Synthesis, Spectral and Thermal Behavior of Some New Four Coordinated Complexes

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Abstract: A new symmetric bidentate Schiff base *N, N'* bis(4-fluorobenzaldehyde)-1,2-diaminoethane(L) and its complexes with general formula MLX_2 ($M = Zn(II)$, $Cd(II)$ and $Hg(II)$ and $X = \text{chloride, bromide, iodide, thiocyanate and azide}$) have been prepared. The ligand and complexes have been established by microanalysis, electronic, FT-IR, 1H and ^{13}C NMR spectra, and by molar conductivity measurements. All compounds are non-electrolytes in chloroform or $DMSO-d_6$. The thermal behavior of the complexes shows weight loss by decomposition of the anions and ligand segments in the subsequent steps. Some activation thermodynamic parameters such as E^* , ΔH^* , ΔS^* and ΔG^* were calculated from thermal analysis.

Keywords: Schiff base ligand, Azomethine, Metal Complex, Spectra, Thermal

Introduction

Compounds containing azomethine group ($RC=N-$) were named Schiff base after Hugo Schiff¹ and are usually formed by the condensation of a primary amine with an active carbonyl compound. Schiff base metal complexes with Schiff base ligands have been prepared and presented in numerous reports ranging from the purely synthetic²⁻⁸ to modern physicochemically such as catalytic application⁹, optical material¹⁰, dyes, luminophores¹¹ and polymer with conductance properties¹² to biochemically relevant studies of these complexes in the points of view such as biologically active substances, antitumor¹³, antiviral¹⁴ and antifungal¹⁵. Because of these applications, synthesis of new Schiff bases and their metal complexes are still the aim of many recent investigations.

In continuation of our previous reports on Schiff base complexes¹⁶⁻¹⁸, the aim of this work is to prepare and investigate the structure of the chelates of zinc(II), cadmium(II) and mercury(II) with a new bidentate Schiff base ligand as *N, N'* bis(4-fluorobenzaldehyde)-1,2-diaminoethane(L) with nitrogen atoms as donor sites. The general formula of these complexes are MLX_2 in which $L =$ bidentate Schiff base ligand Furthermore, thermal behavior of them was investigated and some activation thermodynamic parameters such as A , E^* , ΔH^* , ΔS^* and ΔG^* were calculated from thermal analysis.

Experimental

All the solvents used in the synthesis and analysis, 4-florobenzaldehyde, ethylenediamine, zinc, cadmium and mercury salts and other chemicals were purchased from Aldrich and Merck, and used without any further purification. The FT-IR spectra were recorded on the JASCO-680 model in the range of 400-4000 cm^{-1} using a KBr disk. Elemental analysis (C, N and H) was conducted on a CHNS-932(LECO) elemental analyzer. UV-Vis spectra in the 200-800 nm range were recorded using a JASCO-V570 spectrometer at chloroform and DMSO. ^1H and ^{13}C NMR spectra were recorded using a Bruker DPX FT-NMR spectrometer at 500 MHz with the samples dissolved in DMSO- d_6 using TMS as internal standard. Molar conductance of the Schiff base ligands and their transition metal complexes were determined in chloroform and DMSO (1.0×10^{-3} M) at room temperature using Metrohm 712 conductometer. Thermogravimetric analyses have been obtained with PL-1500 TG Instruments.

Synthesis of Schiff base ligand (L)

Ethylenediamine (0.060 g, 1 mmol) was added to 4-fluorobenzaldehyde (0.2482 g, 2 mmol) and severally stirred and grinded under solvent free conditions. The white product as Schiff base ligand was formed. Ligand was treated with cold water and was filtered. For more purification, ligand was recrystallized from methanol.

