

RESEARCH ARTICLE



SYNTHESIS AND CHARACTERIZATION OF UNSYMMETRICAL AZO-LINKED SCHIFF-BASE: TRANSITION METAL COMPLEXES AND THEIR FLUORESCENCE PROPERTIES

MARYAM LASHANIZADEGAN* , MINA JAMSHIDBEIGI AND MARZIEH SARKHEIL

Department of Chemistry, Faculty of Science, Alzahra University, Vanak, Tehran, Iran, P. O. 1993893973.

Corresponding Author: m_lashani@alzahra.ac.ir

Abstract

Metal Complexes (ML), (M= Mn(II), Cu(II), Ni(II), Zn(II), Co(II) and Cd(II)) of Schiff base ligand were obtained by condensation of 4-(benzeneazo) salicylaldehyde with 1,2-propandiamine. The above complexes have been synthesis by direct reaction of ligand with metal and also template method and characterized by their infrared spectra, electronic spectra and elemental analysis. The ligand and its complexes with Ni(II), Zn(II) and Cd(II) were further identified using ¹H NMR spectra. The complexes display intra ligand (_ *) fluorescence in solid state at room temperature.

Keywords: Azo-link, Transition metal, Luminescence, salicylaldehyde.

Introduction

The interest in Schiff base ligands are due to their easy synthesis process and application of their complexes in the understanding of coordination chemistry of transition metal ions (Katsuki et al., 2003) catalysis (Cozzi et al., 2003) dioxygen uptake (Tovrong et al., 1976). Azo derivatives have been utilized as organic dyes (Hunger, 2003), indicators (Anderson et al., 1967), (Ashutosh et al., 1979) and radical reaction indicator (Athey, 1998), (Sheppard, 1985). In addition, azo derivatives have the potential for use in electronic (Cisnetti et al., 2004), drug delivery applications (Jain et al., 2006). Azo derivatives can serve as an example of the use of the fluorescence increase effect for the quantitative determination of copper (Hu et al., 1998). Therefore azo-linked Schiff base derivatives have potential to be use in all properties of azo and Schiff bases compounds. The oxidation-reduction behaviors of these compounds play important role in its biological activity (Zhou et al., 2000). Here we report the synthesis and characterization of Mn(II), Cu(II), Ni(II), Zn(II), Co(II) and Cd(II) complexes of

Schiff base, N,N'-bis[4(benzeneazo) salicylaldehyde]1,2 propanediamine. We also have studied the luminescence of the prepared complexes.

Experimental

All chemicals used in the present study are of analytical grade. Melting points were analyzed with an electrothermal melting point apparatus. FT-IR spectra were recorded using a Bruker Tensor 27 spectrometer. The visible spectra were determined using a Perkin Elmer, Lambda 35 UV/Vis. Spectrometer. Fluorescent studies were performed on a Varian Eclipse spectrofluorimeter. ¹H NMR spectra were obtained on a Bruker Avance 300 MHz spectrometer using TMS as internal standard.

Preparation of 4-(benzeneazo) salicylaldehyde 4-(benzeneazo) salicylaldehyde (HL') was prepared using standard procedure (Vogel, 1956).

Preparation of ligand (H₂L)

0.05 mole of 1-2 propandiamine was slowly added to a solution of 0.03 mole of 4-(benzeneazo) salicylaldehyde (30 ml ethanol) after refluxing the reaction mixture for 2 h. The solution was left at room temperature and red precipitate was collected by filtering and washing with 15 ml of ethanol and then recrystallized from ethanol and dried at 50 °C overnight. Yield 82% M.P. 84 °C.

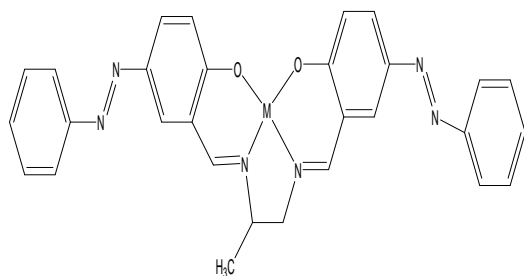
Preparation of the complexes (ML)

Mn(II), Cu(II), Ni(II), Zn(II), Co(II) and Cd(II) complexes were prepared by the addition of 1mmole Mn(CH₃COO)₂ .4H₂O, Cu(CH₃COO)₂ .H₂O, Ni(CH₃COO)₂ .4H₂O, Zn(CH₃COO)₂ .2H₂O, Co(CH₃COO)₂ .4H₂O and Cd(CH₃COO)₂ .2H₂O, respectively, which were dissolved in about 5-10 ml of hot ethanol solution of 1mmol of the ligand. The mixture was then refluxed for 2h. The precipitated solid were filtered off from the ice-cooled reaction mixture. The solid was washed with ethanol and then dried at 50 °C.

Template preparation of the complexes (ML)

All complexes were also prepared by template reaction in one step, 1mmole hydrated metal acetate, 1mmole 1-2 propandiamine and 2mmole 4-(benzeneazo) salicylaldehyde in 30mL ethanol reflux for 4 h. The precipitated solid were filtered off from the ice-cooled reaction mixture. The solid were washed with ethanol and then dried at 50 °C.

