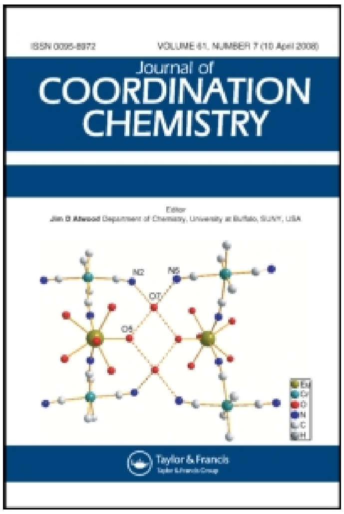

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New homoleptic metal complexes of Schiff bases derived from 2,4-di-*p*-tolyl-3-azabicyclo[3.3.1]nonan-9-one

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New bidentate Schiff-base ligands 2-(2,4-di-*p*-tolyl-3-azabicyclo[3.3.1]nonan-9-ylidene)hydrazinecarbothioamide HL^1 and 2-(2,4-di-*p*-tolyl-3-azabicyclo[3.3.1]nonan-9-ylidene)hydrazinecarboxamide HL^2 were synthesized from the condensation of 2,4-di-*p*-tolyl-3-azabicyclo[3.3.1] nonan-9-one with thiosemicarbazide and semicarbazide, respectively. Homoleptic complexes of these ligands, of general formula $K[Cr(L^n)_2Cl_2]$, $K_2[Mn(L^n)_2Cl_2]$, $K_2[Fe(L^1)_2Cl_2]$ and $[M(L^n)_2]$ (where M = Co(II), Ni(II) Cu(II), Zn(II), Cd(II), and Hg(II) ions; $n = 1$ or 2) are reported. The mode of bonding and overall geometry of the complexes were determined through IR, UV-Vis, NMR and mass spectral studies, magnetic moment measurements, elemental analysis, metal content, and conductance. These studies revealed octahedral geometry for Cr(III), Mn(II), and Fe(II) complexes, square planar for Cu(II), Co(II), and Ni(II) complexes and tetrahedral for Zn(II), Cd(II), and Hg(II) complexes.

Keywords: Schiff bases; 2-(2,4-Di-*p*-tolyl-3-azabicyclo[3.3.1]nonan-9-ylidene)hydrazinecarbothioamide; 2-(2,4-Di-*p*-tolyl-3-azabicyclo[3.3.1]nonan-9-ylidene)hydrazinecarboxamide; Homoleptic metal complexes; Structural study

1. Introduction

Schiff-base compounds have great importance in coordination chemistry due to their ability to form a range of complexes with applications in different fields [1, 2]. Schiff-base metal complexes have applications in biomedical [3, 4], biomimetic, and catalytic systems [5, 6], and in supporting liquid crystalline phases [7]. One approach in the field of Schiff-base chemistry has been to investigate the synthesis of semi- and thiosemicarbazones and their metal complexes. Semi- and thiosemicarbazones have variable bonding modes, ability to form stable chelates with metal ions and structural diversity [8–10]. The sulfur, oxygen, and nitrogen may be involved in coordination providing a useful model for bioinorganic processes [11, 12]. These compounds are also of interest due to their pharmaceutical applications and biological activities [13],

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including enzyme inhibition [14]. The biological activity of uncomplexed semi- and thiosemicarbazones can be increased significantly by the formation of metal complexes [15, 16]. In this article we report the synthesis and characterization of two Schiff-base ligands, 2-(2,4-di-*p*-tolyl-3-azabicyclo[3.3.1]nonan-9-ylidene)hydrazinecarbothioamide HL^1 and 2-(2,4-di-*p*-tolyl-3-azabicyclo[3.3.1]nonan-9-ylidene)hydrazinecarboxamide HL^2, and some of their homoleptic metal complexes. Biological activities of the ligands and their metal complexes against bacteria and fungi are currently under investigation and will be reported elsewhere.

2. Experimental

2.1. *Materials*

All reagents were commercially available and used without purification. Solvents were distilled from appropriate drying agents immediately prior to use.

2.2. *Physical measurements*

Elemental analyses (C, H, and N) were carried out using a Heraeus instrument (Vario EL). Melting points were obtained using a Buchi SMP-20 capillary melting point apparatus and are uncorrected. IR spectra were recorded as KBr or CsI discs using a Shimadzu 8300 FTIR spectrophotometer from 4000 to 250 cm^{-1}. Electronic spectra were measured from 200 to 900 nm for 10^{-3} M solutions in DMSO at 25°C using a Shimadzu 160 spectrophotometer. Mass spectra were obtained by positive Fast Atom Bombardment (FAB) using a VG autospec micromass spectrometer. NMR spectra (^{1}H, ^{13}C, COSY, ^{13}C–^{1}H correlated NMR) were acquired in DMSO-d_6 using Bruker AMX400 MHz and JEOL Lambda 400 MHz spectrometers with tetramethylsilane (TMS) as an internal standard for ^{1}H NMR analysis. Metals were determined using a Shimadzu (A.A) 680 G atomic absorption spectrophotometer. Chloride was determined using the potentiometer titration method using a 686–Titro processor–665Dosimat–Metrohm Swiss. Conductivity measurements were made with DMSO solutions using a Jenway 4071 digital conductivity meter, and at room temperature (25°C) magnetic moments were measured with a magnetic susceptibility balance (Johnson Matthey Catalytic System Division).

