd₂(μ-L)₂(μ_{1,1}-NCS)(μ-NH₄⁺)(NCS)₂] (2): Complex 2 crystallizes in the orthorhombic space group *Pbcn*. The molecular structure of the compound is represented in Fig. 8 and Table-2 lists all of the pertinent metric values. The asymmetric unit contains end-on thiocyanate and double phenoxido bridged dinuclear centrosymmetric Cd(II) complex. Each Cd(II) is hepta-coordinated in a highly distorted pentagonal bipyramidal coordination (Fig. 9).

Each Cd(II) is bonded through the two imine nitrogen atoms of two ligands, two phenoxide oxygen atoms of two ligands, one nitrogen end of the terminal SCN⁻ group, one nitrogen

TABLE-2
SELECTED INTERATOMIC DISTANCES (Å) AND
ANGLES (°) FOR COMPLEXES 1 AND 2

1 (Optimized structural parameters)		2	
Distances		Distances	
Cd1-N1	2.39533	Cd1-Cd1*	3.4326(13)
Cd1-N2	2.39452	Cd1-N1	1.815(2)
Cd1-N3	2.39355	Cd1-O1	2.264(6)
Cd1-O1	2.31835	Cd1-O1*	2.283(6)
Cd1-O2	2.31878	Cd1-N3	2.303(8)
Cd1-O3	2.31872	Cd1-N4	2.215(11)
Cd2-N4	2.39467	Cd1-N2	2.289(7)
Cd2-N5	2.39504	Cd1-N5	2.627(10)
Cd2-N6	2.39426	Angles	
Cd2-O1	2.31855	N1-Cd1-O1	37.79(16)
Cd2-O2	2.31874	N1-Cd1-O1*	37.42(15)
Cd2-O3	2.31833	N1-Cd1-N3	115.73(19)
Cd1-Cd2	3.32493	N1-Cd1-N4	133.2(3)
Angles		N1-Cd1-N2	92.3(3)
N1-Cd1-N2	100.40129	N1-Cd1-N5	68.2(3)
N1-Cd1-N3	100.27718	O1-Cd1-O1*	75.2(3)
N2-Cd1-N3	100.41257	O1-Cd1-N3	78.0(2)
N1-Cd1-O1	109.96059	O1*-Cd1-N3	153.1(2)
N1-Cd1-O2	149.52269	O1-Cd1-N2	106.5(2)
N1-Cd1-O3	77.90845	O1*-Cd1-N2	79.3(3)
N2-Cd1-O1	149.43852	O1*-Cd1-N5	71.7(2)
N2-Cd1-O2	77.91729	O1-Cd1-N5	72.0(2)
N2-Cd1-O3	109.87421	N3-Cd1-N5	100.1(2)
N3-Cd1-O1	77.97877	N4-Cd1-O1*	101.4(3)
N3-Cd1-O2	110.00270	N4-Cd1-O1	150.8(4)
N3-Cd1-O3	149.53009	N4-Cd1-N3	102.1(3)
N4-Cd2-N5	100.37807	N4-Cd1-N2	101.2(4)
N4-Cd2-N6	100.22166	N4-Cd1-N5	79.3(3)
N5-Cd2-N6	100.37753	N2-Cd1-N3	108.6(3)
N4-Cd2-O1	149.48677	N2-Cd1-N5	150.4(3)
N4-Cd2-O2	110.09612	Symmetry code * = -½ x, ½ y, 3/2-z	
N4-Cd2-O3	77.91674		
N5-Cd2-O1	77.89589		
N5-Cd2-O2	149.34126		
N5-Cd2-O3	110.04574		
N6-Cd2-O1	110.10190		
N6-Cd2-O2	77.91050		
N6-Cd2-O3	149.39966		
O1-Cd1-O2	74.202205		
O1-Cd1-O3	74.30127		
O2-Cd1-O3	74.28898		
O1-Cd2-O2	74.19940		
O1-Cd2-O3	74.30480		
O2-Cd2-O3	74.29711		

