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Synthesis and spectral characterization of zinc(II) and cadmium(II) complexes of acetone-N(4)-phenylsemicarbazone: Crystal structures of acetone-N(4)-phenylsemicarbazone and a cadmium(II) complex

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1. Introduction

There has been less attention devoted to the synthesis and biological properties of the structurally analogous semicarbazones and their metal complexes, despite the fact that, for some of these compounds, considerable anticonvulsant [1,2], antimicrobial [3] and antitumor [4] activities have been found, and a great advantage of semicarbazone derivatives over their thiosemicarbazone analogues seems to be their lower toxicity. Semicarbazones are compounds having the formula R₂C=N-NH-(CO)-NH₂ formally derived by condenzation of aldehyde or ketone with semicarbazide. A number of arylsemicarbazones were devoid of sedative-hypnotic activity and exhibited anticonvulsant activity with less neurotoxicity [5].

Semicarbazones are compounds with versatile structural features and can coordinate to the metal either as a neutral ligand or as a deprotonated anion. Semicarbazones exist in two tautomeric forms, keto and enol. The coordination possibilities in the semicarbazones are increased if the substituents of the aldehyde or ketone include additional donor atoms. The π -delocalization and the configurational flexibility of their molecular chain can give rise to a variety of coordination modes [6].

Cadmium [7] and zinc form complexes with chloride, acetate, sulfate and carboxy-ligands to yield both charged and neutral com-

ABSTRACT

Seven Zn(II) and Cd(II) complexes of ON donor acetone-N(4)-phenylsemicarbazone (HL) have been synthesized and physico-chemically characterized by partial elemental analyses, molar conductance measurements, infrared, electronic and ¹H NMR spectral studies. The semicarbazone binds the metal as a neutral bidentate ligand in all the complexes. The crystal structures of acetone-N(4)-phenylsemicarbazone and [Cd(HL)₂Cl₂] have been determined by X-ray diffraction studies. The coordination geometry around cadmium(II) in the complex [Cd(HL)₂Cl₂] is distorted octahedral.

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pounds. The Zn(II) ion has been found to be of catalytic importance in enzymatic reactions [8]. A review on 200 crystal structures of Cd(II) complexes showed that cadmium(II) has coordination numbers of 4, 5 and 6 in about 19%, 18% and 56%, respectively [9]. Here we report the synthesis and spectral characterization of the semicarbazone ligand, acetone-N(4)-phenylsemicarbazone (Scheme 1) and its Zn(II) and Cd(II) complexes. It also describes the single crystal X-ray diffraction studies of ligand acetone-N(4)-phenylsemicarbazone and one of its Cd(II) complexes. To the best of our knowledge, there exist only one previous structural report on cadmium(II) complex of semicarbazone [10].

2. Experimental

2.1. Materials

N(4)-phenylsemicarbazide (Sigma–Aldrich) and acetone (Merck) were of analar grade and used as received. The metal salts of Zn(II) and Cd(II) were used as supplied. Solvent used was methanol (Merck) and used without further purification.

2.2. Synthesis of acetone-N(4)-phenylsemicarbazone (HL)

N(4)-phenylsemicarbazide (0.151 g, 1 mmol) in methanol was refluxed with acetone (1 mmol) in presence of four drops of dilute acetic acid for 3 h. On slow evaporation, colorless crystalline



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Scheme 1. Acetone-N(4)-phenylsemicarbazone.

compound formed was filtered, washed with ether and recrystallized from methanol and dried over P_4O_{10} *in vacuo*. The structure has been determined by single crystal X-ray diffraction studies. Melting point = 152 °C.

HL: Elemental Anal. Calc.: C, 62.80; H, 6.87; N, 21.98. Found: C, 62.76; H, 6.56; N, 21.95%.

2.3. Synthesis of complexes

The complexes were prepared by refluxing the methanolic solution of HL with a methanolic solution of appropriate salts for 6 h. The complexes separated were filtered, washed with methanol and finally with ether and dried over P_4O_{10} *in vacuo*. X-ray quality single crystal of the complex [Cd(HL)₂Cl₂] was obtained by slow evaporation of its solution in methanol over a period of one week.