2.3. *Synthesis*

2.3.1. Preparation of 2,4-di-*p*-tolyl-3-azabicyclo[3.3.1]nonan-9-one. A mixture of 4-methylbenzaldehyde (4.0 mL, 38 mmol), ammonium acetate (1.0 g, 19 mmol), and cyclohexanone (2.0 mL, 19 mmol) in methanol (20 mL) was refluxed for 1 h. An orange solid formed was collected by filtration and washed with methanol (5 mL) and then with diethyl ether (10 mL), and dried under vacuum to give (2.5 g, 95%), m.p. 122–125°C. IR data (cm^{-1}), 3298 ν(N–H), 3022 $\nu(C\text{–}H)_{arom}$, 2860 and 2937 $\nu(C\text{–}H)_{alip}$, 1704 ν(C=O), 1594 ν(C=C), 1510 δ(N–H). NMR data (ppm), δ_H(400 MHz, DMSO-d_6): 1.75 (4H, m, $C_{8,8'}\text{–}H$); 2.1 (2H, m, $C_9\text{–}H$); 2.3 (6H, s, $2 \times CH_3$), 2.6–2.8 (2H, dt, J_{HH} 4 Hz, $C_{7,7'}\text{–}H$), 2.9 (2H, s, $C_{Z,Z'}$–*H*), 4.3 (1H, s, N–*H*), 7.3 (4H, d, J_{HH} 8 Hz, $C_{2,2';\ 6,6'}$–*H*), 7.4 (4H, d, J_{HH} 8 Hz, $C_{5,5';}$ $C_{3,3'}$–*H*); δ_C(100.63 MHz, DMSO-d_6): 20.8 ($2 \times CH_3$), 22.4 ($C_{8,8'}$), 24.9 (C_7), 26.3 ($C_{7'}$), 27.8 ($C_{Z,Z'}$), 30.5 (C_9), 126.6 ($C_{5,5'}$), 128.4 ($C_{3,3'}$), 132.6 ($C_{2,2',6,6'}$), 135.7 ($C_{1,1'}$), 136.3 ($C_{4,4'}$), 206.1(C=O).

2.3.2. Preparation of HL^1. Thiosemicarbazide (0.06 g, 0.65 mmol) dissolved in methanol (20 mL) was added to a solution of 2,4-di-*p*-tolyl-3-azabicyclo[3.3.1]nonan-9-one (0.2 g, 0.62 mmol) in methanol (30 mL). Concentrated hydrochloric acid (2 mL) was then added and the mixture was heated under reflux for 6 h. Slow evaporation gave yellow crystals that were collected by filtration, washed with cold methanol (2 mL), then diethyl ether (10 mL) and dried. Yield (0.15 g, 62%), m.p. 160°C. NMR data (ppm), δ_H(400 MHz, DMSO-d_6): 1.1(4H, m, $C_{8,8'}$–*H*), 1.7 (2H, d, J_{HH} 4, C_9–*H*), 2.3 (6H, s, $2 \times CH_3$), 2.17 (2H, d, J_{HH} 7.2 Hz, $C_{7,7'}$–*H*), 2.9 (2H, t, $C_{Z,Z'}$–*H*), 6.1 (2H, s, $N_{(4)}$–*H*), 7.3 (4H, d, J_{HH} 7.4 Hz, $C_{3,3',5,5'}$–*H*), 7.4 (4H, d, J_{HH} 7.4 Hz, $C_{2,2',6,6'}$–*H*), 7.6 (1H, s, $N_{(2)}$–*H*); δ_C(100.63 MHz, DMSO-d_6): 20.8 ($2 \times CH_3$), 22.4 ($C_{8,8'}$), 27.7 (C_9), 27.8 ($C_{7,7'}$), 34.5 ($C_{Z,Z'}$), 129.1 ($C_{2,2',6,6'}$), 130.2 ($C_{3,3',5,5'}$), 132.6 ($C_{1,1'}$), 135.5 ($C_{4,4'}$), 139.5 (C=N), 188.9 (C=S). The positive FAB mass spectrum of HL^1 showed the parent ion peak at m/z 393.7 corresponding to $(M+H)^+$ and the following fragments: 343.7 (26%) $[M-CH_3SH]^+$, 300 (100%) $[M-\{(CH_3SH+CH_3CH=NH)+H\}]^+$, 241 (36%) $[M-\{(CH_3SH+CH_3CH=NH+(CH_3)_2CHNH)\}]^+$, 104 (7%) $[M-\{(CH_3SH+CH_3CH=NH+(CH_3)_2CHNH)+C_6H_5(CH_2)_2NHNH_2\}]^+$.

