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Analytical and Crystallographic Parameters of Cd(II) Complexes Derived from Substituted Schiff Bases

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Schiff base ligands were synthesized using 5-nitrosalicylaldehyde with *o*-toluidine, *p*-toluidine, *o*-aminobenzoic acid, *p*-aminobenzoic acid and 2-hydroxy-1-naphthaldehyde with *o*-aminobenzoic acid, *p*-aminobenzoic acid. Cadmium(II) complexes of these Schiff bases were synthesized having the metal:ligand stoichiometry 1:2. The Schiff bases and their metal complexes were characterized for analytical parameters and spectral features. The structures of these complexes were proposed on basis of NMR, UV-Visible, IR spectral data.

Key Words: Schiff base, Cd(II) complexes, Spectral investigations.

INTRODUCTION

Interest in coordination chemistry is increasing continuously with the preparation of organic ligands containing a variety of donor groups[1,2]. Schiff bases are important class of ligands having many applications[3]. In recent years, there has been considerable interest in the chemistry of transitional metal complexes of Schiff bases[4-11]. Researchers[12-17] have reported that some drugs have increased activity when administered as metal complexes and number of metal chelates have been used in anticancer and antifungal reagents. The present study deals with the synthesis and characterization of cadmium(II) with Schiff bases obtained by the condensation of 5-nitro salicylaldehyde with *o*-toluidine, *p*-toluidine, *o*-aminobenzoic acid, *p*-aminobenzoicacid and 2-hydroxy-1-naphthaldehyde with *o*-aminobenzoic acid, *p*-aminobenzoic acid and named as L_1, L_2, L_3, L_4, L_5 and L_6, respectively. The Schiff bases and their Cd(II) complexes were characterized for analytical parameters and spectral features.

EXPERIMENTAL

The chemicals used in the present studies were of analytical grade supplied by S.D. Fine Chem (India) and Fluka (Germany). Elemental analysis was carried out in Carl Erba instrument. The metal content of all metal complexes was determined by reported method[18]. Molar conductivity of ligands and there Cd(II) complexes were recorded using 1×10^{-3} M solutions in DMF on Toshniwal TSM-15 conductivity meter. The electronic absorption spectra of ligands and Cd(II) complexes were recorded in UV-Visible region using DMF as solvent on UV-Visible 2100 spectrometer supplied by M/s Shimadzu Corporation. Magnetic susceptibility measurements were carried out at room temperature by the Gouy balance method using $Co[Hg(SCN)]_4$ as the standard[19]. X-ray diffraction spectra were recorded on X-ray diffractometer supplied by M/s Phillips, Holland.

Synthesis of Schiff bases: The Schiff base ligands L_1 and L_2 were synthesized by refluxing 5-nitrosalicylaldehyde with *o*-toluidine and *p*-toluidine in methanol, respectively. The Schiff base ligands L_3 and L_4 were synthesized by refluxing 5-nitrosalicylaldehyde with *o*-aminobenzoic acid and *p*-aminobenzoic acid in methanol, respectively. Similarly, Schiff base ligands L_5 and L_6 were synthesized by refluxing 2-hydroxy-1-naphthaldehyde with *o*-aminobenzoic acid and *p*-aminobenzoic acid in methanol, respectively. The resulting solution was concentrated then cooled to room temperature and filtered. The yields were recorded in the range of 82 to 88 %.

Synthesis of metal complexes: The cadmium complexes of the Schiff base ligands L_1 and L_2 were prepared by mixing an aqueous solution of cadmium(II) chloride monohydrate with a methanolic solution of the ligand respectively and the cadmium complexes of the Schiff base ligands L_3 and L_4 were prepared by mixing an aqueous solution of cadmium(II) chloride monohydrate with a methanolic solution of the ligand, respectively. Similarly, the cadmium complexes of the Schiff base ligands L_5 and L_6 were prepared by mixing an aqueous solution of cadmium chloride monohydrate with a methanolic solution of the ligand respectively. The resulting mixture was refluxed for 4 h on a waterbath and cooled to room temperature. The pH of the mixture was adjusted to 7 by adding alcoholic ammonia. Subsequently, mixture was digested on waterbath for 1 h whereby solid metal complexes were precipitated and filtered, washed with methanol and dried in oven.