2.4. Physical measurements

Elemental analyses were carried out using a Vario EL-III CHN analyzer at SAIF, Cochin University of Science and Technology, India. Infrared spectra were recorded on a Thermo Nicolet, Avator 370 spectrometer in the range $4000-400 \text{ cm}^{-1}$ using KBr pellets. Electronic spectra were recorded in methanol on a Shimadzu UV-2450 UV–Vis spectrophotometer. The ¹H and ¹³C NMR spectra were recorded using Bruker DRX-500 MHz NMR spectrometer, with CDCl₃ as solvent and TMS as the standard at the SAIF, Indian Institute of Technology, Madras, India. The molar conductances of the complexes in methanol solution (10^{-3} M) at room temperature were measured using a Systronics direct reading conductivity meter.

2.5. X-ray crystallography

Single crystals of compounds HL and [Cd(HL)₂Cl₂] (5) of X-ray diffraction quality were grown from their methanol solutions by slow evaporation at room temperature in air and were found to be monoclinic. The crystallographic data and structure refinement parameters are given in Table 1. The data were collected using a Bruker AXS Kappa Apex2 CCD diffractometer, with graphite-monochromated Mo K α (λ = 0.71073 Å) radiation. The unit cell dimensions and intensity data were recorded at 293 K. The program SAINT/XPREP was used for data reduction and APEX2/SAINT for cell refinement [11]. The structure was solved using siR92 [12] and refinement was carried out by full-matrix least squares on F^2 using SHELXL-97 [13]. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms with the exception of those on nitrogen atoms were geometrically fixed and refined using a riding model. The hydrogen atoms on nitrogen atoms were located from the difference Fourier maps and refined isotropically. Molecular graphics employed were DIAMOND Version 3.1f [14], MER-CURY [15] and PLATON [16].

3. Results and discussion

The elemental analyses data obtained is in good agreement with the stoichiometry of acetone-N(4)-phenylsemicarbazone. HL can exist in the keto or enol form or an equilibrium mixture of the

Table I	Та	ble	1
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Crystal data and structure refinement parameters for HL and [Cd(HL)₂Cl₂].

Parameters	HL	$[Cd(HL)_2Cl_2]$
Empirical formula	C ₁₀ H ₁₃ N ₃ O	$C_{20}H_{26}CdCl_2N_6O_2$
Formula weight (M)	191.23	565.77
Temperature (T) (K)	293(2)	293(2)
Wavelength (Mo Kα) (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
Lattice constants		
a (Å)	13.3696(7)	10.9664(5)
b (Å)	5.4201(3)	12.4218(5)
<i>c</i> (Å)	15.8946(8)	9.4043(4)
α (°)	90.00	90.00
β(°)	114.651(2)	110.3120(10)
γ (°)	90.00	90.00
Volume V (Å ³)	1046.83(10)	1201.41(9)
Ζ	4	2
$D_{\text{calc}}(\rho) (\text{mg/m}^3)$	1.213	1.564
Absorption coefficient, μ (mm ⁻¹)	0.082	1.159
F (0 0 0)	408	572
Crystal size (mm)	$0.30 \times 0.20 \times 0.20$	$0.30 \times 0.20 \times 0.20$
Colour, nature	Colorless, block	White, block
 θ Range for data collection (°) 	1.68–27.53	2.57-32.95
Limiting indices	$-17 \leqslant h \leqslant 17$	$-16 \leqslant h \leqslant 16$
	$-5 \leqslant k \leqslant 7$	$-17 \leqslant k \leqslant 19$
	$-20 \leqslant l \leqslant 20$	$-13 \leqslant l \leqslant 14$
Reflections collected	20274	18000
Independent reflections (R_{int})	2395(0.0229)	4476(0.0229)
Observed reflections $[(I > 2\sigma(I)]]$	1598	3381
Completeness to θ	27.53° (99.6%)	25° (99.9%)
Absorption correction	Semi-empirical from	Semi-empirical from
	equivalents	equivalents
Maximum and minimum transmission	0.936 and 0.901	0.85 and 0.68
Refinement method	Full-matrix least	Full-matrix least
	squares on F^2	squares on F^2
Data/restraints/parameters	2395/0/138	4476/0/152
Goodness-of-fit on F^2	1.025	1.032
Final R indices $[(I > 2\sigma(I))]$	$R_1 = 0.0454$	$R_1 = 0.0262$
	$wR_2 = 0.1151$	$wR_2 = 0.0665$
R indices (all data)	$R_1 = 0.0761$	$R_1 = 0.0401$
	$wR_2 = 0.1477$	$wR_2 = 0.0744$
Largest difference peak and hole (e $Å^{-3}$)	0.139 and -0.177	0.379 and -0.300

 $wR_2 = [\Sigma w (F_0^2 - F_c^2)^2 / \Sigma w (F_0^2)^2]^{1/2}.$

 $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|.$

two since it has an amide -NH-C=(O) function. However, the IR spectrum of HL indicates that in the solid state it remains in the keto form. The semicarbazone HL acts as a neutral bidentate ligand in all the complexes.

