

Synthesis and Characterization of Co (II), Ni (II), Cd (II) and Cu (II) Complexes of Bis-Schiff Bases obtained from 1,8-Diaminonaphthalene

NEVİN TURAN* AND MEMET ŞEKERCI

Faculty of Arts and Sciences, Chemistry Department, Firat University, 23119 Elazığ, Turkey.

(Received 15th October 2008, accepted in revised form 31st January 2009)

Summary: The present study deals with the preparation of Schiff base and its chelates with some transition metal ions Co (II), Ni (II), Cu (II) and Cd (II). The ligand was obtained by condensation of 1,8-diaminonaphthalene with salicylaldehyde. The ligand and its complexes have been characterized by elemental analyses, IR, ¹H-NMR, UV-Vis. molar conductance and magnetic susceptibility. The analytical, spectral and magnetic data support the mononuclear formulations of these complexes with M/L 1:1. The Co (II) and Ni (II) complexes of ligand are proposed to be square-planar, while the Cu (II) and Cd (II) complexes are proposed to be tetrahedral.

Introduction

Schiff bases are important class of ligands in coordination chemistry and find extensive applications in different fields [1-3].

In recent years, metal complexes of Schiff bases have attracted considerable attention due to their remarkable antibacterial, antifungal and antitumor activities [4,5]. Schiff base complexes derived from 4-hydroxysalicylaldehyde and amines have strong anticancer activity [6]. In the present paper Co (II), Ni (II), Cu (II) and Cd (II) complexes of the Schiff bases derived from 1,8-diaminonaphthalene and salicylaldehyde are reported. The structures the bis-Schiff base ligands are shown in Fig. 1.

Results and Discussion

The Schiff base ligand (LH₂) was prepared by condensation of 1,8-diaminonaphthalene with salicylaldehyde in DMSO by the reaction (Fig. 2).

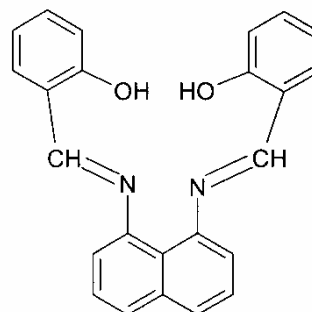


Fig. 1: Structure of the ligand (LH₂).

The elemental analyses and some physical properties of the complexes are listed in Table-1. The analytical data are in good agreement with proposed stoichiometry of the complexes. The ligand LH₂, upon reaction with Co (II), Ni (II), Cu (II) and Cd (II) chlorides yields complexes corresponding to the general formula [ML] and [CdL].2DMSO (Fig. 3).

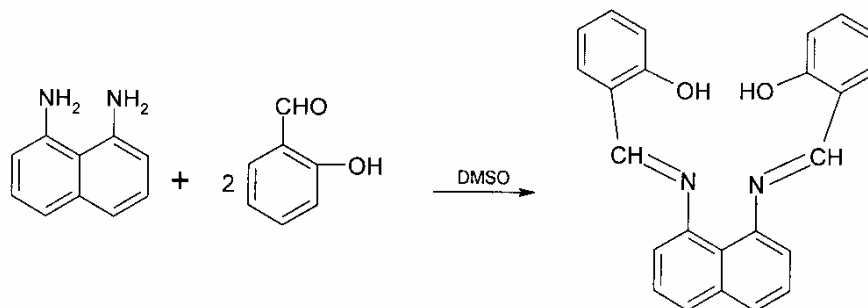
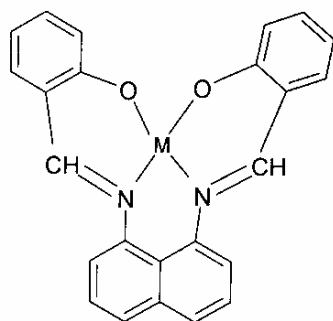


Fig. 2: Synthesis scheme for the preparation of the ligand (LH₂).

*To whom all correspondence should be addressed.

Table-1: The Colors, Formula, Formula Weight, Yields, Melting Points, Magnetic Moments and Elemental Analysis Results of the Ligand (LH₂) and the Complexes.

