

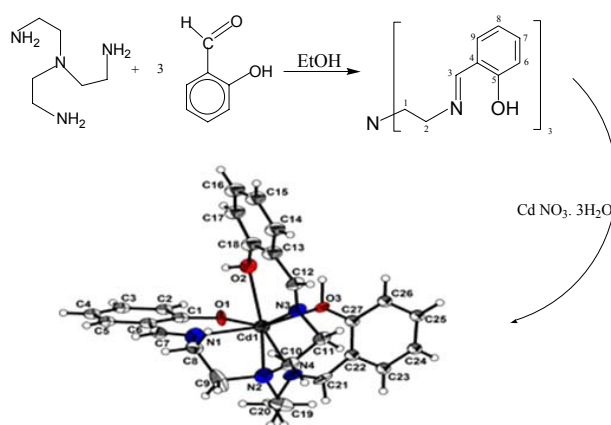
## SYNTHESIS, CHARACTERIZATION AND CRYSTAL STRUCTURE OF Cd(II) COMPLEX WITH POTENTIALLY HEPTADENTATE SCHIFF BASE LIGAND

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The heptadentate  $N_4O_3$ -type Schiff base was derived from the condensation reaction of salicylaldehyde and tris(2-aminoethyl)amine. The heptadentate Schiff base ligand was characterized by elemental analysis,  $^1H$ -,  $^{13}C$ -NMR, IR and UV-VIS spectroscopy techniques. A novel Cadmium (II) complex was also synthesized. The complex was characterized by IR and UV-VIS spectra, and X-ray single crystal diffraction. X-ray structure analysis of the former complex shows mono-capped distorted trigonal antiprism geometry. The complex crystallizes in the monoclinic system with space group  $P2_1/c$ . It is noteworthy that the tripodal heptadentate Schiff base ligand effectively encapsulates the Cadmium (II) ion and enforces seven-coordinate geometry in complex.



### INTRODUCTION

Schiff bases condensation reactions are used in the preparation of an enormous range of macrocyclic compounds. Potential applications of macrocyclic Schiff base as supramolecular devices are contrast agents in magnetic resonance imaging (MRI) and radiopharmaceuticals. It can also be used in nanotechnology and as models for biological systems.<sup>1-4</sup> Macrocyclic tren-Schiff base has gained favor due to both the relatively simple synthesis and the multidentate nature which results in very high binding constants for many d- and f-block metals. As far as we are aware, a range of potentially heptadentate ( $N_4O_3$ ) Schiff base ligand of the type  $N[CH_2CH_2N=CH(2-OH-C_6H_4)]_3$  derived from condensation reactions of tris(2-aminoethyl)amine (tren) with salicylaldehyde or

various ring substituted salicylaldehydes, have been prepared, and their coordination chemistry with a number of lanthanide ions has been extensively investigated.<sup>5,6</sup> This is the first synthesis mononuclear heptadentate complex with Cadmium (II) ion in this report, but in the another reports, The central amine N atom of the tris(2-aminoethyl)amine moiety does not coordinate to the metal atom.<sup>7,8</sup>

### RESULTS AND DISCUSSION

The prepared macrocyclic ligand was synthesized by condensation of salicylaldehyde and tris(2-aminoethyl)amine in ethanol. The reaction proceeded smoothly, producing the corresponding Schiff base ligand in a good yield. The ligand is soluble in common organic solvents.

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The complex is stable at room temperature and soluble in dimethyl sulfoxide (DMSO) and methanol. The purity of the Schiff base ligand and its complex were checked by thin-layer chromatography (TLC). The IR spectrum of the free ligand show the characteristic C=N band in the 1637  $\text{cm}^{-1}$  region which is shifted to lower frequencies in the spectra of the metal complex (1606  $\text{cm}^{-1}$ ), indicating the bonding of nitrogen of the azomethine group to the metal ion which can be explained by the donation of electrons from nitrogen to the empty d-orbital of the metal ion. The ligand spectrum showed band at 3450  $\text{cm}^{-1}$  due to the stretching and deformation of the phenolic OH. Phenolic  $\nu$  (C-O) stretching vibrations appeared at 1247  $\text{cm}^{-1}$  in the Schiff base ligand; however, the signal was shifted in the complex (1022 $\text{cm}^{-1}$ ). This shift confirms the participation of oxygen in the C-O-M bond. The observed new high intensity band at 430  $\text{cm}^{-1}$  in complex is ascribed to  $\nu$  (M-O), suggesting the involvement of the oxygen atoms in the bonding with the metal centers. The electronic spectra of the Schiff base ligand and its complex were recorded in DMSO as a solvent. The absorption bands (in the UV region) at 257, 313 and 414 nm are attributed to transitions  $\pi \rightarrow \pi^*$  (aromatic ring)