2.3.3. Preparation of HL^2. The method used to prepare HL^2 was similar to that used for HL^1, but semicarbazide was used in place of thiosemicarbazide. The product (0.133 g, 56%) was isolated as yellow crystals, m.p. 162°C. NMR data (ppm), δ_H(400 MHz, DMSO-d_6): 1.1 (4H, m, $C_{8,8}'$–*H*), 1.7 (2H, d, J_{HH} 4 Hz, C_9–*H*), 2.35 (6H, s, $2 \times CH_3$), 2.2 (2H, d, J_{HH} 7.2 Hz, $C_{7,7'}$–*H*), 2.9 (2H, t, $C_{Z,Z'}$–*H*), 6.1 (2H, s, $N_{(4)}$–*H*), 7.3 (4H, d, J_{HH} 7.4 Hz, $C_{3,3',\ 5,5'}$–*H*), 7.4 (4H, d, J_{HH} 7.4 Hz, $C_{2,2',\ 6,6'}$–*H*), 7.6 (1H, s, $N_{(2)}$–*H*); δ_C(100.63 MHz, DMSO-d_6): 20.8 ($2 \times CH_3$), 22.4 ($C_{8,8'}$), 27.7 (C_9), 27.8 ($C_{7,7'}$), 34.5 ($C_{Z,Z'}$), 129.1 ($C_{2,2',6,6'}$), 130.2 ($C_{3,3',5,5'}$), 132.6 ($C_{1,1'}$), 135.5 ($C_{4,4'}$), 141.6 (C=N), 190.0 (C=O). The positive FAB mass spectrum of HL^2 showed the parent ion peak at m/z 377.1 (32%) corresponding to $(M+H)^+$ and the following fragments: 315 (16%) $[M-\{NH_2CH_2NOH\}]^+$, 301 (100%) $[M\ \{NH_2CH_2NOH+CH_2\}]^+$, 286 (66%) $[M-\{NH_2CH_2NOH+CH_2+NH\}]^+$, 258 (21%) $[M-\{NH_2CH_2NOH+CH_2+NH+C_2H_4\}]^+$, 154 (14%) $[M-\{NH_2CH_2NOH+CH_2+NH+C_2H_4+C_6H_5CH=CH_2\}]^+$.

2.3.4. General synthesis of the complexes with HL^1 and HL^2. A solution of the appropriate Schiff-base ligand (2 mmol) and potassium hydroxide (2.3 mmol) in ethanol (20 mL) was stirred for 15 min. A methanolic solution (15 mL) of the metal chloride (1 mmol) was then added dropwise. The resulting mixture was refluxed under N_2 for 6 h, resulting in the formation of a solid which was washed several times with ethyl ether and dried under vacuum. Elemental analysis data, colors, and yields for the complexes are given in table 1.

Table 1. Colors, yields, elemental analyses, and molar conductance values.