Compounds	FW, (g/mol)	M.p. (°C)	Yield (%)	μ_{eff} (B.M.)	Elemental Analyses			
					Calculated (Found) (%)			
					C	H	N	S
Ligand (LH ₂) (Dark Brown)	366	252	42.0	—	78.69 (78.15)	4.92 (5.00)	7.65 (7.37)	—
C ₂₄ H ₁₈ N ₂ O ₂								
[CoL] (Black)	422.93	333	60.0	1.42	68.10 (67.98)	3.78 (3.19)	6.62 (6.10)	—
C ₂₄ H ₁₆ N ₂ O ₂ Co								
[NiL] (Black)	422.71	336	54	Dia	68.13 (68.00)	3.79 (3.51)	6.62 (6.41)	—
C ₂₄ H ₁₆ N ₂ O ₂ Ni								
[CuL] (Dark green)	427.55	338	50	1.05	67.36 (67.16)	3.74 (3.65)	6.55 (6.25)	—
C ₂₄ H ₁₆ N ₂ O ₂ Cu								
[CdL]·2DMSO (Gray)	632.66	350	55	Dia	53.11 (53.06)	4.43 (4.35)	4.43 (3.98)	10.12 (10.00)
C ₂₈ H ₂₈ N ₂ O ₄ S ₂ Cd								



M = Co (II), Ni (II) and Cu (II)

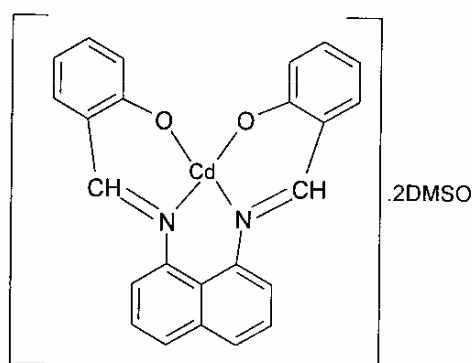
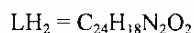
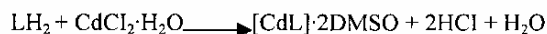
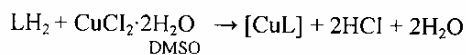
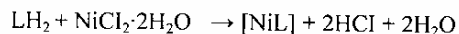
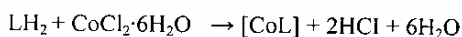


Fig. 3: Suggest structure of the square-planer Co (II), Ni (II) and tetrahedral Cu (II), Cd (II) complexes of the ligand (LH₂).

The complexes were prepared by the general reaction shown below.



The analytical data show that the metal to ligand ratio is 1:1; in addition, the Cd (II) complex has two additional chelating DMSO units. The synthesized Schiff base ligands and their complexes are very stable at room temperature in the solid state. The ligands are soluble in DMSO at room temperature, acetone and chloroform at ambient temperature, but its metal complexes are generally soluble in DMSO and DMF.

Conductance Measurements

According to the molar conductivity measures Co (II), Ni (II), Cu (II) and Cd (II) complexes haven't shown an important conductivity. This proves that complexes are in the non-ionic structure [7].

Magnetic Moment Data

The Co (II) and Cu (II) complexes are paramagnetic. The magnetic susceptibility values of Co (II) and Cu (II) are 1.42, 1.05 B.M., respectively. As Co (II) and Cu (II) complexes are paramagnetic, their ¹H-NMR spectra could not be obtained [7]. Therefore, the Ni (II) and Cd (II) complexes are diamagnetic and their ¹H-NMR spectra cannot be obtained.

Infrared Spectra

Important IR bands of the Schiff base ligand (LH₂) and its complexes are given in Table 2. The

Table-2: Characteristic IR Bands (cm^{-1}) of the Ligand (LH_2) and the Complexes in KBr Pellets.

Assignment	Ligand (LH_2)	[CoL]	[NiL]	[CuL]	[CdL]-2DMSO
ν (OH)	3500-3442				
C-H Aromatic	3080-3060	3045	3041	3055	3050
C=N Azomethine	1628	1617	1619	1618	1610
ν (C=C)	1565	1558	1550	1554	1548
Phenolic C-O stretching	1340	1157	1152	1154	1163
ν (M-N)	—	518	523	517	488
ν (M-O)	—	460	476	470	446

position and/or the intensities of these peaks are expected to be changed upon chelation.

In the IR spectrum of 1,8-diamino naphthalene the characteristic peaks are at 3370 and 3286 cm^{-1} ν (NH_2) and 1578 cm^{-1} δ (NH), respectively [8].

In the IR spectra of the ligand (LH_2), the most characteristic bands are at 3472 cm^{-1} ν (OH) and 1628 cm^{-1} ν ($\text{HC}=\text{N}$) azomethine. Absence of ν (C=O) and ν (NH_2) peaks in the spectra of ligand indicates that the expected imino compound was formed by condensation from 1,8-diamino naphthalene and salicylaldehyde and it is also shown that there are no residual starting materials left in the ligand compound as well [9].

The azomethine ν (C=N) bands in the spectra of ligand (LH_2) lying at 1628 cm^{-1} displayed a shift to lower wave numbers (1610-1619) in the spectra of complexes Co (II), Ni (II), Cu (II) and Cd (II) indicating that the C=N nitrogen atom coordinates to the metal ion in these complexes [10, 11].