L: IR spectrum (KBr, cm^{-1}): 3435 (m), 3035(w), 2927(w), 2907(m), 2848(s), 1651(vs), 1595(s), 1506(s), 1459(m), 1414(m), 1373(m), 1298(m), 1283(m), 1260(w), 1230(s), 1213(s), 1152(s), 1096(m), 1019(s), 984(m), 968(m), 936(w), 874(m), 845(s), 818(m), 804(m), 780(w), 580(s), 470(m), 417(m). UV-Vis spectrum [(DMF), $\lambda(\text{nm})$ (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 251(378570), 276(sh)(15746) and 287(sh)(11864). ^1H -NMR spectrum (DMSO- d_6): 8.31(s, 2H), 7.74(dt, 4H, $J_{\text{HH}} = 6.11$ Hz, $J_{\text{HF}} = 5.98$ Hz and $J = 2.05$ Hz), 7.22(t, 4H, $J_{\text{HF}} = 8.80$ Hz and $J = 8.75$ Hz), 3.84(s, 4H) ppm. ^{13}C -NMR spectrum (DMSO- d_6): 163.40(d, $J = 985.5$ Hz), 160.51, 132.60, 129.87(d, $J = 34.55$ Hz), 115.50(d, $J = 86.90$ Hz), 60.67 ppm.

Preparation of MLX_2 complexes ($M = \text{Zn(II)}$, Cd(II) and Hg(II) , and $X = \text{Cl}^-$, Br^- , I^- , SCN^- and N_3^-)

A solution of 1 mmol of ligand (0.272 g) in 20 mL of methanol or ethanol was added dropwise under stirring to the solution of 1 mmol of MX_2 in methanol (20 mL). The mixture was stirred for 3h and complexes as a precipitate were filtered and for purification washed twice with methanol. Then complexes were dried at (80-100 $^\circ\text{C}$) under vacuum and were kept in a desiccator over silica-gel.

ZnLCl_2 : IR spectrum (KBr, cm^{-1}): 3441(m), 3061(m), 2944(m), 1647(vs), 1603(s), 1510(s), 1438(m), 1390(m), 1336(m), 1304(m), 1230(s), 1160(s), 1107(w), 1091(m), 1041(s), 1011(w), 972(m), 949(w), 936(m), 879(m), 855(s), 831(s), 794(m), 783(w), 712(w), 607(w), 578(s), 516(s), 492(m), 419(m). UV-Vis spectrum [(CHCl $_3$), $\lambda(\text{nm})$ (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 271 (33037). ^1H -NMR spectrum (DMSO- d_6): 8.24(s, 2H), 7.68(dt, 4H, $J_{\text{HH}} = 6.20$ Hz, $J_{\text{HF}} = 6.12$ Hz and $J = 2.00$ Hz), 7.15(t, 4H, $J_{\text{HF}} = 8.80$ Hz and $J_{\text{HH}} = 8.80$ Hz), 3.77(s, 4H) ppm. ^{13}C -NMR spectrum (DMSO- d_6): 163.49(d, $J = 986.5$ Hz), 160.71, 132.61(d, $J = 9.90$ Hz), 129.99(d, $J = 34.60$ Hz), 115.56(d, $J = 87.15$ Hz), 60.69 ppm.

ZnLBr_2 : IR spectrum (KBr, cm^{-1}): 3435(m), 3059(m), 2941(m), 1644(vs), 1603(s), 1509(s), 1435(m), 1391(m), 1336(m), 1305(m), 1230(s), 1161(s), 1107(w), 1091(m), 1043(s), 1012(w), 970(m), 948(w), 936(m), 876(m), 853(s), 838(s), 794(m), 783(w), 712(w), 608(w), 576(s), 515(s), 494(m), 418(m). UV-Vis spectrum [(CHCl $_3$), $\lambda(\text{nm})$ (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 272 (35273). ^1H -NMR spectrum (DMSO- d_6): 8.30(s, 2H), 7.73(dd, 4H, $J_{\text{HH}} = 8.28$ Hz and $J_{\text{HF}} = 5.80$ Hz), 7.21(t, 4H, $J_{\text{HF}} = 8.70$ Hz and $J_{\text{HH}} = 8.70$ Hz), 3.83(s, 4H) ppm. ^{13}C -NMR spectrum (DMSO- d_6): 163.46(d, $J = 986.80$ Hz), 160.65, 132.62(d, $J = 9.90$ Hz), 129.96(d, $J = 34.55$ Hz), 115.58(d, $J = 86.85$ Hz), 60.68 ppm.

