

Synthesis and identification of some new cadmium(II) halide complexes

Shiva Joohari

Department of Basic Science, Yasouj Branch, Islamic Azad University, Yasouj, (IRAN)

ABSTRACT

The new Schiff base derived from 3-Phenyl-propenal and 2,2-Dimethyl-propane-1,3-diamine and its cadmium(II) complexes have been synthesized and characterized by various physical and spectral techniques such as elemental analysis, molar conductance measurements, FT-IR, ^1H and ^{13}C NMR and UV-Visible spectroscopy. The spectral studies confirm that the ligand act as bidentate molecule and coordinates metal through azomethine nitrogen. The elemental analysis data exhibit the molar ratio between ligand and cadmium salts is 1:1 and low molar conductivities of complexes are the reason for stabilization of molecular structure and non-electrolyte nature of these complexes. The changes in the location and shape of the peaks in UV-visible, FT-IR, and the ^1H and ^{13}C NMR spectra of complexes rather than free ligand are the other evidence to form Schiff base complexes. In respect to resulting data, the CdLX_2 (X= Cl, Br and I) as general formula and pseudo-tetrahedral structure has been suggested for these complexes.

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KEYWORDS

Schiff base;
Spectroscopic;
Conductivity;
Cadmium complex.

INTRODUCTION

The most important moiety of Schiff base ligands is azomethine ($-\text{C}=\text{N}$) moiety that is functional group for this type of ligands. The significant role of Schiff base ligands to development of coordination chemistry is undeniable because of their ability to bond to more transition metals with donor nitrogen site of iminic moiety and other electron donor such as oxygen and sulfur in the structure of Schiff base ligands and formation very stable complexes^[1-8]. Application of Schiff base complexes in inorganic, biologic and industrial fields are the reason for attention to synthesis and characterization of various Schiff base complexes in these years. Some of the most application are as antiviral, antimicrobial, antifungal and antibacterial agents, biomimetic enzyme models, anticancer, as catalyses in chemical reactions,

liquid crystal, polymer stabilizers, DNA cleavage agent^[9-19].

For the above mentioned reasons, new bidentate Schiff base ligand, 2,2-Dimethyl-N,N'-bis-(3-phenyl-allylidene)-propane-1,3-diamine (L), and its Cd(II) complexes have been synthesized. The resulting complexes and ligand were studied by elemental analyses, molar conductivity, IR, UV-Vis, ^1H and ^{13}C NMR spectra and the general formula MLX_2 suggested for cadmium complexes wherein X= Cl, Br and I.

EXPERIMENTAL

Materials and methods

All the solvents used in the synthesis and analysis, 3-Phenyl-propenal, 2,2-Dimethyl-propane-1,3-di-

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amine, cadmium salts and other chemicals were purchased from Aldrich and Merk, 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 DMF. ^1H and ^{13}C NMR spectra were recorded using a Bruker DPX FT-NMR spectrometer at 400 MHz with the samples dissolved in DMSO-d_6 and CDCl_3 using TMS as internal standard. Molar conductance of the Schiff base ligands and their transition metal complexes were determined in CHCl_3 (1.0×10^{-3} M) at room temperature using Metrohm 712 conductometer. The melting points ($^\circ\text{C}$) of the complexes were recorded on Kruss instrument.

Synthesis of Schiff base ligand 2,2-Dimethyl-N,N'-bis-(3-phenyl-allylidene)-propane-1,3-diamine (L)

New Schiff base was synthesized by drop wise adding of a methanolic solution of 2,2-Dimethyl-propane-1,3-diamine (0.1022 g, 1mmol) to the 2mmol 3-Phenyl-propenal (0.2643 g) dissolved in 20 mL methanol at room temperature condition and severally stirred. Ligand as orange precipitation was filtered and washed twice with cooled ethanol. For more purification, ligand recrystallized in ethanol-dichloromethan solvent.