and  $n \rightarrow \pi^*$  (C-O) and  $n \rightarrow \pi^*$  (C=N) respectively. In the metal complex, these bands were shifted to some extent, because the imine nitrogen is involved in coordination with the metal ion. In the electronic spectra of complex, we observed the new band at 222 nm, while that was not observed in ligand, the new band is assigned to the ligand to metal charge transfer and confirming the coordination of the ligand to the metal ions. The  $^1\text{H-NMR}$  spectrum of the ligand showed a peak at 13.65 ppm for phenolic OH group. The azomethine proton was seen at 8.23 ppm (singlet). In the  $^{13}\text{C-NMR}$  spectrum of the ligand, the phenolic C-OH observed at 161.33 ppm and the signal due to the azomethine carbon atom appeared at 166.62 ppm. In the X-ray Crystallographic Analysis, each asymmetric unit cell contains four methanol, two nitrate anions, one water and four complexes  $[\text{C}_{112}\text{H}_{131}\text{Cd}_4\text{N}_{18}\text{O}_{23}]$  (Fig. 1). As shown in Fig. 2 (a)  $[\text{Cd1 L}]$ , Cd1-N distances are of two types; an average of 2.31 Å to the three imine nitrogen atoms, and a significantly shorter interaction of 2.67 Å with the apical amine nitrogen. Selected bond distances and angles for the complex are presented in Table 1. Details of the method are given in Table 2.

Table 1

Selected bond lengths (Å) and bond angles (°) for complex Cd 1

Cd1—O1	2.288 (9)	N3—Cd1—O2	75.4 (4)
Cd1—N3	2.298 (12)	N1—Cd1—O2	88.4 (4)
Cd1—N1	2.321 (14)	N4—Cd1—O2	155.2 (4)
Cd1—N4	2.339 (13)	O3—Cd1—O2	82.0 (3)
Cd1—O3	2.403 (10)	O1—Cd1—N2	132.4 (4)
Cd1—O2	2.458 (11)	N3—Cd1—N2	68.7 (4)
Cd1—N2	2.675 (11)	N1—Cd1—N2	70.3 (4)
O1—H501	1.42 (9)	N4—Cd1—N2	69.8 (4)
O2—H201	0.95 (7)	O3—Cd1—N2	124.9 (4)
O3—H301	1.1036	O2—Cd1—N2	132.4 (4)
N1—C7	1.247 (18)	N3—Cd1—N4	110.7 (4)
N3—C12	1.281 (18)	N1—Cd1—N4	112.7 (5)
N4—C21	1.290 (19)	O1—Cd1—O3	88.6 (3)
O1—Cd1—N3	154.5 (4)	N3—Cd1—O3	87.2 (4)
O1—Cd1—N1	77.8 (4)	N1—Cd1—O3	164.6 (3)
N3—Cd1—N1	102.1 (4)	N4—Cd1—O3	74.5 (4)
O1—Cd1—N4	92.3 (4)	O1—Cd1—O2	79.1 (3)

Table 2

X-Ray single-crystal data

Color/shape	Yellow/plate
Chemical formula	$\text{C}_{112}\text{H}_{131}\text{Cd}_4\text{N}_{18}\text{O}_{23}$
M	2546.99
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293

Table 2 (continued)

a, b, c (Å)	15.859 (3), 35.568 (7), 20.299 (4)
$\beta$ (°)	101.47 (3)
V (Å <sup>3</sup> )	11221 (4)
Z	4
$\mu$ (mm <sup>-1</sup> )	0.83
Density (Mg m <sup>-3</sup> )	1.508
Crystal size (mm)	0.5 × 0.2 × 0.35
N° of refl. Measured	49895
N° of unique refl.	16093
N° of observed refl. [I > 2 $\sigma$ (I)]	6443
N° parameters refined	938
Final R indices [I > 2 $\sigma$ ]	R1 = 0.0922 wR2 = 0.1145
R indices for all data	R1 = 0.2242 wR2 = 0.1482
Goodness of fit [all refl.]	0.87
F(000)	5219
$\Delta\rho$ /(e Å <sup>-3</sup> )	1.52, -0.52