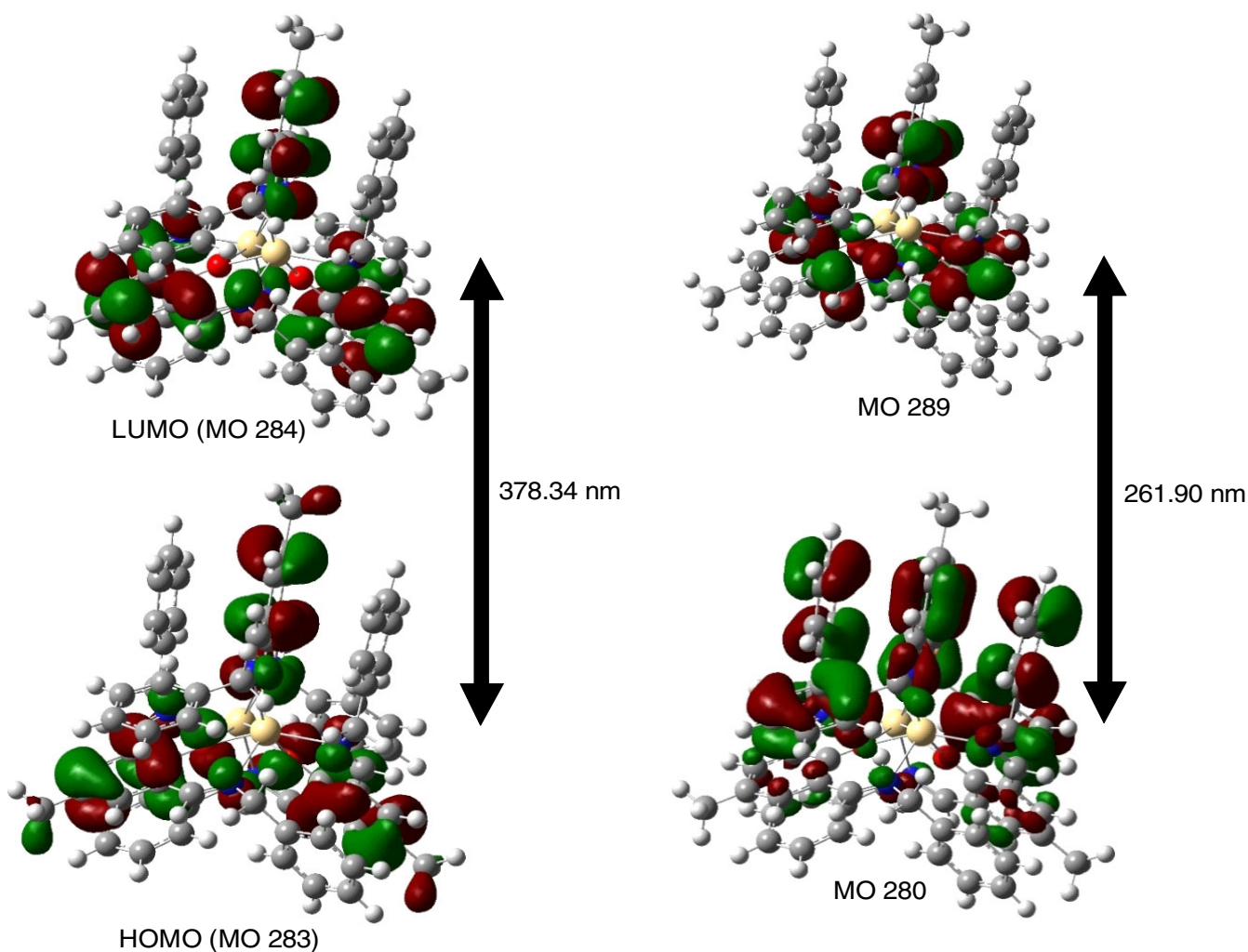


Fig. 5. HOMO-LUMO gap of complex 1

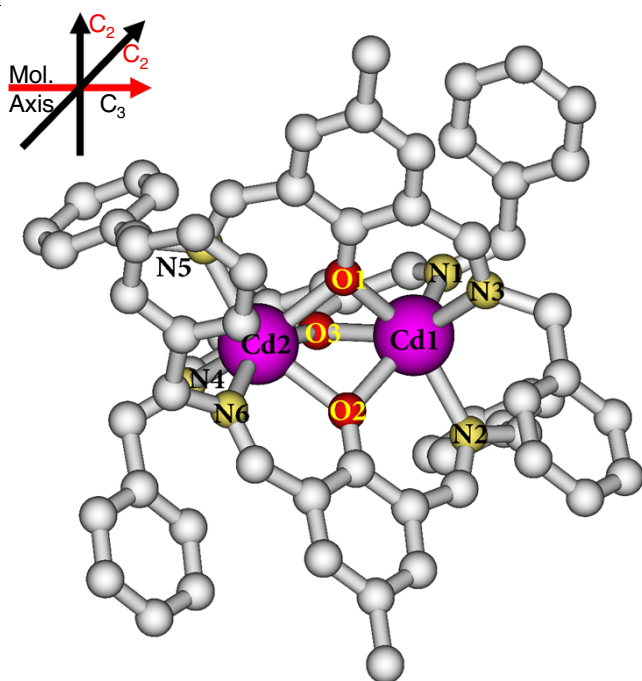


Fig. 6. Optimized structure of complex 1

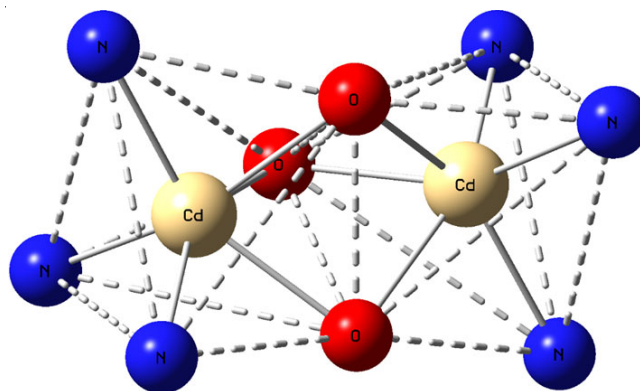


Fig. 7. Distorted octahedral geometry around the Cd(II) in the structure of 1

atom of the end-on bridged SCN⁻ group and one nitrogen atom of the NH₄⁺ ion. The axial N2-Cd1-N5 angle is 150.4°, which departs from the optimum angle of 180°, demonstrating the significant degree of geometric