Phenolic ν (C-O) stretching vibration band is observed at 1340 cm^{-1} in the free ligand. In all complexes, this band appears at lower frequency in 1152-1163 cm^{-1} region, confirming the involvement of the phenolic group in complex formation [12, 13].

In the complexes, weak bands in the 476-446 cm^{-1} and 523-488 cm^{-1} range, can be attributed to ν (M-O) and ν (M-N), respectively. From the IR results, it may be concluded that the Schiff base ligand is bidentate and coordinates with the metal ion through the phenolic oxygen and azomethine nitrogen atoms [14, 15].

¹H-NMR Spectra

The ¹H-NMR spectrum of Schiff base and its Ni (II) and Cd (II) complexes were recorded in

DMSO- d_6 solution using tetramethylsilane (TMS) as internal standart. The ¹H-NMR spectrum of the free ligand showed wide singlet 9.90 ppm due to phenolic protons, a singlet at 8.10 ppm due to imine protons, multiplet in the range 6.50-7.04 ppm due to the aromatic protons and DMSO proton at 2.52 ppm.

The ¹H-NMR spectrum of Ni (II) and Cd (II) complexes showed approximately the same peaks similar to those of the free ligand with the exception of phenolic group. The phenolic-OH signal, appeared in the spectrum of ligand (LH_2) at 9.90 ppm is completely disappeared in the spectra of its Ni (II) and Cd (II) complexes indicating that the OH protons are removed by the chelation with Ni (II) and Cd (II) ions. In the spectra of Schiff bases protons of the azomethine group undergo downfield shift in the Ni (II) and Cd (II) complexes indicating participation of this group in coordination of the metals ions.

Electronic Spectra

The UV-vis spectra of the ligand and its complexes were recorded in the DMF solution in the wavelength range from 200 to 800 nm.

The band appearing in the range of 250-340 nm is attributed to $\pi \rightarrow \pi^*$ transition of the benzene ring of the ligand (LH_2). In the spectra of the complexes, these bands are slightly to lower wavelength. In the spectrum of the ligand the bands in the 377-436 nm range are assigned to the $n \rightarrow \pi^*$ transitions of the azomethine group. During the formation of the complexes these bands are shifted to lower wavelength suggesting that the nitrogen atom of the azomethine group is coordinated to the metal ion.

The electronic spectrum of the Co (II) complex shows absorption bands at 600 nm and 685 nm, attributed to the ${}^2A_{1g} \rightarrow {}^2E_g$ and ${}^2A_{1g} \rightarrow {}^2B_{2g}$ transitions, which is compatible with this complex having a low spin square-planar structure [16].

The electronic spectrum of the Ni (II) complex shows an absorption band at 445 nm attributed to the ${}^1A_{1g} \rightarrow {}^1B_{1g}$ transition, which is compatible with this complex having a square-planar structure [17].

The appearance of the weak d-d transition band around 685 nm suggests that the chaletes of the Cu (II) have tetrahedral geometry, because the d-d

transition of tetrahedral geometry gives a specific band around 685 nm [18]. The electronic spectrum of the Cu (II) complex shows an absorption band around 685 nm attributed to the ${}^2T_{2g} \rightarrow {}^2E$ transition, which is compatible with this complex having tetrahedral structure [19].

The electronic spectrum of the Cd (II) complex shows only a band at 455 nm attributed to the ligand-metal charge transfer transition. The Cd (II) complexes are diamagnetic as expected for its d^{10} configuration. Thus, from IR, electronic and analytical data it is clear that LH_2 reacts with Cd (II) in 1:1 molar ratio with tetrahedral coordination around this metal ions [20, 21].

Experimental

Materials and Measurements

All solvents were of analytical grade. The metal salts $CoCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $NiCl_2 \cdot 2H_2O$ and $CdCl_2 \cdot H_2O$ and starting materials for the ligand were Merck, Aldrich, Fluka and Alfa Aesar products.

The electronic spectra of the ligand and the complexes in the UV-Vis. region were recorded in DMF solutions using a pharmacia LKB-Ultraspec III. UV Spectrophotometer. IR spectra were recorded on a ATI-LNICAM MATTSON 1000 series FTIR spectrometer on KBr pellets in the wave number range of 400-4000 cm^{-1} . 1H -NMR spectra were recorded on a jeol FX 90 Q, 90 MHz in $DMSO-d_6$, magnetic susceptibilities measurements were performed using the standard Gouy tube technique using $Hg[Co(SCN)_4]$ as a calibrant. The elemental analyses were conducted on a LECO CHNS-O model 932 instrument.