RESULTS AND DISCUSSION

The chemical composition, colour and molar conductance of the ligands and the Cd(II) complexes are summarized in Table-1. The percentage yields of these complexes are satisfactory, ranging between 55 to 65 %. The elemental analysis indicates that the cadmium complexes have a 1:2 metal:ligand stoichiometry. All the complexes are coloured. The solubility of the complexes is very poor in various polar and non-polar solvents. However, they are soluble in DMSO, DMF and nitrobenzene. The molar conductance values are in the range $7.5\text{-}9.4 \times 10^{-3}$ Siemens. The low molar conductance suggests their non-electrolytic nature. Literature[20-26] has reported the complexes with low molar conductance as non-electrolytes. The measurements of magnetic susceptibility suggests that all the complexes are diamagnetic in nature. The complexes are of tetrahedral geometry. Researchers[27-31] have reported tetrahedral geometry for cadmium complexes.

Infrared spectra and UV-visible spectra: In IR spectra of ligand the band pointed in the region 1638-1620 cm^{-1} is assigned to $\nu(C=N)$. The lowering of position of these band in the region 1619-1590 cm^{-1} in corresponding Cd(II) complexes suggest that the azomethine nitrogen atom of ligand is involved in coordination.

TABLE-1
PHYSICAL AND ANALYTICAL DATA OF THE SCHIFF BASES AND THEIR Cd(II) COMPLEXES

Compd. / ligand	m.f. (colour)	m.w. (Yield, %)	m.p. (°C) (Decomp. °C)	Mol. Cond. × 10^{-3} Siemens	Elemental analysis (%): Found (Calcd.)			
					C	H	N	Cd
L_1	$C_{14}H_{12}N_2O_3$	256	162	5.7	65.19	4.28	10.44	-
	(Yellow)	(84.2)	(-)		(65.62)	(4.68)	(10.93)	
$Cd(L_1)_2(H_2O)$	$CdC_{28}H_{22}N_4O_6(H_2O)$	622	-	8.6	53.60	3.27	8.70	17.63
	(Yellow)	(62.4)	(310)		(54.06)	(3.53)	(9.00)	(18.07)
L_2	$C_{14}H_{12}N_2O_3$	256	155	9.8	65.15	4.24	10.47	-
	(Yellow)	(82.4)	(-)		(65.62)	(4.68)	(10.93)	
$Cd(L_2)_2(H_2O)$	$CdC_{28}H_{22}N_4O_6(H_2O)$	622	-	7.5	53.66	3.55	8.68	17.58
	(Yellow)	(55.6)	(315)		(54.06)	(3.53)	(9.00)	(18.07)
L_3	$C_{14}H_{10}N_2O_5$	286	264	5.6	58.28	3.84	9.35	-
	(Orange)	(86.1)	(-)		(58.74)	(4.19)	(9.79)	
$Cd(L_3)_2(H_2O)$	$CdC_{28}H_{18}N_4O_{10}(H_2O)$	682	-	7.8	48.89	2.46	7.88	16.09
	(Yellow)	(60.2)	(342)		(49.31)	(2.64)	(8.21)	(16.48)
L_4	$C_{14}H_{10}N_2O_5$	286	235	7.9	58.30	3.77	9.31	-
	(Yellow)	(83.4)	(-)		(58.74)	(4.19)	(9.79)	
$Cd(L_4)_2(H_2O)$	$CdC_{28}H_{18}N_4O_{10}(H_2O)$	682	-	8.6	49.12	2.39	7.76	15.98
	(Yellow)	(61.4)	(356)		(49.31)	(2.64)	(8.21)	(16.48)
L_5	$C_{18}H_{13}NO_3$	291	189	8.6	73.75	4.11	4.46	-
	(Yellow)	(85.6)	(-)		(74.22)	(4.46)	(4.81)	
$Cd(L_5)_2(H_2O)$	$CdC_{36}H_{24}N_2O_6(H_2O)$	692	-	9.4	62.08	3.24	3.56	15.74
	(Yellow)	(64.2)	(320)		(62.48)	(3.46)	(4.04)	(16.24)
L_6	$C_{18}H_{13}NO_3$	291	210	6.6	73.83	4.27	4.59	-
	(Yellow)	(87.2)	(-)		(74.22)	(4.46)	(4.81)	
$Cd(L_6)_2(H_2O)$	$CdC_{36}H_{24}N_2O_6(H_2O)$	692	-	9.1	62.14	3.39	3.55	15.94
	(Yellow)	(63.6)	(319)		(62.48)	(3.46)	(4.04)	(16.24)