IR(KBr, cm^{-1}): 3422(m), 3058(w), 3025(w), 2954(w), 2924(w), 2866(w), 2830(w), 1635(vs), 1577(w), 1448(s), 1385(m), 1160(w), 1026(w), 978(s), 748(s), 690(s), 508(m). UV-vis [(DMF), $\lambda(\text{nm})$]: 282. $^1\text{H-NMR}$ (CDCl_3): 8.08(d, 2H, J=7.20 Hz), 7.44(bd, 4H), 7.37(bm, 6H), 7.31(bd, 2H), 6.93(bd, 2H), 3.71(q, 4H), 1.24(t, 6H) ppm. $^{13}\text{C-NMR}$ (CDCl_3): 173.01, 163.72, 138.07, 128.82, 128.53, 127.26, 126.42, 58.22, 46.25, 18.46 ppm.

Preparation of CdLX_2 complexes (X= Cl, Br and I)

Chloride, bromide and iodide salts of cadmium dissolved in 10 mL absolute ethanol and 1mmol (0.3305 g) of the Schiff base ligand that dissolved in 20 mL methanol, was added to metal solution in several steps and the mixture was severe stirred at room temperature. The ratio that used for reaction is 1:1 metal to

ligand. The precipitated material was filtered off and then the product was washed with cooled ethanol and dried on the vacuum apparatus.

[CdLCl₂]

IR(KBr, cm^{-1}): 3443(m), 3054(w), 3022(w), 2956(w), 2897(w), 2842(w), 1632(vs), 1595(w), 1447(m), 1270(m), 1163(s), 1064(w), 1002(s), 967(m), 907(m), 752(s), 690(s), 510(m), 455(w). UV-vis [(DMF), $\lambda(\text{nm})$]: 286. $^1\text{H-NMR}$ (DMSO-d_6): 8.09(d, 2H, J= 7.20 Hz), 7.68(bd, 4H, J= 7.60 Hz), 7.41(m, 6H), 7.20(bs, 4H), 3.40(bs, 4H), 0.91(s, 6H) ppm. $^{13}\text{C-NMR}$ (DMSO-d_6): 169.84, 149.95, 135.49, 129.30, 128.66, 127.34, 121.20, 69.91, 36.17, 24.21 ppm.

[CdLBr₂]

IR(KBr, cm^{-1}): 3444(m), 3057(w), 3021(w), 2961(w), 2901(w), 2851(w), 1631(vs), 1611(m), 1593(m), 1447(m), 1264(m), 1160(w), 1055(w), 987(s), 955(m), 751(s), 692(s), 513(m), 459(w). UV-vis [(DMF), $\lambda(\text{nm})$]: 285. $^1\text{H-NMR}$ (CDCl_3): 7.98(d, 2H, J=9.20 Hz), 7.85(dd, 2H, J=9.60 Hz and J=9.20 Hz), 7.59(dd, 4H, J=2.00 Hz and J=4.40 Hz), 7.33(m, 6H), 7.11(d, 2H, J=12.00 Hz), 3.71(s, 4H), 0.88(s, 6H) ppm. $^{13}\text{C-NMR}$ (CDCl_3): 170.17, 149.52, 134.39, 130.99, 129.08, 128.61, 124.61, 72.28, 37.65, 24.75 ppm.

[CdLI₂]

IR(KBr, cm^{-1}): 3455(m), 3054(w), 3026(w), 2958(w), 2916(w), 2867(w), 1627(vs), 1592(m), 1448(m), 1267(m), 1165(s), 1064(w), 982(m), 953(m), 750(s), 685(s), 509(m), 438(w). UV-vis [(DMF), $\lambda(\text{nm})$]: 285. $^1\text{H-NMR}$ (CDCl_3): 8.04(d, 2H, J=9.60 Hz), 7.89(dd, 2H, J=9.60 Hz and J=9.20 Hz), 7.59(m, 4H), 7.34(m, 6H), 7.12(d, 2H, J=15.20 Hz), 3.65(s, 4H), 0.89(s, 6H) ppm. $^{13}\text{C-NMR}$ (CDCl_3): 170.12, 149.55, 134.44, 131.00, 129.09, 128.61, 124.64, 71.45, 37.55, 24.81 ppm.