ZnLi₂: IR spectrum (KBr, cm⁻¹): 3435(m), 3057(w), 2934(w), 1639(vs), 1601(s), 1508(s), 1433(m), 1397(m), 1336(m), 1305(m), 1229(s), 1160(s), 1105(w), 1091(m), 1038(m), 981(w), 945(w), 934(w), 875(m), 851(s), 834(s), 793(m), 782(w), 710(w), 608(w), 576(s), 514(s), 493(m), 413(w). UV-Vis spectrum [(CHCl₃), λ(nm) (ε, M⁻¹cm⁻¹)]: 270(41847). ¹H-NMR spectrum (DMSO-d₆): 8.29(s, 2H), 7.72(dt, 4H, J_{HH}= 6.20 Hz, J_{HF}= 6.15 Hz and J= 2.90 Hz), 7.19(t, 4H, J_{HF}= 8.80 Hz and J_{HH}= 8.80 Hz), 3.81 (s, 4H) ppm. ¹³C-NMR spectrum (DMSO-d₆): 163.47(d, J= 985.75 Hz), 160.64, 132.65, 130.00(d, J= 34.50 Hz), 115.62(d, J= 86.95 Hz), 60.71 ppm.

ZnL(SCN)₂: IR spectrum (KBr, cm⁻¹): 3435(m), 3073(w), 2942(w), 2089(vs), 2068(vs), 1637(vs), 1598(s), 1508(s), 1442(m), 1402(m), 1343(m), 1305(m), 1261(w), 1235(s), 1158(s), 1107(w), 1092(m), 1037(m), 982(w), 952(m), 875(w), 835(s), 798(m), 785(w), 712(w), 598(m), 577(m), 517(s), 483(m), 419(w). UV-Vis [(DMSO), λ(nm) (ε, M⁻¹cm⁻¹)]: 257(35418) and 276(sh)(29487). ¹H-NMR spectrum (DMSO-d₆): 8.28(s, 2H), 7.72(dd, 4H, J_{HH}= 8.58 Hz and J_{HF}= 5.75 Hz), 7.18 (t, 4H, J_{HF}= 8.80 Hz and J_{HH}= 8.80 Hz), 3.82(s, 4H) ppm. ¹³C-NMR spectrum (DMSO-d₆): 163.50(d, J= 986.35 Hz), 160.58, 135.45, 132.68, 129.96(d, J= 34.50 Hz), 115.57(d, J= 87.00 Hz), 60.75 ppm.

ZnL(N₃)₂: IR spectrum (KBr, cm⁻¹): 3375(m), 2919(w), 2856(w), 2065(vs), 1641(vs), 1601(s), 1507(s), 1451(m), 1370(s), 1342(s), 1302(m), 1260(w), 1230(s), 1152(s), 1095(m), 1039(m), 1017(m), 985(w), 956(m), 873(w), 834(s), 795(m), 782(w), 712(w), 597(m), 576(s), 519(s), 485(w), 420(m). UV-Vis [(DMSO), λ(nm) (ε, M⁻¹cm⁻¹)]: 258(29735) and 281(sh)(19564). ¹H-NMR spectrum (DMSO-d₆): 8.29(s, 2H), 7.73(dd, 4H J_{HH}= 8.65 Hz and J= 5.70 Hz), 7.21(t, 4H, J_{HF}= 8.80 Hz and J_{HH}= 8.85 Hz), .3.83(s, 4H) ppm. ¹³C-NMR spectrum (DMSO-d₆): 163.52(d, J= 986.65 Hz), 160.68, 132.38, 129.99(d, J= 34.55 Hz), 112.60(d, J= 87.20 Hz), 60.73 ppm.

CdLi₂: IR spectrum (KBr, cm⁻¹): 3435(m), 3055(w), 2936(w), 1641(vs), 1601(s), 1509(s), 1338(m), 1302(m), 1259(w), 1229(s), 1158(s), 1105(w), 1092(w), 1036(m), 1011(w), 977(w), 943(w), 930(w), 872(w), 852(m), 829(s), 792(m), 779(w), 710(w), 634(w), 583(m), 571(m), 513(s), 481(m), 412(m). UV-Vis [(CHCl₃), λ(nm) (ε, M⁻¹cm⁻¹)]: 261(52089). ¹H-NMR spectrum (DMSO-d₆): 8.31(s, 2H), 7.75(m, 4H), 7.21(t, 4H, J_{HF}= 8.40 Hz and J_{HH}= 8.15 Hz), 3.84(s, 4H) ppm. ¹³C-NMR spectrum (DMSO-d₆): 163.42(d, J= 985.45 Hz), 160.54, 132.62, 129.91(d, J= 34.90 Hz), 115.49(d, J= 86.55 Hz), 60.67 ppm.