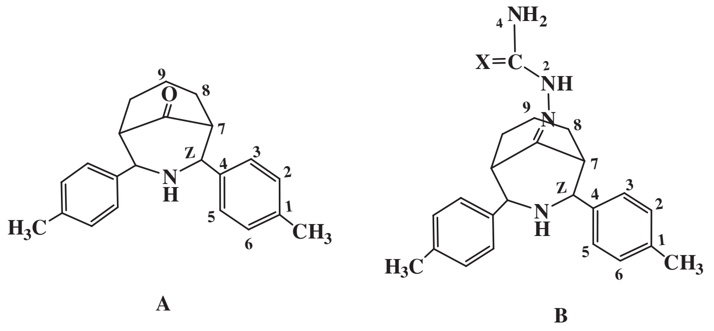
Compound	Color	Yield (%)	m.p. (°C)	Found (Calcd) (%) M	C	H	N	Cl	Λ_M ($cm^2\,\Omega^{-1}\,mol^{-1}$)
HL^1	Yellow	62	160	–	70.2 (70.4)	7.2 (7.1)	14.2 (14.3)	–	–
$K[Cr(L^1)_2Cl_2]$	Greenish yellow	65	>300	5.5 (5.4)	58.8 (58.8)	5.8 (6.0)	11.8 (11.7)	7.3 (7.4)	33
$K_2[Mn(L^1)_2Cl_2]$	Green	60	$280_{\text{(dec.)}}$	5.4 (5.5)	56.3 (56.3)	5.8 (5.7)	11.6 (11.8)	7.1 (7.1)	71
$K_2[Fe(L^1)_2Cl_2]$	Gray	64	$284_{\text{(dec.)}}$	5.8 (5.7)	56.2 (56.3)	5.6 (5.7)	11.4 (11.2)	5.5 (5.6)	77
$[Co(L^1)_2]$	Green	68	$240_{\text{(dec.)}}$	6.8 (7.0)	65.8 (65.9)	6.8 (6.7)	13.2 (13.1)	–	6
$[Ni(L^1)_2]$	Pale green	71	>300	7.0 (6.9)	65.6 (65.9)	6.5 (6.7)	13.0 (13.1)	–	8
$[Cu(L^1)_2]$	Brown	62	$244_{\text{(dec.)}}$	7.7 (7.5)	65.2 (65.3)	6.4 (6.6)	13.3 (13.2)	–	17
$[Zn(L^1)_2]$	Pale yellow	80	>300	7.8 (7.6)	65.3 (65.4)	6.8 (6.7)	13.1 (13.0)	– –	12
$[Cd(L^1)_2]$	Yellow	73	$240_{\text{(dec.)}}$	12.5 (12.4)	61.7 (62.0)	6.3 (6.1)	12.2 (12.3)	–	9
$[Hg(L^1)_2]$	Pale yellow	67	$241_{\text{(dec.)}}$	19.8 (20.1)	56.9 (56.5)	5.2 (5.8)	11.3 (11.2)	–	13.5
HL^2	Yellow	56	162	–	70.2 (70.4)	7.2 (7.1)	14.2 (14.3)	–	–
$K[Cr(L^2)_2Cl_2]$	Pale yellow	72	>300	5.5 (5.6)	60.6 (60.8)	6.3 (6.2)	11.9 (12.0)	7.8 (7.6)	31
$K_2[Mn(L^2)_2Cl_2]$	Green	58	$200_{\text{(dec.)}}$	5.6 (5.7)	58.0 (58.2)	5.9 (5.9)	11.5 (11.6)	7.3 (7.3)	74
$[Co(L^2)_2]$	Deep purple	82	$240_{\text{(dec.)}}$	7.2 (7.1)	68.5 (68.4)	7.3 (7.0)	13.7 (13.6)		16.6
$[Ni(L^2)_2]$	Pale yellow	55	$200_{\text{(dec.)}}$	7.0 (7.1)	68.1 (68.5)	6.8 (7.0)	13.4 (13.6)	–	9
$[Cu(L^2)_2]$	Deep green	77	$230_{\text{(dec.)}}$	7.7 (7.7)	68.0 (68.1)	6.9 (7.0)	13.6 (13.5)	–	11
$[Zn(L^2)_2]$	Light brown	76	>300	8.1 (7.9)	67.7 (67.9)	6.8 (6.9)	13.8 (13.5)	–	
$[Cd(L^2)_2]$	Pale yellow	66	224–225	13.0 (12.8)	63.9 (64.3)	6.3 (6.6)	12.9 (12.8)	–	5
$[Hg(L^2)_2]$	Yellow	70	260	21.1 (20.8)	57.9 (58.4)	5.5 (6.0)	11.7 (11.6)	–	6

(dec.) = decomposed.

3. Results and discussion

The precursor 2,4-di-*p*-tolyl-3-azabicyclo[3.3.1]nonan-9-one (scheme 1A) was obtained in almost quantitative yield by a Mannich condensation [17] using two equivalents of *p*-methylbenzaldehyde, one equivalent of ammonium acetate, and one equivalent of cyclohexanone. The compound was characterized by elemental analysis, IR, ^{1}H-, and ^{13}C-NMR spectra. The IR spectrum shows characteristic bands due to the ν(C=O), ν(N–H), and ν(C=C) functional groups.

Condensation of 2,4-di-*p*-tolyl-3-azabicyclo[3.3.1]nonan-9-one with one equivalent of thiosemicarbazide or semicarbazide afforded the new Schiff bases 2-(2,4-di-*p*-tolyl-3-azabicyclo[3.3.1]nonan-9-ylidene)hydrazinecarbothioamide HL^1 and 2-(2,4-di-*p*-tolyl-3-azabicyclo[3.3.1]nonan-9-ylidene)hydrazinecarboxamide HL^2 in moderate



X= S = HL^1
X= O = HL^2

Scheme 1. Chemical structures of precursor and ligands.

Table 2. IR frequencies (cm^{-1}) of the compounds.