RESULTS AND DISCUSSION

The resulting data that were given from analytical and physical methods show that the molar ratio between metal halides and ligand are 1:1 in all the complexes. These data are listed in TABLE 1 and TABLE

2. All compounds are very stable at room temperature in the solid state. The melting point of ligand was 93°C and for complexes was in the range of 171 to 291 °C. The molar conductivity of ligand and its complexes were recorded in 10⁻³ molar DMF solutions at room temperature. The range of 6.68-52.03 cm² Ω⁻¹M⁻¹ that

shows the low molar conductivity for all compounds, confirm that all of them are non-electrolytes and the anions in the structure of complexes are coordinated to central metal ion^[20]. The complexes can be presented by the general formula of CdLX₂ (X=Cl, Br and I) as shown in Figure 1.

TABLE 1 : Analytical and physical data of the Schiff base ligand (L) and its cadmium(II) complexes

| Compound | Color | Melting point (dec.) | Yield (%) | Found (Calcd.) (%) | | | ΛM (cm ² Ω ⁻¹ M ⁻¹) |
|----------------------|--------|----------------------|-----------|--------------------|------------|------------|---|
| | | | | C | N | H | |
| 1 Ligand(L) | Orange | 93 | 65 | 83.35(83.59) | 8.75(8.48) | 7.46(7.93) | 6.68 |
| 2 CdLCl ₂ | cream | 291 | 72 | 53.80(53.77) | 5.59(5.45) | 5.02(5.10) | 17.22 |
| 3 CdLBr ₂ | White | 211 | 79 | 45.70(45.84) | 4.81(4.65) | 4.26(4.35) | 17.55 |
| 4 CdLI ₂ | Cream | 171 | 71 | 39.60(39.65) | 4.17(4.02) | 3.64(3.76) | 52.03 |

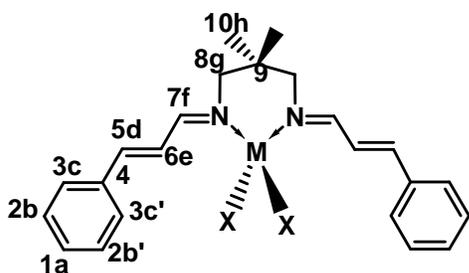


Figure 1 : The suggested structure for cadmium complexes with new bidentate Schiff base ligand X = Cl⁻, Br⁻ and I⁻

IR spectra

The more importance peaks of ligand and its cadmium complexes are given in the TABLE 2. In the spectrum of ligand, strong vibration band of azomethin moieties as functional groups for Schiff base are appeared in the 1635 cm⁻¹. This peak in the spectra of all complexes shifted to the lower frequencies by 3-8 cm⁻¹ after coordination ligand to metal indicating coordination through the iminic nitrogen of the Schiff base^[21,22]. The ligand stretching frequencies assigned to C-H of aromatic, olefinic, aliphatic and iminic groups located at 3058, 3025, (2954, 2924) and (2866, 2830) cm⁻¹ respectively. After coordination to metal ion, these peaks have shift to the lower or higher energies. The absorption bands at 1577, 748 and 690 cm⁻¹ were attributed

to vibration frequency corresponding to ν(C=C), out of plane CH aromatic and out of plane C-C aromatic bands in the Schiffbase have shifted to lower of higher frequencies after complexation. In the IR spectra of complexes new absorption band that was not observed in the spectrum of Schiff base ligand attributed to the vibration of M-N moieties located at 435-459 cm⁻¹ which have strongly supported the coordination of nitrogen donor sites of Schiff base ligand to metal ion^[23,24].