The colors and elemental analyses of HL and its complexes are presented in Table 2. The complexes are soluble in CH₃OH, CHCl₃, DMF and DMSO. The conductivity measurements were made in methanol solutions and the values (Table 2) show that the complexes are non-electrolytes.

3.1. Crystal structure of HL

The molecular structure of HL along with atom numbering scheme is given in Fig. 1. Selected bond lengths and bond angles of HL are given in Table 3. The compound crystallized into a monoclinic space group P_{2_1}/n . The molecule exists in the Z conformation with respect to the C(2)–N(1) bond. However, the O(1) and N(1) atoms are in *E* conformation with respect to the N(2)–C(4) bond and hence the semicarbazone moiety as a whole exists in the ZE conformation [17]. A torsion angle of $-179.43(18)^{\circ}$ corresponding to the O(1)–C(4)–N(2)–N(1) moiety implies a *trans* alignment of

Table 2	
Colors and elemental analyses of HL and its Zn(II) and Cd(II) complexe	es.

Compound	Color	Calc. (found) (%)	Calc. (found) (%)		
		С	Н	Ν	
HL	Colorless	62.80(62.76)	6.87(6.56)	21.98(21.95)	
$[Zn(HL)_2Cl_2]$ (1)	White	46.30(46.23)	5.06(5.15)	16.20(16.07)	10.3
$[Zn(HL)_2(CH_3COO)_2]$ (2)	Yellow	50.93(51.01)	5.71(5.84)	14.85(14.89)	10.2
$[Zn(HL)_2(NO_3)_2]$ (3)	Pale yellow	42.01(41.98)	4.59(4.65)	19.60(19.67)	8.3
$[Zn(HL)_2(SO_4)]$ (4)	Pale yellow	44.16(44.11)	4.83(4.73)	15.46(15.49)	12.3
$[Cd(HL)_2Cl_2]$ (5)	White	42.46(42.40)	4.64(4.71)	14.86(14.75)	8.2
$[Cd(HL)_2(CH_3COO)_2]$ (6)	Yellow	47.03(46.91)	5.27(5.39)	13.71(13.77)	11.3
$[Cd(HL)_2(NO_3)_2]$ (7)	White	38.82(38.87)	4.24(4.34)	18.11(18.31)	9.1

^a Molar conductivity, 10⁻³ M methanol at 298 K.



Fig. 1. The molecular structure of HL, showing the atom numbering scheme. Ellipsoids are drawn with 50% probability. Hydrogen atoms are omitted for clarity.

the keto carbonyl O(1) atom in HL. The azomethine bond, C(2)–N(1) 1.270(2) Å is in conformity with a formal C=N double bond (1.28 Å) and the C(4)–O(1) bond distances of 1.220(2) Å, is very close to a formal C=O bond length 1.21 Å. It confirms the existence of the semicarbazone in the keto form in the solid state. The N(1)–N(2) (1.380(2) Å) and N(2)–C(4) (1.354(2) Å) bond distances in HL are intermediate between ideal values of corresponding single [N–N, 1.45 Å; C–N, 1.47 Å] and double bonds [N=N, 1.25 Å, C=N, 1.28 Å], giving evidence for an extended π -delocalization along the semicarbazone chain [18].

The packing of the molecule in a unit cell along the *b*-axis is given in Fig. 2. The assemblage of molecules in the respective manner in the unit cell is resulted by the H-bonding and C-H- π interactions as depicted in Table 4. The intramolecular hydrogen bonding interaction N(3)–H(3)···N(1), leads to the formation of one five membered ring comprising of atoms N(1), N(2), C(4), N(3), H(3) and one intermolecular hydrogen bonding interaction O(1)–H(2)···N(2) is also observed in Fig. 2. A weak intramolecular hydrogen bonding interaction is observed between C(10)–H(10A) and O(1) with an angle of 122°. The C–H– π interactions C(1)–H(1C) \rightarrow Cg(1) (atom numbering according to Fig. 1) at a distance of 2.886 Å contribute stability to the unit cell packing.