CdL(SCN)₂: IR spectrum (KBr, cm⁻¹): 3435(m), 3075(w), 2951(m), 2906(w), 2122(vs), 2096(vs), 1647(vs), 1604(s), 1510(s), 1459(w), 1434(m), 1383(m), 1347(m), 1303(m), 1272(w), 1234(s), 1158(s), 1094(m), 1023(m), 999(s), 966(m), 941(w), 861(m), 834(s), 785(m), 712(w), 595(m), 572(s), 525(s), 464(m), 421(w). UV-Vis [(DMSO), λ(nm) (ε, M⁻¹cm⁻¹)]: 258(49529) and 273(47179). ¹H-NMR spectrum (DMSO-d₆): 8.46(s, 2H), 7.86(m, 4H), 7.28(t, 4H, J_{HF}= 7.20 Hz and J_{HH}= 8.65 Hz), 3.63(s, 4H) ppm. ¹³C-NMR spectra (DMSO-d₆): 163.49(d, J= 931.9 Hz), 160.58, 133.01, 131.84, 129.93(d, J= 34.55 Hz), 115.52(d, J= 87.10 Hz), 60.68 ppm.

HgLiCl₂: IR spectrum (KBr, cm⁻¹): 3465(m), 2917(w), 1637(vs), 1600(s), 1507(s), 1443(m), 1392(w), 1344(m), 1295(m), 1234(s), 1152(s), 1102(w), 1040(m), 987(w), 941(m), 855(w), 829(s), 781(w), 585(m), 512(s), 477(w), 417(w). UV-Vis [(DMSO), λ(nm) (ε, M⁻¹cm⁻¹)]: 258(67911) and 275(66595). ¹H-NMR spectrum (DMSO-d₆): 8.56(s, 2H), 7.92(t, 4H, J_{HH}= 8.00 Hz and J_{HF}= 5.85 Hz), 7.24(t, 4H, J_{HF}= 7.35 Hz and J_{HH}= 8.80 Hz), 3.79(s, 4H) ppm. ¹³C-NMR spectrum (DMSO-d₆): 163.95(d, J= 992.80 Hz), 160.83, 132.46(d, J= 10.65 Hz), 129.92(d, J= 34.30 Hz), 115.53(d, J= 87.55 Hz), 60.59 ppm.

HgLiBr₂: IR spectrum (KBr, cm⁻¹): 3442(m), 3057(w), 3037(w), 2921(m), 2894(m), 1644(vs), 1602(s), 1508(s), 1459(w), 1442(m), 1415(m), 1373(m), 1338(w), 1300(m), 1285(m), 1232(s), 1154(s), 1096(m), 1038(m), 1017(s), 972(m), 938(m), 875(m), 833(s),

780(m), 712(w), 688(w), 605(m), 581(s), 520(s), 480(m), 421(w). UV-Vis [(DMSO), λ (nm) (ϵ , M⁻¹cm⁻¹)]: 275(60414). ¹H-NMR spectrum (DMSO-d₆): 8.63(s, 2H), 7.97(t, 4H, J_{HH}= 5.90 Hz and J_{HF}= 5.95 Hz), 7.28(dt, 4H, J_{HF}= 8.85 Hz, J_{HH}= 8.70 Hz and J= 2.15 Hz), 3.79(s, 4H) ppm. ¹³C-NMR spectrum (DMSO-d₆): 163.98(d, J= 993.6 Hz), 161.08, 132.35, 131.22(d, J= 35.55 Hz), 115.56(d, J= 87.00 Hz), 60.57 ppm.