Electronic spectra

Electronic spectra of the ligand and its complexes were recorded in DMF at room temperature conditions and the spectral data including the λ_{max} values are listed in TABLE 2. For this type of chelate ligand, π-π* charge transfer occur in the electrons of aromatic rings, double bond of carbon-carbon and π electrons of iminic moieties. In some cases, these absorption bands can overlap together. In the UV-Vis spectrum of ligand the band that appeared at 278 nm is corresponding to ligand to ligand charge transfer (LLCT) as π-π* charge transfer. Coordination of ligand to metal ion influenced the location of π-π* charge transfer transition band and for complexes exhibited at 285-286 nm regions. The most important bands in d¹⁰ electron con-

TABLE 2 : Vibrational (cm⁻¹) and electronic (nm) spectral data of the Schiff base (L) and its complexes

| Compound | νCH _{arom.} | νCH _{alkene} | νCH _{aliph.} | νCH _{imin} | νC=N | νC=C | νCH _{arom(oop)} | νC-C _{arom(oop)} | νM-N | λ _{max} |
|----------------------|----------------------|-----------------------|-----------------------|---------------------|------|------|--------------------------|---------------------------|------|------------------|
| 1 Ligand | 3058 | 3025 | 2954, 2924 | 2866, 2830 | 1635 | 1577 | 748 | 690 | - | 278 |
| 2 CdLCl ₂ | 3054 | 3022 | 2956, 2897 | 2842 | 1632 | 1595 | 752 | 690 | 455 | 286 |
| 3 CdLBr ₂ | 3057 | 3021 | 2961, 2901 | 2851 | 1631 | 1593 | 751 | 692 | 459 | 285 |
| 4 CdLI ₂ | 3054 | 3026 | 2958, 2916 | 2867 | 1627 | 1592 | 750 | 685 | 438 | 285 |

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figuration metal complexes are charge transfer (MLCT) transition that may be overlap with $\pi-\pi^*$ transitions of the ligand as seen in the electronic spectra of titled complexes.

^1H and ^{13}C NMR spectra

Deuterated solvent that used for recording ^1H and ^{13}C NMR at the 400 MHz were CDCl_3 except for CdLCl_2 that used DMSO-d_6 . Figure 2 show the ^1H NMR and ^{13}C NMR spectra of ligand and cadmium iodide complexes respectively. All data of NMR spectra of ligand and its cadmium complexes were listed in experimental. In the ^1H NMR spectrum of ligand, the H_f as iminichydrogens due to coupling with H_e appeared as a doublet peak at the 8.08 ppm with coupling constant 7.20 Hz. After coordination of ligand to metal, the signal of azomethin hydrogen in the spectra of all complexes had a blueshift to lower fields except for CdLCl_2 that shifted smoothly to higher fields. In the spectrum of ligand, the hydrogens of aromatic rings appeared the signals at 7.44-7.37 ppm included by the signal of H_c and H_e at 7.44 as broad doublet and the signal of H_b , H_b , and H_a as multiplet peak at 7.37 ppm. After coordination in all complexes the signal of $\text{H}_{c,c}$ shifted to the weaker fields but the signal of $\text{H}_{b,b}$ and a shifted to the strong fields. The broad doublet signal at the 7.31 and 6.93 ppm are assigned to H_e and H_d . In the ^1H NMR of CdLCl_2 , the signal of H_e and H_d had a blue and red shift respectively and these signals appeared together at 7.20 ppm as a broad single peak. In the other complexes the signal of H_e as doublet of doublet peak due to coupling with H_d and H_f shifted to the 7.85-7.89 ppm and the doublet peak that is appeared at 7.11-7.12 ppm is attributed to the resonance of H_d that coupled with H_e . H_g of the ligand appeared as a quartet at 3.71 ppm due to coupling with H_h that shifted to 3.40-3.71 ppm in the complexes. H_h signal of the ligand at 1.24 ppm as a triplet is appeared at strong fields in the 0.88-0.91 ppm regions after coordination. In the ^{13}C NMR spectrum of ligand the peak at 173.01 ppm is assigned to carbon of iminic moieties that after coordination to metal ion shifted to lower fields to 169.84-170.17 ppm, suggesting well coordination of the iminic nitrogens to metal ions. The aromatic carbons in structure of ligand showed the signal at 138.07 (C_4), 128.82 (C_1), 128.53 (C_3) and 127.26 (C_2). Also the sig-

nals of olefinic carbons resonance exhibited at 163.72 ppm for C_6 and 126.42 ppm for C_5 . The signals reso-