3.2. Crystal structure of [Cd(HL)₂Cl₂]

The molecular structure of the complex $[Cd(HL)_2Cl_2]$ along with the atom numbering scheme is represented in Fig. 3 and selected bond lengths and bond angles are summarized in Table 3. The compound crystallizes in a monoclinic space group $P2_1/c$. The molecular structure of Cd(II) semicarbazone complex obtained from single crystal X-ray diffraction studies showed a six coordinate Cd(II) cen-

Table 3	
Selected bond lengths (Å) and bond a	angles (°) of HL and $[Cd(HL)_2Cl_2]$

	HL	$[Cd(HL)_2Cl_2]$
Bond lengths		
C(2)-N(1)	1.270(2)	1.2765(19)
C(4)-O(1)	1.220(2)	1.2292(17)
C(4)-N(3)	1.354(2)	1.3480(19)
C(4)-N(2)	1.354(2)	1.3665(19)
C(5)-N(3)	1.402(2)	1.407(2)
N(1)-N(2)	1.380(2)	1.3770(2)
N(1)-Cd(1)		2.3995(12)
O(1)-Cd(1)		2.3234(11)
Cl(1)-Cd(1)		2.5418(5)
Bond angles		
N(1)-C(2)-C(1)	116.90(16)	117.99(14)
N(1)-C(2)-C(3)	125.59(16)	124.56(15)
O(1)-C(4)-N(3)	123.80(16)	124.42(14)
O(1)-C(4)-N(2)	121.18(15)	121.15(15)
N(3)-C(4)-N(2)	115.02(15)	112.58(13)
C(6)-C(5)-N(3)	116.88(15)	124.79(17)
C(10)-C(5)-N(3)	123.95(15)	115.64(16)
C(2)-N(1)-N(2)	118.58(14)	117.91(12)
C(4)-N(2)-N(1)	120.17(14)	119.54(12)
C(4) - N(3) - C(5)	128.26(15)	129.25(14)
C(2)-N(1)-Cd(1)		131.41(10)
N(2)-N(1)-Cd(1)		110.31(9)
C(4) - O(1) - Cd(1)		116.57(10)
O(1)-Cd(1)-N(1)		70.36(4)
O(1)-Cd(1)-O(1')		180
O(1')-Cd(1)-N(1)		109.64(4)
N(1)-Cd(1)-N(1')		180
O(1)-Cd(1)-Cl(1')		88.36(4)
O(1') - Cd(1) - Cl(1')		91.64(4)
N(1) - Cd(1) - Cl(1')		91.04(4)
N(1')-Cd(1)-Cl(1')		88.96(4)
CI(1') - Cd(1) - CI(1)		180

ter. The Cd(II) center is coordinated by azomethine nitrogen, carbonyl oxygen from the semicarbazone and two chloro ligands. The chloro and semicarbazone ligands serve as monodentate and bidentate ligands. The semicarbazone ligand is coordinated to cadmium as a neutral bidentate N, O-donor forming two five membered chelate rings. The bond angles of O(1)-Cd(1)-O(1'), N(1)-Cd(1)-N(1') and Cl(1)-Cd(1)-Cl(1') are 180° so the complex is centrosymmetric with the Cd atom situated on an inversion centre. The distortion from an ideal octahedral stereochemistry is suggested by the values for the orthogonal bite angles N(1)-Cd(1)-O(1) and N(1')-Cd(1)-O(1') (70.36(4)°). The two semicarbazones and chloro ligands have occupied trans position. The Cd(II) ion in the monomer exhibit distorted octahedral geometry with O(1), N(1), O(l'), N(1') atoms defining the equatorial plane and the terminal chlorine atoms takes the axial position. It is interesting to note that the azomethine and carbonyl bond distances are slightly increased in the complex, when compared to the corresponding values in the free ligand HL, and this supports coordination.



Fig. 2. Unit cell packing diagram of HL viewed along b-axis.

Table 4

Interaction parameters of the compound HL.