HgLi₂: IR spectrum (KBr, cm⁻¹): 3435(m), 3056(w), 2924(m), 2898(m), 1639(vs), 1600(s), 1508(s), 1416(w), 1387(w), 1337(m), 1300(m), 1227(s), 1156(s), 1102(w), 1082(w), 1036(m), 974(w), 940(w), 872(w), 854(m), 833(s), 790(w), 710(w), 570(m), 517(s), 470(w), 414(m). UV-Vis [(CHCl₃), λ (nm) (ϵ , M⁻¹cm⁻¹)]: 253(48516) and 278(28685). ¹H-NMR spectrum (DMSO-d₆): 8.62(s, 2H), 7.96(m, 4H), 7.26(m, 4H), 3.67(s, 4H) ppm. ¹³C-NMR spectrum (DMSO-d₆): 163.89(d, J= 993.35 Hz), 161.01, 132.27, 129.97(d, J= 34.45 Hz), 115.41(d, J= 87.55 Hz), 60.52 ppm.

HgL(SCN)₂: IR spectrum (KBr, cm⁻¹): 3434(s), 3036(w), 2908(m), 2849(m), 2110(vs), 1646(vs), 1601(s), 1507(s), 1460(w), 1415(m), 1374(m), 1298(m), 1229(s), 1153(s), 1094(m), 1018(s), 983(m), 937(w), 874(m), 843(s), 780(m), 714(w), 580(s), 530(s), 485(w), 418(m). UV-Vis [(CHCl₃), λ (nm) (ϵ , M⁻¹cm⁻¹)]: 252(64099) and 270(42722). ¹H-NMR spectrum (DMSO-d₆): 8.31(s, 2H), 7.75(bs, 4H), 7.21(bs, 4H), 3.84(s, 4H) ppm. ¹³C-NMR spectrum (DMSO-d₆): 163.45(d, J= 986.10 Hz), 160.59, 132.60, 131.75, 129.90(d, J= 34.65 Hz), 115.51(d, J= 86.85 Hz), 60.69 ppm.

HgL(N₃)₂: IR spectrum (KBr, cm⁻¹): 3435(m), 3035(w), 2921(w), 2064(vs), 2023(vs), 1648(vs), 1601(s), 1508(s), 1443(w), 1361(s), 1299(m), 1232(s), 1154(m), 1098(w), 1039(m), 976(m), 946(w), 833(s), 786(m), 713(w), 580(s), 512(m), 487(w), 407(m). UV-Vis [(DMSO), λ (nm) (ϵ , M⁻¹cm⁻¹)]: 258(48161). ¹H-NMR spectrum (DMSO-d₆): 8.58(s, 2H), 7.90(bs, 4H), 7.31(bs, 4H), 3.70(bs, 4H) ppm. ¹³C-NMR spectrum (DMSO-d₆): 163.90(d, J= 992.10 Hz), 160.61, 132.65, 129.93(d, J= 34.55 Hz), 115.67(d, J= 86.95 Hz), 60.66 ppm.

Results and Discussion

Physical data

The new Schiff base ligand (L) was prepared with the condensation reaction between ethylenediamine and 4-florobenzaldehyde. In continue, the reaction of bidentate Schiff base ligand (L) with MX₂ salts (X= chloride, bromide and iodide thiocyanate and azide, M= zinc and mercury and cadmium) in a equimolar ratio give complexes with general formula MLX₂. Elemental analyses and other physical properties of the ligands and their complexes are summarized in Table 1. Elemental analysis are confirmed the stoichiometry of complexes.

The molar conductivity of complexes in chloroform or DMSO as solvent (1×10⁻³ M) was measured at room temperature. The low molar conductivity for complexes shows them to be non-electrolytes¹⁹⁻²¹.