Compound	ν(C=N)	ν(C=O)	ν(C=S)	ν(N–N)	ν(M–N)	ν(M–O)	ν(M–S)	ν(M–Cl)
HL^1	1660	–	1311, 867	1020	–	–	–	–
$K[Cr(L^1)Cl_2]$	1620	–	1295, 837	1047	420	–	350	289
$K_2[Mn(L^1)Cl_2]$	1647	–	1294, 800	1027	460	–	320	293
$K_2[Fe(L^1)_2Cl_2]$	1630	–	1306, 820	1060	430	–	312	278
$[Co(L^1)_2]$	1634	–	1303, 836	1023	480	–	324	–
$[Ni(L^1)_2]$	1632	–	1280, 830	1048	445	–	380	–
$[Cu(L^1)_2]$	1665	–	1300, 855	1036	440	–	370	–
$[Zn(L^1)_2]$	1670	–	1301, 859	1326	450	–	365	–
$[Cd(L^1)_2]$	1674	–	1302, 860	1048	440	–	373	–
$[Hg(L^1)_2]$	1675	–	1299, 862	1050	451	–	360	–
HL^2	1629	1688		1016	–	–	–	–
$K[Cr(L^2)_2Cl_2]$	1635	1675		1048	440	503	–	281
$K_2[Mn(L^2)_2Cl_2]$	1658	1673		1033	480	513	–	269
$[Co(L^2)_2]$	1635	1674		1030	470	505	–	–
$[Ni(L^2)_2]$	1637	1664		1047	474	512	–	–
$[Cu(L^2)_2]$	1638	1668		1049	480	500	–	–
$[Zn(L^2)_2]$	1636	1670		1050	435	505	–	–
$[Cd(L^1)_2]$	1647	1675		1027	442	511	–	–
$[Hg(L^2)_2]$	1633	1672		1040	480	504	–	–

yield (scheme 1B). The Schiff bases were characterized by elemental analysis (table 1), IR (table 2) and UV-Vis (table 3), mass spectroscopy, and ^{1}H- and ^{13}C-NMR spectroscopy.

Complexes of the ligands with Cr^{III}, Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II}, and Hg^{II} were synthesized by heating 2 mmol of each ligand with 1 mmol of metal chloride using methanolic potassium hydroxide as a base. The use of a base in these reactions was essential since otherwise only starting materials were recovered. In methanolic potassium hydroxide, deprotonation of the ligands occurs facilitating formation of $K[Cr(L^n)_2Cl_2]$, $K_2[Mn(L^n)_2Cl_2]$, $K_2[Fe(L^1)_2Cl_2]$ and $[M(L^n)_2]$, where $M = Co(II)$, Ni(II) Cu(II), Zn(II), Cd, and Hg(II), $L^n = L^1$ or L^2 (scheme 2). The complexes are air-stable solids, soluble in DMSO but not in other common organic solvents. The analytical data (table 1) agree well with the suggested formulas.

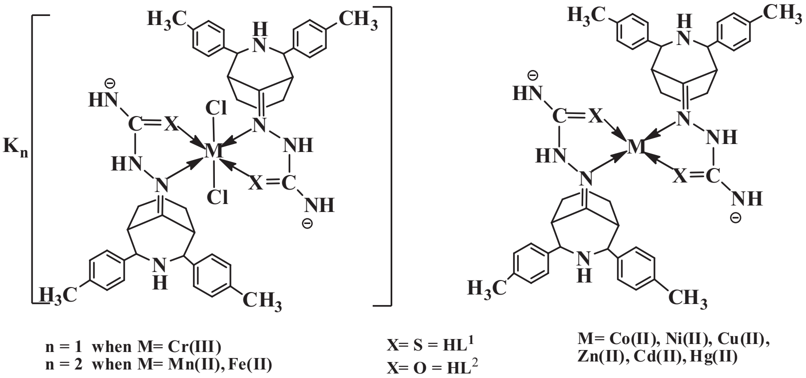
Table 3. Magnetic moment and UV-Vis spectral data in DMSO.