distortion. The atoms N1, O1, O1*, N3 and N4 almost entirely occupy the same plane and make up the equatorial plane of the bipyramid because the sum of the angles formed at the Cd(II) ion in the pentagonal plane is 356.71°. In the direction of the axial N2 atom, Cd1 is

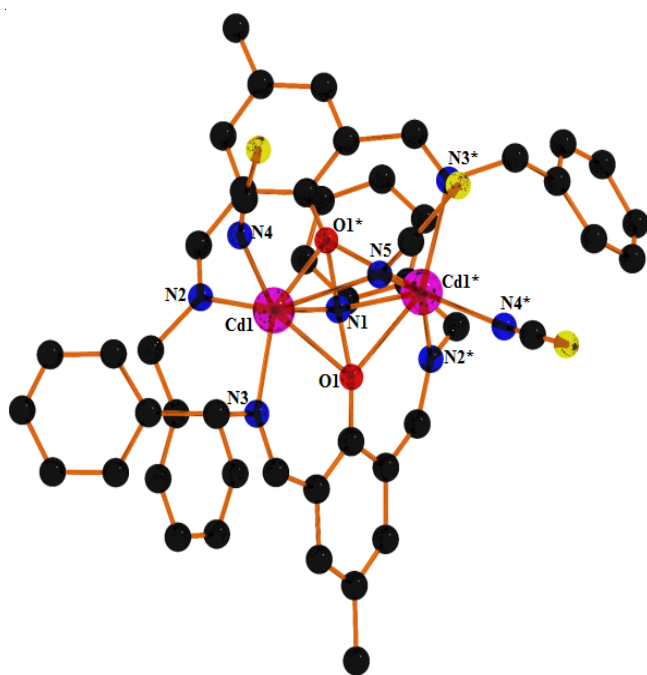


Fig. 8. Molecular structure representation of **2** with atom numbering scheme and H atoms are omitted for clarity, symmetry code (*) $-\frac{1}{2} + x, \frac{1}{2} + y, \frac{3}{2} - z$