Synthesis of the Schiff Base (LH_2)

1,8-Diaminonaphthalene (3.16 g, 0.02 mol) in 15 mL DMSO was added slowly and drop wise into a solution of salicylaldehyde (4.88 g, 0.04 mol), the mixture was stirred at 120 °C for 30 min. Five drops of 3 mL glacial acetic acid solution were added to the above-mentioned solution to keep pH~5. The resultant solution was refluxed for 6 h. The resulting dark brown coloured precipitation was filtered and washed with ethanol and ether, then dried at room temperature. Yield: 3.07 g (42 %).

Synthesis of Co (II), Ni (II), Cu (II) and Cd (II) Complexes

The ligand (LH_2) (1.10 g, 0.003 mol) was dissolved in 50 ml DMSO in a 100 mL round-bottom flask. A solution of 0.003 mol the metal salt [$CoCl_2 \cdot 6H_2O$ (0.71 g), $NiCl_2 \cdot 6H_2O$ (0.50 g), $CuCl_2 \cdot 2H_2O$ (0.51 g) and $CdCl_2 \cdot H_2O$ (0.60 g) in 10 mL of absolute ethanol was added dropwise in a 10 min. period with continuous stirring at room temperature. The reaction mixture were then further refluxed for 8 h at 100-120 °C. The resulting precipitates were filtered off, and washed with DMSO and ether, respectively. It was then dried in room temperature. Yields: 0.76 g (60 %), 0.69 g (54 %), 0.64 (50 %), 1.04 g (55 %), respectively.

References

1. K. M. Patel, K. N. Patel, N. H. Patel and M. N. Patel, *Synthesis Reactivity Inorganic, Metal-Organic Chemistry*, **31**, 239 (2001).
2. H. Temel, Ü. Çakir, H. I. Ugraş and M. Şekerci, *Journal of Coordination Chemistry*, **56**, 943 (2003).
3. Y. Liang, B. Su, J. Zhao and W. Sun, *Synthetic Communications*, **34**, 3235 (2004).
4. V. K. Patel, A. M. Vasanwala and C. R. Jejurkar, *Indian Journal of Chemistry*, **28A**, 719 (1989).
5. N. Turan and M. Şekerci, *XVIII. National Chemistry Congress*, Kars, Turkey, 424 (2004).
6. M. Şekerci, C. Alkan, A. Çukurovalı and S. Saydam, *XIII. National Chemistry Congress*, Samsun, Turkey, 182 (1999).
7. H. Temel, Ü. Çakir, B. Otludil and H. İ. Ugraş, *Synthesis Reactivity Inorganic, Metal-Organic Chemistry*, **31**, 1323 (2001).
8. S. M. Abu-El-Wafa, N. A. El-Wakiel, R. M. Issa and R. A. Mansour, *Journal of Coordination Chemistry*, **58**, 683 (2005).
9. M. T. El-Haty and F. A. Adam, *Bulletin De La Societe Chimique De France*, No. 5 (1986).
10. C. H. Lin, *Synthesis Reactivity Inorganic, Metal-Organic Chemistry*, **23**, 1097 (1993).
11. A. Kolawole and K. S. Patel, *Journal of the Chemical Society Dalton Transactions*, 1241 (1991).
12. H. Temel and M. Şekerci, *Synthesis Reactivity Inorganic, Metal-Organic Chemistry*, **31**, (2001).
13. N. Turan and M. Şekerci, Master Thesis, *Synthesis and characterization of Co (II), Ni (II), Cu (II) complexes of Schiff base obtained from*

- 1,8-diaminonaphthalene*. University of Fırat, Elazığ, Turkey, 2003.
14. Z. H. Chosan and H. Pervez, *Synthesis Reactivity Inorganic, Metal-Organic Chemistry*, **23**, 1061 (1993).
 15. N. Turan and M. Şekerci, *XVII. National Chemistry Congress*, Istanbul, Turkey, 237 (2003).
 16. M. Nath, A. Kumar and S. Vashista, *Synthesis Reactivity Inorganic, Metal-Organic Chemistry*, **28**, 893 (1998).
 17. H. Temel, S. İlhan, M. Şekerci and R. Ziyadanoğulları, *Spectroscopy Letters*, **35**, 219 (2002).
 18. M. Şekerci, C. Alkan and A. Çukurovalı, *Russian journal of Inorganic Chemistry*, **45**, 8 (2000).
 19. E. Taş and M. Şekerci, *Heteroatom Chemistry*, **11**, 4 (2000).
 20. M. Şekerci and C. Alkan, *Journal of Science and Engineering*, University of Fırat, **11**, 119 (1999).
 21. N. Turan, N. Çolak and M. Şekerci, *International Journal of Natural and Engineering Sciences*, **2**, 28 (2008).