Compound	μ_{eff} (BM)	Band position (λ nm)	Extinction coefficient ε_{max} ($dm^3 mol^{-1} cm^{-1}$)	Assignments
$K[Cr(L^1)_2Cl_2]$	3.86	295	600	$\pi \rightarrow \pi^*$
		375	420	CT
		527	95	${}^4A_{2g}{}^{(F)} \rightarrow {}^4T_{1g}{}^{(F)}$ (υ_2)
		637	65	${}^4A_{2g}{}^{(F)} \rightarrow {}^4T_{2g}{}^{(F)}$ (υ_1) (10Dq)
$K_2[Mn(L^1)_2Cl_2]$	5.35	268	320	$\pi \rightarrow \pi^*$
		350	190	CT
		433	90	${}^6A_{2g} \rightarrow {}^4A_{1g}, {}^4E_g$
		520	70	${}^6A_{2g} \rightarrow {}^4T_{1g}$
$K_2[Fe(L^1)_2Cl_2]$	5.12	265	720	$\pi \rightarrow \pi^*$
		330	1200	CT
		590	150	$A_{1g} \rightarrow T_{2g}$
$[Co(L^1)_2]$	1.81	288	1100	$\pi \rightarrow \pi^*$
		380	850	CT
		520	250	${}^2E_g \rightarrow {}^2T_{2g}$
		667	155	${}^2E_g \rightarrow {}^2T_{1g}$
$[Ni(L^1)_2]$	Diamagnetic	300	1050	$\pi \rightarrow \pi^*$
		360	625	CT
		424	180	${}^1A_{1g} \rightarrow {}^1B_{1g}$
		500	140	${}^1A_{1g} \rightarrow {}^1A_{2g}$
$[Cu(L^1)_2]$	1.82	264	264	$\pi \rightarrow \pi^*$
		345	770	CT
		478	80	${}^2B_{1g} \rightarrow {}^2E_g$
		630	100	${}^2B_{1g} \rightarrow {}^2B_{2g}$
$[Zn(L^1)_2]$	Diamagnetic	267	605	$\pi \rightarrow \pi^*$
		323	1325	CT
$[Cd(L^1)_2]$	Diamagnetic	266	750	$\pi \rightarrow \pi^*$
		337	1110	CT
$[Hg(L^1)_2]$	Diamagnetic	266	700	$\pi \rightarrow \pi^*$
		335	1200	CT
$K[Cr(L^2)_2Cl_2]$	3.84	271	160	$\pi \rightarrow \pi^*$
		345	375	CT
		476	55	${}^4A_{2g} \rightarrow {}^4T_{1g}{}^{(F)}$ (υ_2)
		653	25	${}^4A_{2g} \rightarrow {}^4T_{2g}{}^{(F)}$ (υ_1) (10Dq)
$K_2[Mn(L^2)_2Cl_2]$	5.41	270	375	$\pi \rightarrow \pi^*$
		320	365	CT
		420	100	${}^6A_{1g} \rightarrow {}^4T_{2g}{}^{(G)}$
		525	40	${}^6A_{1g} \rightarrow {}^4T_{1g}{}^{(G)}$
$[Co(L^2)_2]$	1.81	299	1050	$\pi \rightarrow \pi^*$
		374	750	CT
		477	190	${}^2E_g \rightarrow {}^2T_{2g}$
		548	150	${}^2E_g \rightarrow {}^2T_{1g}$
$[Ni(L^2)_2]$	Diamagnetic	285	980	$\pi \rightarrow \pi^*$
		377	190	CT
		665	140	${}^1A_{1g} \rightarrow {}^1B_{1g}$
$[Cu(L^2)_2]$	1.83	272	420	$\pi \rightarrow \pi^*$
		340	880	CT
		510	90	${}^2B_{1g} \rightarrow {}^2E_g$
		660	120	${}^2B_{1g} \rightarrow {}^2B_{2g}$
$[Zn(L^2)_2]$	Diamagnetic	273	280	$\pi \rightarrow \pi^*$
		343	400	CT

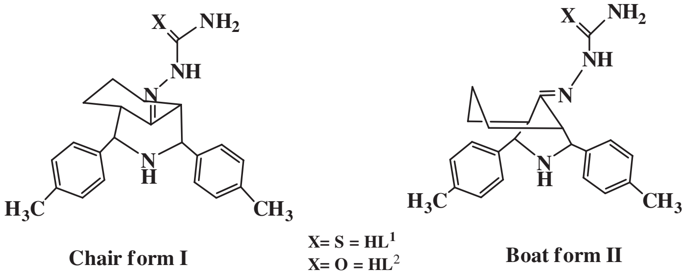
(*Continued*)

Table 3. Continued.

Compound	μ_{eff} (BM)	Band position (λ nm)	Extinction coefficient $\varepsilon_{\max}$ ($\text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-1}$)	Assignments
$[\text{Cd}(\text{L}^2)_2]$	Diamagnetic	255	174	$\pi \rightarrow \pi^*$
		350	1520	CT
$[\text{Hg}(\text{L}^2)_2]$	Diamagnetic	263	200	$\pi \rightarrow \pi^*$
		336	1500	CT



Scheme 2. Proposed structures of homoleptic metal complexes.



Scheme 3. Expected conformational forms of ligands in solution.