IR spectra

The infrared spectra of ligand and its complexes were recorded in the region 4000-400 cm⁻¹. The most characteristic absorptions of the Schiff base ligand and its complexes are presented in experimental section. The absence of symmetric and asymmetric vibration related to (-NH₂) of amine and carbonyl stretching of aldehyde in the IR spectrum of ligand and appearance a new strong peak at 1651 cm⁻¹ suggested that the amino and aldehyde functional groups have been converted to iminic group (C=N) as a new bound. IR spectra of the complexes showed obviously change in the location of absorbance band especially for ν (C=N) indicated that the Schiff base was coordinated to the metals atom. The band appearing at 1651 cm⁻¹ due to the azomethine group (C=N)²²⁻²⁴ was shifted to lower frequency by 4–14 cm⁻¹ indicating participation of the azomethine nitrogen in the complexation. Schiff base ligand spectrum showed the stretching frequencies at 3035, (2927

and 2907) and 2848 cm^{-1} assigned to C-H of aromatic, aliphatic and iminic groups respectively. These bonds are shifted to higher frequency after its coordination to metal ions. The absorption band assigned to C=C bonds appeared at 1595 cm^{-1} that shifted to high frequency by 3-9 cm^{-1} after complexation. The stretching frequency at 1230 cm^{-1} can be attributed to the $\nu(\text{C-F})$ smoothly affected by coordination of the ligand. The strong out of plane bending vibration of the aromatic C-H is present²⁵ at 845 cm^{-1} . This band is shifted to lower frequency by 2-16 cm^{-1} after binding of ligand to metal. Furthermore conclusive evidence that confirmed coordination of Schiff bases with the metal ions appearance of weak low-frequency new bands at 512-530 cm^{-1} assigned to the metal-nitrogen $\nu(\text{M-N})$ ²⁶⁻²⁷. The absorption at 2065 cm^{-1} in $\text{ZnL}(\text{N}_3)_2$ and the absorptions at 2064 and 2023 cm^{-1} in $\text{HgL}(\text{N}_3)_2$ is assigned to coordinated N_3 ²⁸ and the absorption frequencies at 2068 cm^{-1} in $\text{ZnL}(\text{NCS})_2$ is assigned to N-coordinated SCN, the absorption at 2110 cm^{-1} in $\text{HgL}(\text{SCN})_2$ and at 2122-2096 cm^{-1} in $\text{CdL}(\text{SCN})_2$ are assigned to S-coordinated coordinated SCN²⁹⁻³². This observation for azide and thiocyanate complexes confirms well coordination of these anions (and somewhat halide ions in other complexes) as well as Schiff base ligand to metal centers.

Table 1. Elemental analysis, color, %yield and molar conductivity of the ligand and its complexes.

Entry	Compound	$\Lambda M, \text{cm}^2 \Omega^{-1} \text{M}^{-1}$	Found (Calcd.) %			Yield, %	Color
			H	N	C		
1	Ligand	-	5.3 (5.18)	10.4 (10.29)	70.3 (70.58)	81	White
2	ZnLCl_2	0.04 ^a	3.5 (3.45)	6.9 (6.86)	46.9 (47.03)	83	White
3	ZnLBr_2	0.074 ^a	-	-	-	79	White
4	ZnLI_2	0.098 ^a	2.2 (2.39)	4.9 (4.74)	31.9 (32.49)	85	White
5	$\text{ZnL}(\text{SCN})_2$	62.17 ^b	-	-	-	69	White
6	$\text{ZnL}(\text{N}_3)_2$	35.46 ^b	3.2 (3.35)	27.1 (26.57)	45.1 (45.57)	72	cream
7	CdLI_2	0.186 ^a	2.33 (2.21)	4.27 (4.39)	29.97 (30.10)	78	White
8	$\text{CdL}(\text{SCN})_2$	76.28 ^b	-	-	-	80	White
9	HgLCl_2	4.63 ^b	2.40 (2.59)	5.27 (5.15)	35.12 (35.34)		White
10	HgLBr_2	14.19 ^b	-	-	-	83	cream
11	HgLI_2	2.40 ^b	2.1 (1.94)	3.9 (3.85)	26.7 (26.44)	79	cream
12	$\text{HgL}(\text{SCN})_2$	0.412 ^a	2.3 (2.40)	9.7 (9.51)	36.3 (36.70)	70	Pale Yellow
13	$\text{HgL}(\text{N}_3)_2$	26.96 ^b	-	-	-	68	White

a= the solvent is CHCl_3 , *b*= the solvent is DMSO.