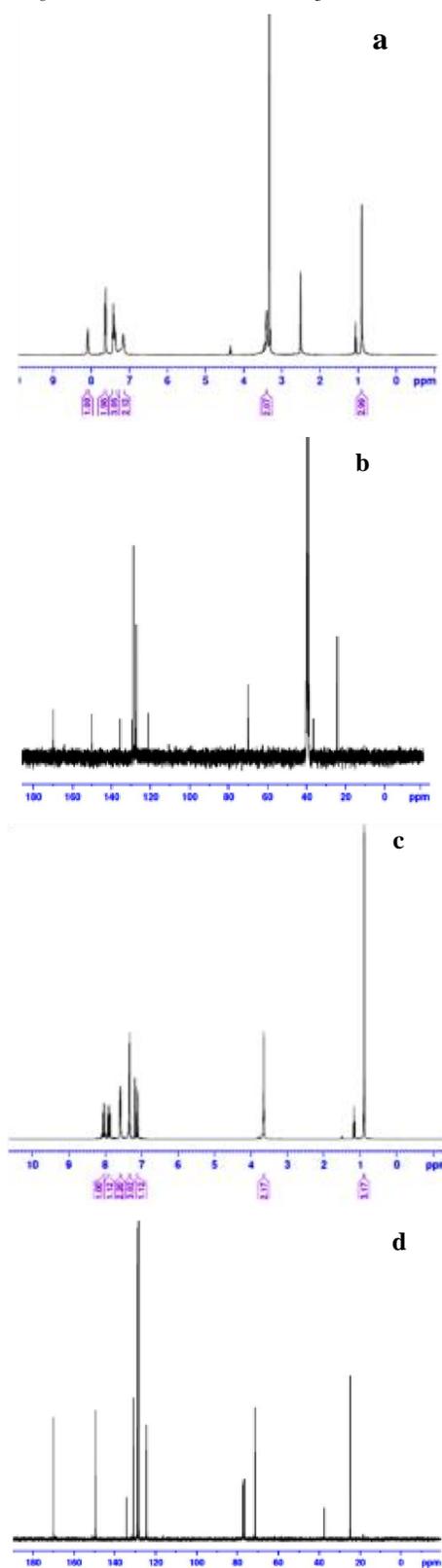


Figure 2 : The ^1H and ^{13}C NMR spectra of CdLCl_2 (a, b) and CdLI_2 (c, d) complex

nance of aliphatic carbons moieties were appeared at 58.22(C₈), 46.25(C₉) and 18.46(C₁₀). These ten signals in the ¹³C NMR spectrum of ligand are agree with the supposed structure of ligand at figure 1. Coordination of iminicnitrogens as donor sits to the metal cadmium cause to change in the location of carbons signals and in the spectra of complexes the aromatic carbons shifted to 134.39-135.49(C₄), 129.30-131.00(C₁), 128.66-129.09(C₃) and 127.34-128.61(C₂), the carbons of olefin moieties shifted to 149.52-149.95(C₆) and 121.20-124.64(C₅) and the aliphatic carbons had a shift to 69.91-72.28(C₈), 36.17-37.65(C₉) and 24.21-24.81(C₁₀). The resulting data from ¹H and ¹³C NMR are the reason to confirm the ligand and its cadmium complexes have been synthesized successfully with the structure that supposed in figure 1.

CONCLUSION

In this paper, we reported synthesis and characterization of some new cadmium halide complexes of a new bidentate ligand. The ligand and its complexes were characterized by spectral (IR, UV-Visible and H and CNMR) and physical data. The suggested structure for the complexes was considered pseudo-tetrahedral.

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