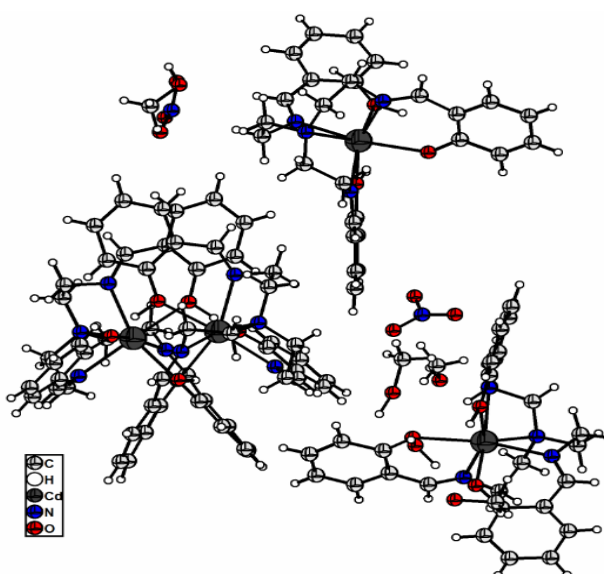
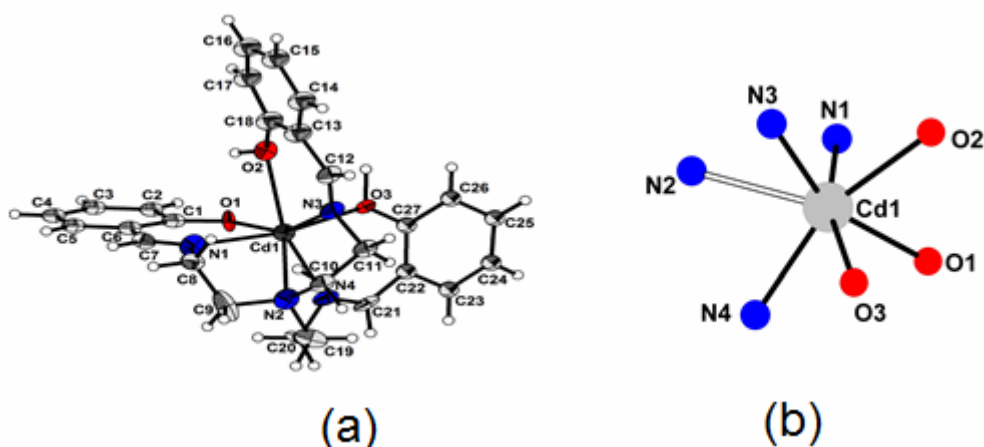
Fig. 1 – Crystal structure of asymmetric unit cell [C<sub>112</sub>H<sub>131</sub>Cd<sub>4</sub>N<sub>18</sub>O<sub>23</sub>].

Fig. 2 – (a) Crystal structure of complex Cd 1. (b) Plot showing the coordination sphere of Cd (II).

These results are similar to the all reported neutral complexes of lanthanide ions with Schiff bases derived from condensation reactions of tren

with various ring substituted salicylaldehydes are seven-coordinate.<sup>5, 6</sup> The Cd1—O1 bond distance is shorter than those of the Cd1—O bonds. The

bond lengths of C=N in complex are 1.290 (19) Å, 1.247 (18) Å and 1.281(18) Å. Also, the dihedral angles of C10—C11—N3—C12, C9—C8—N1—C7 and C19—C20—N4—C21 are 103.1 (16) Å, 120.0 (16) Å and 114.8 (16) Å, respectively. Therefore, we believe that the coordination geometry of cadmium atom in the Schiff base complex under consideration here is probably capped octahedral (or distorted capped trigonal antiprism) (Fig. 2 (b)). And there are several intra-molecular hydrogen bonds which include O1...H501 [1.42(9) Å] and O6...H301 [1.3434 Å], making the compound more stable.

## EXPERIMENTAL

### Materials and spectral measurements

All starting materials were purchased from Aldrich and Merck and were used without further purification. IR spectra were recorded in KBr on a Perkin-Elmer 78 spectrophotometer. UV—VIS spectra were recorded in DMSO on a Shimadzu UV-1601 spectrophotometer. Melting point was obtained on a (Buchi SMP-20 capillary melting point apparatus). NMR spectra (<sup>1</sup>H, <sup>13</sup>C-NMR) were acquired in DMSO-d<sub>6</sub> solution using Bruker AMX 250 MHz spectrometer with tetramethylsilane (TMS) as internal standard for <sup>1</sup>H-NMR analysis.