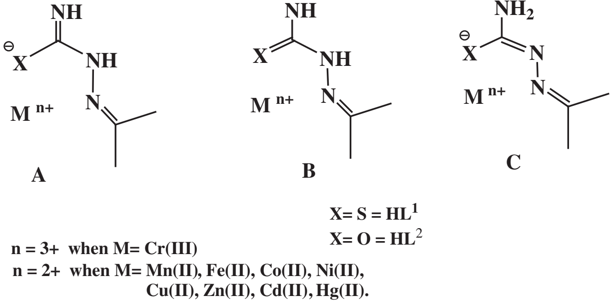
3.1. *NMR and IR spectra*

The ^{1}H- and ^{13}C-NMR spectra of the compounds displayed signals corresponding to the various proton and carbon nuclei consistent with the proposed structural formula (section 2). In solution, the ligands can exist in two conformation forms: the chair form I and the boat form II (scheme 3). Analysis of the NMR spectra of the ligands shows that in HL^1 two conformational isomers are symmetrical, but HL^2 gives two conformations that are not symmetrical. ^{13}C-NMR spectra show the chemical shifts of $C_{7,7'}$ in HL^1 are equivalent and appear at 36.5 ppm, while the chemical shifts in HL^2

are nonequivalent at 37.0 and 34.5 ppm. This is perhaps due to the ease of rotation of the chelating portion of the molecule; rapid rotation would give an averaged symmetrical spectrum while slow rotation could give one or two conformations that are not symmetrical.

Important infrared bands of the ligands and their complexes together with their assignments are collected in table 2. IR spectra of the free ligands show bands due to ν(C=S), ν(C=O), ν(C=C), δ(N–H), and ν(N–H). In the spectra of HL^1 complexes, coordination *via* thione sulfur is indicated by the appearance of bands at 1280–1306 and 800–860 cm^{-1} attributed to the ν(C=S). These bands were observed at 1311 and 867 cm^{-1}, respectively, in the free ligand [18]. The shift to lower frequencies is due to electron transfer from metal center to sulfur [19]. Analogous shifts are seen for δ(N–H) of the thiosemicarbazone, observed at 1502–1485 cm^{-1} in the complex, lower than the observed in the free ligand (1567 cm^{-1}). The ν(C=N) at 1660 cm^{-1} in the free ligand shifts to 1620–1647 cm^{-1} for the complexes of chromium(III), manganese(II), iron(II), cobalt(II), and nickel(II). This can be attributed to delocalization of metal electron density (t_{2g}) to the π-system of the ligand [20, 21]. However, the shift of ν(C=N) to higher frequencies in spectra of the complexes of copper(II), zinc(II), cadmium(II), and mercury(II) may indicate the decreasing interaction between metal and ligand [20]. The hydrazinic ν(N–N) at 1020 cm^{-1} in free HL^1 is shifted to higher frequency, around 1023–1050 cm^{-1}, due to the reduction in repulsion between lone pairs on nitrogen due to complexation *via* azomethine nitrogen [22]. The spectra of the complexes also exhibited bands around 420–480 and 312–380 cm^{-1} assigned to ν(M–N) and ν(M–S), respectively. Additional bands around 278–293 cm^{-1} in $K[Cr(L^1)Cl_2]$, $K_2[Mn(L^1)Cl_2]$, and $K_2[Fe(L^1)_2Cl_2$ are assigned to ν(M–Cl) [23, 24]. The IR spectra of complexes of HL^2 exhibit ν(C=O) around 1664–1675 cm^{-1}, observed in the free ligand at 1680 cm^{-1}. This is consistent with coordination *via* the oxygen of C=O to the metal [25]. At lower frequency the complexes exhibited bands around 503–512, 435–480, and 281–296 cm^{-1} assigned to the ν(M–O), ν(M–N) and ν(M–Cl), respectively [23–26]. Due to larger dipole moment change for M–O compared to M–N, ν(M–O) usually appears at higher frequency than ν(M–N) [27].

Thiosemicarbazones and semicarbazones are versatile ligands with variable bonding modes to metals (scheme 4). In the solid state deprotonated bidentate Schiff-bases HL^1 and HL^2 adopt resonance form B upon coordination to metal (scheme 4) in accord with that reported by Pavlishchuk *et al.* [28] in Ni(II) complexes with 4,7-dithiadecane-2,9-dione *bis*(thiosemicarbazone) and with that reported by Chandra and Tyagi [25] in the



Scheme 4. Alternative resonance structures for homoleptic metal complexes.

Ni(II), Pd(II), and Pt(II) complexes with the thiosemicarbazone and semicarbazone of *p*-tolualdehyde. In solution it is difficult to determine the exact bonding mode of ligands. The ^{1}H NMR spectrum of $[Zn(L^1)_2]$ in DMSO-d_6 showed peaks of coordinated ligand, shifted slightly downfield, 2.34 (12H, s, 4 × CH_3), 1.05 (8H, m, $C_{8,8'}$–*H*), 1.23 (4H, dd, J_{HH} 8.5 Hz, C_9–*H*), 2.9 (4H, dd, J_{HH} 8 Hz, $C_{7,7'}$–*H*), 3.2 (4H, m, $C_{Z,Z'}$–*H*), 4.4 (4H, br, N–*H*), 7.3 (8H, d, J_{HH} 7.5 Hz, Ar–*H*) and 7.4 (8H, d, J_{HH} 7.5 Hz, Ar–*H*). Upon complex formation, the N–H protons in A, B, and C forms (scheme 4) exchange rapidly and, therefore, only one peak at 4.4 ppm for the combined N–H resonances is observed. The NMR spectrum of the Zn(II) complex is consistent with the symmetric nature.