D-H-A	D–H (Å)	H–A (Å)	D-A (Å)	D-H-A (°)
H bonding N(2)-H(2)-O(1) ^a N(3)-H(3)-N(1) Equivalent position	0.86 0.86 code: a = -x, 2	2.03 2.20 2 - y, 2 - z	2.870(2) 2.620(2)	164 110
X-H(I)-Cg(J)	H···Cg	(Å)	X–H· · ·Cg (°)	X···Cg (Å)
$CH-\pi$ interactions $C(1)-H(1C))-Cg(1)^b$ 2.886 135.59 Equivalent position code: $b = \frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$ $Cg(1) = C(5), C(6), C(7), C(8), C(9), C(10)$				3.634(2)

D = donor, A = acceptor, Cg = centroid.



Fig. 3. Structure of $[Cd(HL)_2Cl_2]$ showing the atom numbering scheme. Ellipsoids are drawn with 50% probability. Hydrogen atoms are omitted for clarity.

In the case of this Cd(II) complex the coordination of carbonyl oxygen from the semicarbazone ligand occurs through ketonic form. It was confirmed by the C(4)–O(1) bond length 1.2292(17) Å, which is slightly longer than the standard C=O bond length (1.21 Å) [19] and the N(2)–C(4) bond length 1.3665(19) Å. which is considerably shorter than the standard N–C single bond

length (1.47 Å). The Cd–O, Cd–N and Cd–Cl bond distances are 2.3234(11) Å, 2.3995(12) Å and 2.5418(5) Å. The bond angle, O(1)–Cd(1)–N(1) is 70.36(4)° indicating that the compound has distortion from octahedral geometry. The azomethine bond, C(2)–N(1) 1.2765(19) Å is very close to an ideal C=N double bond (1.28 Å). The Cd–N azomethine bond length is comparable with the previously reported Cd-semicarbazone complex [10]. The N(1)–N(2) 1.3770(17) Å and N(2)–C(4) 1.3665(19) Å bond distances in the complex are intermediate between ideal values of corresponding single and double bonds, giving evidence for an extended π -delocalization along the semicarbazone chain.

The packing of the molecule is stabilized by intermolecular hydrogen bonding interactions are given in Table 5. Two intermolecular hydrogen bonding interactions $[N(3)-H(3)\cdots Cl(1)]$ and $[N(2)-H(2)\cdots Cl(1)]$ [symmetry code: x, 1/2 - y, z - 1/2; with a $H(3)\cdots Cl(1)$ and $H(2)\cdots Cl(1)$ distance 2.40(2) Å and 2.53(2) Å] are observed in Fig. 4. The two chloro ligands attached to the metal ion are intermolecularly hydrogen bonded to the hydrogens of N(2) and N(3) of the N(4)-phenylsemicarbazone moiety.

3.3. IR spectra

The tentative assignments for the IR spectral bands useful for determining the ligand's mode of coordination are listed in Table 6. The strong band at 3375 cm⁻¹ in the spectrum of HL has been assigned to $v(^{4}NH)$, shift to lower energies in all the complexes [20]. The medium band at 3196 cm⁻¹ in the ligand due to $v(^{2}NH)$ vibration indicates that the ligand remains in the keto form in the solid state [21]. In all the complexes, the presence of a band corresponds

 Table 5

 H-bonding interactions of the compound [Cd(HL)₂Cl₂].

D-H-A	D–H (Å)	H–A (Å)	D-A (Å)	D-H-A (°)
H bonding N(2)–H(2)–Cl(1) N(3)–H(3)–Cl(1) ^a Equivalent position c	0.81(2) 0.80(2) rode: a = x, 1/2	2.53(2) 2.40(2) $2 - y, -1/2 + z$	3.2875(15) 3.1843(15)	155.5(19) 166.2(18)

D = donor, A = acceptor.



Fig. 4. Intermolecular bonding interactions of [Cd(HL)₂Cl₂] (hydrogen atoms other than involved in hydrogen bonds are removed for clarity).

to $v(^{2}NH)$ vibration indicates that the semicarbazone is coordinated in the neutral form. A sharp band at 1682 cm⁻¹ in the ligand has significant contribution from C=O stretching vibration and the presence of band in the region 1662–1642 cm⁻¹ supports the keto form of the ligand in these complexes [10].