### Synthesis of [Tris(2-(salicylaldeneimino)ethyl)amine]

The heptadentate ligand [Tris(2-(salicylaldeneimino)ethyl)amine] (trensal) was prepared according to the method described by Joy Chakraborty *et al.*<sup>9</sup> To a solution of salicylaldehyde (0.06 mol, 7.3 g) in absolute ethanol (25 ml) was added tris(2-aminoethyl)amine (0.02 mol, 2.92 g) in absolute ethanol (25 mL). Then the solution was refluxed for 1 h. After evaporation of the solvent, the product (Fig. 3) was obtained as a bright yellow precipitate, [C<sub>27</sub>H<sub>30</sub>N<sub>4</sub>O<sub>3</sub>]. Yield 89.12%, mp 191-193 °C. IR data (ν, cm<sup>-1</sup>): 3450.32 (O-H), 3054.25 (C-H) aromatic, 2939.49 (C-H) aliphatic, 1637.24 (C=N), 1278.47 (C-N), 1068.53 (C-O), 1573.31, 1498.60 (C=C). UV—VIS (λ<sub>max</sub>/nm): 257, 313, and 414. <sup>1</sup>H NMR data (δ, ppm): 2.84 t (6H, 9-H), 3.59 t (6H, 8-H), 8.23 s (3H,

7-H), 6.87 s (3H, 6-H), 6.74 t (3H, 5-H), 7.30 t (3H, 4-H), 6.84 d (3H, 3-H), 13.65 s (3H, OH). <sup>13</sup>C NMR data (δc, ppm): 55.33 (C-9), 57.39 (C-8), 166.62 (C-7), 116.96, 118.75, 118.84, 131.97, 132.60, 161.33 (C-1 to C-6).

### Preparation of complex

To a solution of ligand (3 mmol) in 20 mL ethanol was added hydrated metal nitrate (3 mmol) in 20 ml ethanol. The solution was stirred at room temperature overnight. Then the solution was refluxed for 5 h. The solution was left in Refrigerator overnight. Then the precipitate was filtered off and washed with cold absolute ethanol, and dried in vacuum. Light yellow precipitate. Yield 82.25%, m.p 141-146°C. IR data (ν, cm<sup>-1</sup>): 3166 (C-H) aromatic, 2999 (C-H) aliphatic, 1606 (C=N), 1476(C=C), 1294(C-N), 1022(C-O), 467(M-N), 430(M-O).UV—VIS (λ<sub>max</sub>/nm): 222, 257, 317, 375.

### Crystal structure determination

The X-ray diffraction measurements were made on a STOE IPDS-II diffractometer with graphite monochromated Mo K<sub>α</sub> radiation. The yellow plate shaped crystals were chosen using a polarizing microscope and were mounted on a glass fiber which was used for data collection. Data were integrated using the Stoe X-AREA<sup>10</sup> software package. A numerical absorption correction was applied using the X-RED<sup>11</sup> and X-SHAPE<sup>12</sup> software. The data were corrected for Lorentz and polarizing effects. The structure was solved by direct methods and subsequent difference Fourier maps and then refined on F<sup>2</sup> by a full-matrix least-squares procedure using anisotropic displacement parameters.<sup>13</sup> All hydrogen atoms in structure were added at idealized positions. The atomic factors were taken from the International Tables for X-ray Crystallography<sup>14</sup> All refinements were performed using the X-STEP32 crystallographic software package.<sup>15</sup>

### X-ray data collection and refinement of crystal structure

A little synthesis complex was solved in solution of methanol at 60 °C. The solution was filtered, and then placed in a container with a lid mesh. After one month, the crystals of complex were obtained, which were characterized by X-ray crystallography (CCDC Code: 1402703 contains the supplementary crystallographic data. These data can be obtained from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)).

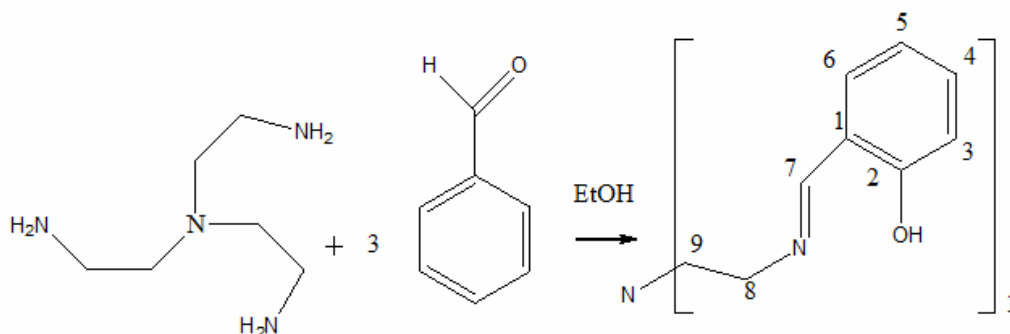


Fig. 3 – Scheme for synthesis of the ligand.

## CONCLUSIONS

In conclusion, a potentially heptadentate ligand ( $N_4O_3$ ) and its Cd(II) complex were synthesized and characterized. X-ray analyzes reveal that Cd atom in this complex is coordinated with three imine, three hydroxyl and unique tertiary nitrogen donor atoms arranged at apices of a distorted capped trigonal antiprism.

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