Maurya and Khurana[32] have reported that lowering in the ν(C=N) stretching vibration by 60-20 cm^{-1} when azomethine nitrogen is coordinated with metal ion. Several authors[33-35] have reported lowering of ν(C=N) frequency during chelation. The ligand exhibits ν(C-O) stretching vibration at 1468-1442 cm^{-1}. In metal complexes ν(C-O) phenolic absorption band appears at 1440-1411 cm^{-1}, which is 20-50 cm^{-1} lower than the corresponding ν(C-O) vibration of the free ligand. This indicates bonding of phenolic oxygen to the metal ion[36]. Literature[37-41] have reported that ν(Cd-N) and ν(Cd-O) stretching vibrations appears in the range of 600-500 cm^{-1} and 500-400 cm^{-1}, respectively. The involvement of azomethine nitrogen and phenolic oxygen atom of the ligand in the complexation is further confirmed by appearance of new additional bands in the lower region of IR spectra. The absorption band in the range of 649 to 570 cm^{-1} is assigned to ν(Cd-N) while band appearing in the range of 492-408 cm^{-1} is assigned to ν(Cd-O). The electronic absorption spectra of the complexes are dominated by the broad band corresponds to the intra-ligand transition and charge transfer transition. The IR and UV-Visible spectral data is summarized in Table-2.

TABLE-2
UV-VISIBLE AND IR SPECTRAL DATA OF LIGAND AND METAL COMPLEXES

Ligand / complex	IR spectral data (cm^{-1})					Electronic spectral data (cm^{-1}) (ε = dm^3 mol^{-1} cm^{-1} × 10^4)
	ν(OH)	ν(C=N)	ν(C-O)	ν(Cd-N)	ν(Cd-O)	Change transfer
L_1	3100w	1624s	1468s	-	-	41,665 (2.41)
$Cd(L_1)_2(H_2O)$	3241w	1598s	1411s	607m	438w	31,645 (3.74)
L_2	3085w	1638s	1442s	-	-	46,728 (3.33)
$Cd(L_2)_2(H_2O)$	3305w	1619s	1430s	611m	492w	27,777 (5.41)
L_3	3125w	1625s	1452s	-	-	41,493 (2.60)
$Cd(L_3)_2(H_2O)$	3264w	1610s	1440s	570m	460w	28,735 (6.99)
L_4	3095w	1622s	1449s	-	-	38,610 (1.42)
$Cd(L_4)_2(H_2O)$	3127w	1615s	1415s	649m	457w	29,069 (6.02)
L_5	3030w	1620s	1448s	-	-	47,619 (2.39)
$Cd(L_5)_2(H_2O)$	3258w	1599s	1422s	588m	408w	31,545 (10.09)
L_6	3059w	1628s	1456s	-	-	48,210 (2.88)
$Cd(L_6)_2(H_2O)$	3170w	1590s	1438s	590m	415w	31,250 (5.66)

X-Ray diffractogram: The crystal lattice parameters of the complexes were found out by X-ray diffraction method. The X-ray diffractogram of the complexes were recorded in the range 5 to 60° 2 θ value. The major refluxes were measured and corresponding d-values were obtained. An independent indexing for each of these refluxes were carried out by least square method. The Miller indices (hkl) were calculated and refined using Back-cal programme by computational method and data has been summarized in Table-3. All the complexes are monoclinic with space group P2/m and crystallized by 16 molecules (Z) per unit cell as reported in the literature[42].

TABLE-3
CRYSTAL LATTICE PARAMETERS OF METAL COMPLEXES

Complex	a (Å)	b (Å)	c (Å)	β°	Volume (Å^3)	δobs (g/cm^3)	δcal (g/cm^3)	Porosity (%)
$Cd(L_1)_2(H_2O)$	20.5166 ±0.0580	21.0864 ±0.2434	28.9838 ±0.2619	86.77	12508	1.2762	1.3598	6.14
$Cd(L_2)_2(H_2O)$	20.1981 ±0.0476	22.0554 ±0.2070	30.2696 ±0.3310	86.06	13439	1.2389	1.2656	2.10
$Cd(L_3)_2(H_2O)$	20.1725 ±0.0452	21.9921 ±0.2114	30.3480 ±0.3130	87.61	13415	1.3157	1.3866	5.11
$Cd(L_4)_2(H_2O)$	20.3519 ±0.0382	23.4386 ±0.1433	31.0113 ±0.2413	88.87	12192	1.4631	1.5258	4.10
$Cd(L_5)_2(H_2O)$	20.5792 ±0.0339	21.7278 ±0.0817	28.6115 ±0.1954	86.35	12791	1.3846	1.4751	6.13
$Cd(L_6)_2(H_2O)$	20.3523 ±0.0497	21.2286 ±0.1407	31.0664 ±0.1334	86.15	13395	1.3611	1.4086	3.37