A sharp band at 1591 cm⁻¹ in the semicarbazone can be attributed to the characteristic >C=N group. On coordination of the azomethine nitrogen, the IR stretching frequency v(C=N) at 1591 cm⁻¹ shows an upward shift and is observed in the region 1598–1620 cm⁻¹ for complexes [22–24]. It is further supported by the appearance of bands in the region 408–416 cm⁻¹ and 445–456 cm⁻¹ which correspond to v(Zn-N) [25] and v(Cd-N) [26]. The increase in the v(N-N) value in the spectra of the complexes is due to the increase in double bond character offsetting the loss of electron density *via* donation to the metal and it is a confirmation of the coordination of the ligand through the azomethine nitrogen.

The acetato complexes **2** and **6** show asymmetric stretching bands at 1571 and 1565 cm⁻¹ and symmetric stretching bands at 1368 and 1372 cm⁻¹ suggest the presence of unidentate type of acetato group [27,28]. The nitrato complexes **3** and **7** have two strong bands at 1331 and 1448 cm⁻¹, with a separation of 117 cm⁻¹ corresponding to v_1 and v_4 and a medium band at 1031 cm⁻¹ corresponding to v_2 of the nitrato group [28]. In com-

l able 6								
IR spectral	assignments	for HL	and it	s Zn(II) and	Cd(II) comp	lexes.

Compound	v(C=0)	v(C=N)	$v(^{2}NH)$	$v(^{4}NH)$	v(N-N)	v(M-N)
HL	1682	1591	3196	3375	1129	-
[Zn(HL) ₂ Cl ₂] (1)	1643	1601	3113	3276	1148	416
$[Zn(HL)_2(CH_3COO)_2]$	1655	1599	3154	3249	1150	408
(2)						
$[Zn(HL)_2(NO_3)_2]$ (3)	1657	1600	3158	3268	1143	415
$[Zn(HL)_2(SO_4)]$ (4)	1648	1598	3110	3276	1177	416
$[Cd(HL)_2Cl_2](5)$	1662	1620	3148	3249	1142	445
$[Cd(HL)_2(CH_3COO)_2]$	1661	1603	3150	3255	1153	456
(6)						
$[Cd(HL)_2(NO_3)_2](7)$	1652	1599	3157	3298	1139	453

plex **4**, the spectral data indicates the bidentate nature of the sulphate anion.

The distorted octahedral structure of the complex $[Cd(HL)_2Cl_2]$ was established by single crystal X-ray diffraction studies. For the other complexes the coordination geometry was arrived at by IR spectral and conductance data. The conductance data of the complexes support the non-electrolytic nature of the complexes. The IR spectral data show that the other complexes are also hexa coordinate with the semicarbazone acting as a neutral bidentate ligand satisfying the four coordination positions and the ions satisfying the other two coordination sites.

3.4. Electronic spectra

The electronic absorption bands of the Zn(II) and Cd(II) complexes, recorded in methanol solution, are given in Table 7. The semicarbazone HL has a ring $\pi \rightarrow \pi^*$ band at 41,150 cm⁻¹ and a band at 33,960 cm⁻¹ due to $n \rightarrow \pi^*$ transition associated with the azomethine linkage. These bands in the complexes have shown a bathochromic shift due to the donation of a lone pair of electrons to the metal and hence the coordination of azomethine [29]. The moderately intense broad bands for the complexes in the region 24,000–28,900 cm⁻¹ are assigned to Zn(II) \rightarrow O and Cd(II) \rightarrow O metal to ligand charge transfer transition (MLCT). The complexes show no appreciable absorption in the region below 22,000 cm⁻¹ in methanol solution, in accordance with the d¹⁰ electronic configuration of the Zn(II) and Cd(II) ions.

3.5. ¹H NMR spectra

The ¹H NMR signals of the ligand HL and one each of the Zn(II) and Cd(II) complexes recorded in CDCl₃ are listed in Table 8. The ¹H NMR spectrum of HL, shows a singlet, integrating as one hydrogen, at δ = 8.21 ppm which is assigned to the proton attached to the N(2)H. The N(4)H is observed as a singlet at δ = 8.04 ppm. The low field position of N(4)H can be attributable to the deshielding caused by phenyl group. This downfield shift also explains the intramolecular H-bonding interaction with nitrogen atom N(1). This is confirmed from the crystal structure. Hydrogen bonding decreases the electron density around the proton and thus moves the proton absorption to a lower field. Absence of any coupling interaction by N(2)H and N(4)H protons due to lack of availability of protons on neighboring atoms render singlet peaks for the imine protons. The ligand does not show any peak attributable to –OH proton indicating that it exists in the keto form. IR spectral data are also in con-

Table 7		
Electronic spectral assignments, $\lambda(cm^{-1})$	for HL and its Zn(II)	and Cd(II) complexes.