3.2. *Mass spectra*

The mass spectra of the ligands were also consistent with the proposed structural formula (section 2). The positive ion FAB mass spectrum for $[Cd(L^1)_2]$ showed several peaks corresponding to successive fragmentation of the molecule. The first peak observed at *m*/*z* 895.7 (7%) represents the molecular ion of the complex. Peaks at *m*/*z* 827 and 175 can be assigned to $[M - (NH{=}CH{-}CH{=}NH)]^+$ and $(CdSN_2H_3)$ fragment, respectively.

3.3. *Electronic spectra, magnetic moments, and conductivity measurements*

The electronic spectrum of HL^1 exhibits an intense absorption at 312 nm assigned to $\pi \rightarrow \pi^*$. The expected $n \rightarrow \pi^*$ transition occurs at 380 nm. The spectrum of HL^2 exhibits a similar intense absorption band at 320 nm assigned to $\pi \rightarrow \pi^*$, and at 360 nm attributed to $n \rightarrow \pi^*$ transition. Electronic spectra of the complexes of HL^1 exhibited various extents of hypsochromic shift of the intraligand $\pi \rightarrow \pi^*$ transition (table 3). Bands related to CT transitions were observed in the spectra of the complexes (table 3). The electronic spectrum of the Cr(III) complex displayed two additional bands, attributed to spin allowed d–d transitions [29–31]. These data together with the magnetic moment indicate an octahedral geometry around Cr(III) [31]. The Mn(II) complex showed the $\pi \rightarrow \pi^*$, CT transitions plus two additional bands which could be attributed to spin forbidden transitions in octahedral geometry [29, 31, 32]. The magnetic moment of this complex is typical for a high-spin octahedral structure. The electronic spectrum of the Fe(II) complex is consistent with octahedral geometry [29, 32]. The magnetic moment of this complex is typical for a high-spin octahedral structure. The low magnetic moment values of the green Co(II) complex and the brown Cu(II) complex, as well as the other analytical data, indicate square planar structures [29, 33, 34]. The Ni(II) complex is diamagnetic suggesting square planar geometry [26]. The electronic spectrum of this complex was consistent with this assignment.

The spectra of the Zn(II), Cd(II), and Hg(II) complexes exhibited bands assigned to ligand $\pi \rightarrow \pi^*$ and M → L charge transfer [29]. These complexes are diamagnetic as expected. The molar conductivity values of the Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) complexes were in the range of 6–17 $cm^2\,\Omega^{-1}mol^{-1}$ indicating nonelectrolytes, while those of the Cr(III), Mn(II), and Fe(II) complexes were consistent with 1 : 1 and 2 : 1 electrolytes (table 1) [35].

The electronic spectra of most complexes of HL^2 exhibited hypsochromic shifts of the $\pi \rightarrow \pi^*$, and the Co(II), Ni(II), and Cu(II) complexes showed bathochromic shifts of the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ ligand transitions (table 3). The spectra of the Cr(III) and Mn(II) complexes of HL^2 showed similar behavior to those of HL^1 suggesting octahedral geometry. As for $[Co(L^1)_2]$ and $[Cu(L^1)_2]$ the spectra of Co(II) and Cu(II) complexes of HL^2 together with the μ_{eff} values (table 3) suggest square planar geometries [29–34, 36]. The spectrum of the Ni(II) complex displayed bands characteristic of square planar Ni(II) complexes [29, 26]. The diamagnetism also indicates square planar Ni(II). The spectra of the Zn(II), Cd(II), and Hg(II) complexes of HL^2 showed similar behavior to those of HL^1, suggesting tetrahedral geometries [29]. The molar conductivities indicate that the Cr(III) is a 1 : 1 electrolyte while the Mn(II) complex is 2 : 1, and the rest are non electrolytes (table 1) [35].

4. Conclusion

We have explored the synthesis and coordination chemistry of some homoleptic complexes obtained from reaction of bidentate Schiff-base ligands HL^1 and HL^2 with metal ions. The mode of bonding and overall structure of the complexes were determined through physico-chemical and spectroscopic methods. The results revealed that in the solid state the Schiff bases adopt resonance form B (scheme 4) upon coordination to the metal center. In solution the exact bonding mode of ligands is difficult to determine.

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