Electronic spectra

Electronic spectra of the ligand and its complexes were recorded in DMF and or chloroform at room temperature as can see in experimental section. In the spectrum of ligand, an independent absorption band appeared and two shoulder bands appeared at 251, 276 and 287 nm regions that first two cases may be due to π - π^* transition of aromatic rings and the third may be related to azomethine group. In the electronic spectra of most of complexes(entries 2,3,4,7 10 and 13), the bands assigned to aromatic rings and azomethine group are merged

together and shifted to lower energies after coordination. In zinc thiocyanate and azide, mercury bromide, iodide and thiocyanate complexes, the first band of ligand shift to higher wavelengths and a strong shoulder is appeared at 276 and 281 nm after coordination. Finally in cadmium thiocyanate and mercury chloride complexes two independent strong bands were detectable for $\pi\text{-}\pi^*$ transition of aromatic rings and azomethine group of ligand due to coordination. The $d\text{-}d$ transition bands for complexes of these transition metals due to d^{10} electron configuration won't be observed. Though metal to ligand charge transfer are predictable for this type of complexes but these transition were not observed.

^1H and ^{13}C NMR spectra

The results data of NMR spectra of the ligand and its metal complexes have been entered in experimental section. ^1H and ^{13}C NMR spectra were recorded at 500 MHz, using DMSO as solvent. ^1H NMR and ^{13}C NMR of ligand are depicted in Figure 2. Studies of ^1H and ^{13}C NMR spectra exhibit that the data have excellent correlation with pseudo-tetrahedral structure that proposed before for complexes. As a functional group signal, resonance of azomethine proton (H_b and H_b') appeared at 8.31 ppm²². These signals are red shifted to 8.46-8.63 ppm with respect to TMS for entries 8, 9, 10, 11 and 13 or shifted to down filed 8.24-8.30 ppm for entries 2, 3, 4, 5 and 6 and unchanged in spectra of entries 7 and 12, suggesting coordination by the azomethine nitrogens to metal ion. In the spectrum of ligand $\text{H}_{d,d'}$ appeared at 7.74 ppm as a doublet of triplet due to coupling with $\text{H}_{e,e'}$ and fluorine atom at benzene ring with coupling constants of 6.11, 5.98 and 2.05 Hz. In the spectra of complexes, the signals of $\text{H}_{d,d'}$ have shown a change in location, so that shifted to up fields (entries 7-13) or down fields (entries 2-6). Also the type of splitting of this signal changed due to coordination of ligand and appeared as doublet of doublet for entries 3, 5 and 6; as triplet for entries 9 and 10, as multiple for entries 7 and 8 and as broad singlet for entries 12 and 13. $\text{H}_{e,e'}$ due to coupling whit $\text{H}_{d,d'}$ and then fluorine atom are observed at 7.22 ppm as a triplet signal with coupling constants of 8.70 and 8.75 Hz. In the spectra of complexes, the signals of $\text{H}_{e,e'}$ are almost unchanged or shifted to upfields (entries 2, 4 and 5) or down fielded (entries 8-11 and 13). On the other hand, in the spectra of HgLBr_2 and HgLi_2 , these signals appeared as doublet of triplet and multiple signals respectively. For $\text{HgL}(\text{SCN})_2$ and $\text{HgL}(\text{N}_3)_2$ these signals are seen as broad singlet that these chemical shifts and signal shapes confirm coordination of ligand to metal centers. The signal of $\text{H}_{a,a'}$ protons in the ligand are exhibited as a singlet at 3.84 ppm that are appeared as singlet in all complexes but are shifted to down fields after coordination.

Figure 1. ^1H NMR and ^{13}C NMR of ligand.

In the ^{13}C NMR spectrum of the ligand, two azomethine carbons C(5,5') resonances are observed as a single peak at 160.51 ppm¹⁶⁻¹⁸. These peaks are shifted to up field in all complexes, suggesting well coordination of the azomethine nitrogen to metal ion. Also, the

^{13}C NMR spectrum of the ligand showed a doublet peak at 163.40 ppm for C(1, 1') carbons due to coupling with fluorine atom with $J = 985.50$ Hz that shifted to lower energies after coordination. C(2, 2') and C(3, 3') also are effected with fluorine atom and exhibit doublet peak at 115.50 and 129.87 ppm with coupling constants of 34.55 and 86.90 Hz. After coordination, these peaks are stayed as doublet but with a smoothly change in their chemical shifts. A singlet peak at 132.60 and 60.67 ppm is assigned to C(4, 4') and C(6, 6') respectively. The peaks of C(4, 4') is stayed singlet in all complexes except for entries 2, 3 and 9 that were transformed to doublet signals due to the coupling effect of fluorine atom. The signals related to C(6, 6') are being almost unchanged in all complexes. The carbon of thiocyanate group in $\text{ZnL}(\text{NCS})_2$, $\text{CdL}(\text{SCN})_2$ and $\text{HgL}(\text{SCN})_2$ are found at 135.45, 131.84 and 131.75 ppm respectively.