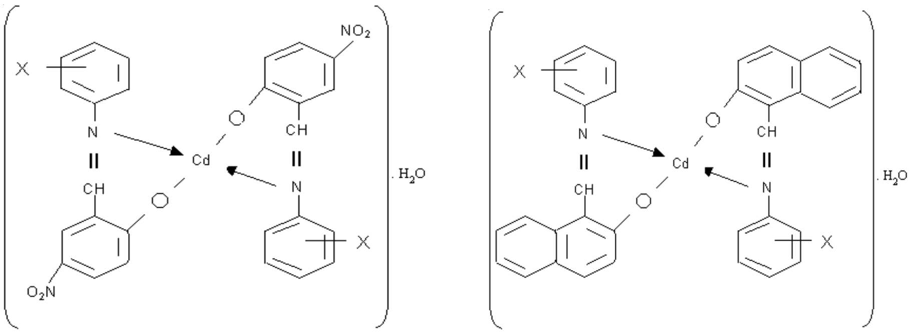
^{1}H NMR Spectra: The proton NMR of Cd(II) complexes were recorded using TMS as a reference in DMSO solvent. From the Table-4, it is clear that the spectral data of the cadmium complexes does not show any proton signal to the phenolic OH range. The PMR of the complexes suggests that the phenolic oxygen participates in the coordination, after complete deprotonation. The assignments to the aromatic proton and the phenolic proton are supported by the literature[43].

TABLE-4
^{1}H NMR SPECTRAL DATA OF LIGAND AND METAL COMPLEXES

Ligand/Complex	^{1}H NMR spectral data (ppm)			
	δ (aromatic)	δ(CH=N)	δ(phenolic)	δ(carboxylic)
$C_{14}H_{12}N_2O_3$	6.48-7.68 (m, 7H)	8.72 (s, 1H)	10.32 (s, 1H)	-
$CdC_{28}H_{22}N_4O_6(H_2O)$	6.64-7.93 (m, 14H)	8.45 (s, 2H)	-	-
$C_{14}H_{12}N_2O_3$	6.54-7.56 (m, 7H)	8.92 (s, 1H)	10.24 (s, 1H)	-
$CdC_{28}H_{22}N_4O_6(H_2O)$	6.68-7.67 (m, 14H)	8.86 (s, 2H)	-	-
$C_{14}H_{10}N_2O_5$	6.81-7.48 (m, 7H)	8.84 (s, 1H)	10.28 (s, 1H)	14.86 (s, 1H)
$CdC_{28}H_{18}N_4O_{10}(H_2O)$	6.92-7.98 (m, 14H)	8.24 (s, 2H)	-	14.45 (s, 2H)
$C_{14}H_{10}N_2O_5$	6.46-7.82 (m, 7H)	8.53 (s, 1H)	10.36 (s, 1H)	14.82 (s, 1H)
$CdC_{28}H_{18}N_4O_{10}(H_2O)$	6.62-7.92 (m, 14H)	8.44 (s, 2H)	-	14.37 (s, 2H)
$C_{18}H_{13}NO_3$	6.53-7.86 (m, 12H)	8.53 (s, 1H)	10.38 (s, 1H)	14.88 (s, 1H)
$CdC_{36}H_{24}N_2O_6(H_2O)$	6.72-7.98 (m, 24H)	8.22 (s, 2H)	-	14.63 (s, 2H)
$C_{18}H_{13}NO_3$	6.84-7.79 (m, 12H)	8.47 (s, 1H)	10.22 (s, 1H)	14.84 (s, 1H)
$CdC_{36}H_{24}N_2O_6(H_2O)$	6.85-7.92 (m, 24H)	8.41 (s, 2H)	-	14.52 (s, 2H)

Conclusion

On basis of analytical data, magnetic measurements and spectral data the complexes may be assigned the following structures as shown in Fig. 1.



where X = o-CH_3, p-CH_3, o-COOH or p-COOH

where X = o-COOH or p-COOH

Fig. 1. Structures of the Cd(II) complexes

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