Compound	$\pi \to \pi^*$	$n \to \pi^*$	MLCT
HL	41,150	33,960	-
$[Zn(HL)_2Cl_2]$ (1)	43,010	34,130	28,940
$[Zn(HL)_2(CH_3COO)_2]$ (2)	46,940	34,430	25,920
$[Zn(HL)_2(NO_3)_2]$ (3)	46,940	40,980	24,090
$[Zn(HL)_2(SO_4)]$ (4)	45,770	40,810	26,040
$[Cd(HL)_2Cl_2]$ (5)	45,450	40,840	25,740
$[Cd(HL)_2(CH_3COO)_2]$ (6)	44,840	34,130	28,940
$[Cd(HL)_2(NO_3)_2]$ (7)	45,350	40,660	28,940

Table 8				
¹ H NMR (CDCl ₃) assign	ments of HL and	its Zn(II) and Co	d(II) complexes (δ	in ppm).

Compound	$-^{2}NH$	$-^{4}NH$	$-^{1}CH_{3}$	$-{}^{3}CH_{3}$	Aromatic protons
HL	8.21	8.04	2.03	1.90	7.02–7.50
$[Zn(HL)_2Cl_2]$ (1)	8.45	8.30	2.04	1.91	7.03–7.52
$[Cd(HL)_2Cl_2]$ (5)	8.48	8.31	2.04	1.91	7.04–7.52

Table 9	
^{13}C NMR (CDCl ₃) assignments of HL (δ in ppm)	

Compound	C(4)	C(2)	C(5)	C(7) and C(9)	C(8)	C(6) and C(10)	C(3)	C(1)
HL	153.69	147.72	138.25	128.90	123.10	119.36	25.28	16.52

firmity with these observations. Two singlets at δ values 2.03 and 1.90 ppm are attributed to the methyl protons which are chemically and magnetically equivalent. The resonances for the phenyl group appear as triplet at 7.02 and 7.33 ppm for para and meta protons and as doublet at 7.53 ppm for ortho phenyl protons.

In the ¹H NMR spectra of the complexes, a signal observed as singlet at δ value 8.45 and 8.48 ppm is assigned to the proton attached to the nitrogen atom N(2). The presence of signal due to N(2)H in the complexes indicates that there is no enolization of ligand in the complexes. Another singlet observed at δ value 8.30 and 8.31 ppm is assigned to the N(4) proton. The N(4) phenyl protons observed within the range 7.04–7.52 ppm in both the complexes. Also two singlets observed at δ values 2.04 and 1.91 ppm are assigned to methyl protons.

3.6. ¹³C NMR spectrum

The ¹³C NMR spectrum provides direct information about the carbon skeleton of the molecule is given in Table 9. There are 8 unique carbon atoms in the molecule, which give a total of 8 different peaks in the 13 C NMR spectrum. The C(4) carbon atom resonance is observed farthest downfield of 153.69 ppm, resultant of the conjugative effect of the -N(1)-N(2)-C(0)-N(4) - semicarbazone skeleton. The non-protonated carbon atom at C(2) is shifted downfield in the spectrum (δ 147.72 ppm). The methyl carbon atoms are observed at δ 25.28 and 16.52 ppm. The three different types of aromatic carbons on the substituted phenyl ring are clearly distinguishable in the ¹³C NMR spectrum. The peak corresponding to the para positioned carbon atom C(8) is observed rather upfield when compared to its ortho [C(6) and C(10)] and meta [C(7) and C(9)] counterparts. The N(4) phenyl resonances are: C(6) and C(10), 119.36 ppm; C(7) and C(9), 128.90 ppm; C(8), 123.10 ppm; C(5), 138.25.

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Appendix A. Supplementary data

CCDC 750911 and 751638 contain the supplementary crystallographic data for compounds HL and $[Cd(HL)_2Cl_2]$. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/ retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2010.03.011.

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