In final, based on the current evidences and according to previous report on this type of ligands^{4,7}, the suggested structure for the complexes is pseudo-tetrahedral as drawn in Scheme 1.

Scheme 1. Structure of complexes.

Thermal investigation of Schiff base complexes

Thermal behavior (TG/DTG) of compounds was studied on PL-1500 TG instrument from room temperature to 600 °C at the heating rates of 10 degree per minute under oxygen atmosphere. The mass loss versus temperature data of the complexes extracted from the plots are seen in Table 2. Thermogravimetric investigations of the complexes indicate some information about the thermal stability of them. Complexes lose 81.2-100% of their weight during room temperature to 600 °C. The mass loss under 100 °C for some compounds indicates existence of a few lattice water molecules (6.99, 6.8, 3.4, 2.3% for Entries of 5-8 respectively). In other complexes weight loss was not observed until 200 °C indicating no water molecule (as lattice water or coordinated) in the compounds.

The thermodynamic activation parameters of decomposition processes of complexes including Arrhenius constant(A), activation energy (E^*), enthalpy (ΔH^*), entropy (ΔS^*) and Gibbs free energy of decomposition step (ΔG^*) are evaluated based on plots using Coats–Redfern relation³¹.

The calculated data are collected in Table 3. The activation energies of decomposition are found to be in the range of 8–127kJ/mol. This range of values of the activation energies indicates relative thermal stability of the complexes. ΔS^* values are negative in most of investigated steps that states decomposition reactions proceed with lower rates than normal ones. ΔH^* and ΔG^* values are positive and placed at ranges of 4.38-124 kJ/mol and 106- 258 kJ/mol respectively.

HgLBr ₂	60-165	1.10*10	7.55*10 ⁻²	-2.69*10 ²	7.73	1.14*10 ²
	195-260	7.02*10	7.98*10 ⁴	-1.56*10 ²	6.60*10	1.45*10 ²
	280-360	4.32*10	1.77*10	-2.27*10 ²	3.82*10	1.75*10 ²
HgLi ₂	70-145	2.73*10	2.34*10	-2.21*10 ²	2.41*10	1.09*10 ²
	185-230	1.17*10 ²	3.50*10 ¹⁰	-4.72*10	1.13*10 ²	1.36*10 ²
	230-325	5.03*10	1.50*10 ²	-2.09*10 ²	4.56*10	1.64*10 ²
HgL(SCN) ₂	110-215	6.73*10	2.40*10 ⁵	-1.46*10 ²	6.34*10	1.31*10 ²
	280-500	1.62*10	6.96*10 ⁻²	-2.73*10 ²	1.11*10	1.77*10 ²
	510-635	2.99*10	1.39*10 ⁻¹	-2.70*10 ²	2.26*10	2.58*10 ²
HgL(N ₃) ₂	70-120	3.26*10	1.83*10 ²	-2.04*10 ²	2.95*10	1.06*10 ²
	145-175	1.21*10 ²	2.34*10 ¹²	-1.14*10	1.17*10 ²	1.22*10 ²
	180-205	1.27*10 ²	2.51*10 ¹²	-1.13*10	1.24*10 ²	1.29*10 ²
	205-250	1.02*10 ²	3.38*10 ⁸	-8.60*10	9.78*10	1.41*10 ²
	315-425	1.98*10	1.56*10 ⁻¹	-2.67*10 ²	1.45*10	1.85*10 ²
	425-525	1.38*10	1.48*10 ⁻¹	-2.69*10 ²	7.25	2.18*10 ²

^arefers to selected decomposition temperature range.

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