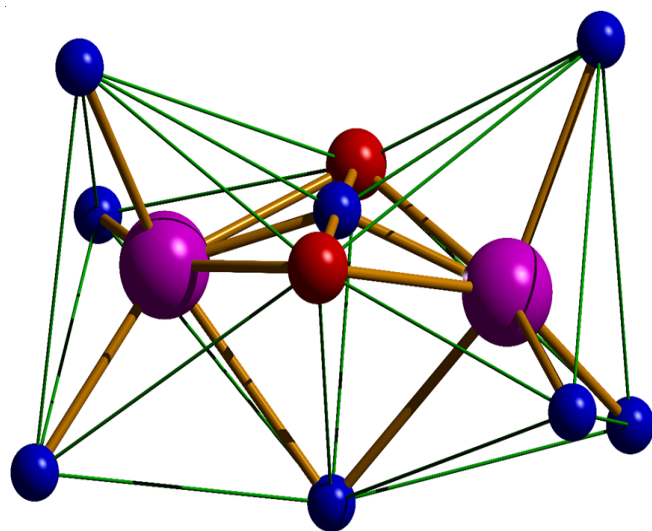


Fig. 9. Distorted pentagonal bipyramidal geometry around the Cd(II) in the crystal structure of **2** Colour code: O = red, N = blue, Cd = pink

located at 0.299 Å above the mean basal plane. In the equatorial plane, the angles surrounding Cd(II) deviate significantly from the optimum value of 72° [N3-Cd1-O1 78.0°, O1-Cd1-N1 37.79°, N1-Cd1-O1* 37.42°, O1*-Cd1-N4 101.4° and N3-Cd1-N4 102.1°]. An interesting feature of this crystal structure is that one NH₄⁺ cation bridges two Cd(II) ions each bonded in a symmetric fashion (1.816 Å). The two hydrogen atoms attached to NH₄⁺ cation form exceptionally strong hydrogen bonds with the two phenoxide oxygen atoms (1.388 Å). The NH₄⁺ cation lies at the center of the diamond core. The [Cd₂O₂] diamond core is produced through the asymmetric bridging [Cd1-O1 = 2.264 Å and Cd1-O1* = 2.283 Å] of two phenoxide oxygens and two Cd(II) ions. The Cd-N_{imine} (imine nitrogen) bond lengths,

related to the imine nitrogen atoms in the ligand, are between 2.289 Å and 2.303 Å. The terminal Cd-N_{NCS} (thiocyanate nitrogen) distances are similar [Cd1-N4 = 2.215 Å; Cd1*-N4* = 2.215 Å] and a little less compared to the av. Cd-N_{imine} bond length [23,43]. The bridging Cd-N_{NCS} bond (2.627 Å) is significantly longer than that of the terminal ones. The N-C-S angles of 173.38° support the essential linearity of the terminal SCN⁻ anions. They are angularly bound to the Cd(II), as suggested by the Cd-N-C angles of 155.81°. The non-coplanar arrangement of the two ligands around the two Cd(II) ions is caused by the pendant benzyl groups of the ligands. The N-benzyl groups are not included in the optimum mean planes of the two ligands, which are angled at 74.03° [44].

Role of NO₃⁻ and SCN⁻ anions for different molecular assemblies: The selection of anions is unquestionably important in controlling the molecular architectures of the resulting complexes as discussed earlier. Therefore, contrasting the impact of the anions in the formation of these Cd(II) compounds should be both fascinating and important. The structure of these two Cd(II) compounds differs from one another in the present investigation for reasons that are mostly related to the anions' nature (bonding capability). The poor bonding capacity of the anion NO₃⁻ with metal ions in complex **1** is illustrated in **Scheme-II** and as a result, it is not able to bond with Cd(II) ions, resulting in the formation of dinuclear complex **1** via ligand coordination only. A versatile bonding types, which includes bridging- or terminal-ligating, may be displayed by the thiocyanate anion. In current work, complex **2** exhibits dinuclearity through the thiocyanate bridge as well as the terminal.

Conclusion

In current study, two Cd(II) Schiff base complexes have been synthesized. Complex **1** features a face-shared octahedral *tris*-ligand complex. Complex **2** is an example of an ammonium cation trapped as well as an end-on thiocyanate-bridged dinuclear complex. Changes in the presence or absence of suitable coordinated anions (NO₃⁻, SCN⁻ and HO⁻) in the reaction medium control variations in the architectures of the complexes. Weakly coordinating NO₃⁻ anion gives only ligand-coordinated complex. The presence of the thiocyanate anion helps form complex containing the thiocyanate bridge as well as the terminal.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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