Scheme 1



M= Cu, Ni, Mn, Co, Zn, Cd

Results and Discussion

The complexes (Scheme 1) are air –stable colored solid, insoluble in water, partly soluble in ethanol and methanol and soluble in DMSO and DMF. Analytical data given in Table 1 suggest that the metal-ligand stoichiometry is 1:1. The complexes

were characterized by spectral studies. The elemental analysis and physical properties of the ligand and metal complexes listed in Table 1.

Infrared spectra

The IR spectrum of the H₂L (Table2) shows a (C=N) peak at 1631 cm⁻¹ and the absence of the (C=O) peak around 1700 cm⁻¹ is indicative of Schiff base condensation. The IR spectra of all the complexes show (C=N) band (LashanizadeganandBoghaei, 2000) at 1612-1632 cm⁻¹ and it is found that the (C=N) bands in the complexes are shifted by about 5-20 cm⁻¹ compared to the free ligand (H₂L). This phenomenon appears to be due to the coordination of the azomethinenitrogens to the metal ion (Chiswell et al., 1980), (Sharma and Prasad, 1982), (Toeo et al., 1997). The phenolic C-O stretching vibration appeared at 1283 cm⁻¹ in the Schiff base (Biradar andKulkarni, 1971) under the shift toward lower frequencies in the complexes. This shift confirms the participation of oxygen in the C-O-M bond (Wang and Chang, 1994).

¹H NMR spectra of the compound

The ¹H NMR data and assignments of the compounds are shown in Table 3. The ¹H NMR spectrum of the free ligand shows a multiplet in the range 7-7.9 ppm due to aromatic protons, and O-H protons of the two phenolic groups are at 13.28 ppm. The azomethine protons in the free ligand appear at 8.46, 8.48 ppm due to unsymmetrical azomethine protons. The methylene protons appear as a doublet at 3.8 ppm due to the coupling with -CH- proton. Also a multiple peaks at 3.8-4 ppm and a sharp peak at 1.51 ppm with integrals correspond to one CH and three CH₃ protons, respectively, confirm the proposed stoichiometry and structure for the Schiff base ligand(H₂L). The ¹H NMR of Ni(II), Zn(II) and Cd(II) complexes show the different types of protons as was observed in the ligand with a little shift, and disappearing of phenolic O-H proton. These observations suggested that the ligand coordinates to the metal atoms through the charged phenolic oxygen and the nitrogen atoms of azomethine groups of the N₂O₂ in the complex.

Electronic absorption spectroscopy

The electronic spectra data of the ligand and their complexes are shown in Table 4. The spectra of H₂L exhibit 2 main peaks at 280 and 345nm.

Table 1. Analytical Data of the Ligand and its Complexes.

Formula	M.P. (dec.)	Color	Yield %	Found (Caled.) %		
				C	H	N
H ₂ L C ₂₉ H ₂₆ N ₆ O ₂	84	Orange	82	70.49 (71.23)	5.23 (5.30)	17.23 (17.14)
NiL C ₂₉ H ₂₄ NiN ₆ O ₂	195	Red	96	62.02 (63.73)	4.45 (4.39)	15.24 (15.38)
CuL C ₂₉ H ₂₄ CuN ₆ O ₂	291	Brown	75	60.94 (61.15)	4.26 (4.21)	14.51 (14.76)
ZnL, H ₂ O C ₂₉ H ₂₆ ZnN ₆ O ₃	(215)	Orange	80	57.54 (57.33)	4.10 (3.95)	13.74 (13.83)
CdL C ₂₉ H ₂₄ CdN ₆ O ₂	(286)	red	46	57.6 (57.96)	4.2 (3.99)	13.81 (13.9)
CoL1.5H ₂ O C ₂₉ H ₂₇ CoN ₆ O _{3.5}	(205)	Dark brown	13	60 (60.63)	4.4 (4.7)	14.4 (14.6)
MnL0.5H ₂ O C ₂₉ H ₂₅ MnN ₆ O _{2.5}	(250)	Brown	33	63.1 (63.0)	4.3 (4.53)	15.0 (15.22)

Table 2. Important IR Absorption Bands (cm⁻¹) of the Ligand and its Complexes.

Compound	€(N=N)	€(C=N)	€(C-O)
H ₂ L	1436	1631	1283
CuL	1417	1629	1255
MnL	1422	1623	1261
NiL	1419	1612	1257
CoL	1419	1607	1255
ZnL	1418	1601	1259
CdL	1414	1632	1282

Table 3. ¹H NMR Chemical shifts (PPM) of Ligand and metal Complexes

Compound	O-H	CH=N	CH ₃	Aromatic H	CH ₂	CH
H ₂ L	13.28 (s, 2H)	8.46,8.50 (s, 2H)	1.51 (s, 3H)	7 - 7.9 (m, 16H)	3.7-3.8 (d, 2H)	3.8-4 (m, 1H)
NiL	--	7.94-7.95 (m, 2H)	1.52 (s,3H)	7.3 – 7.9 (m, 16H)	3 (d, 2H)	3.6 (m, 1H)
ZnL	--	8.4 (s, 2H)	1.36 (s, 3H)	6.9 – 7.9 (m, 16H)	3.4-3.5 (d, 2H)	4-4.05 (m, 1H)
CdL	-	8.44,8.48 (s, 2H)	1.29 (s, 3H)	7-7.9 (m, 16H)	3.7-3.8 (m, 2H)	3.91-3.94 (m, 1H)

Table 4. The electronic spectra data of the ligand and its complexes

Compound	Bands nm, (log)
H ₂ L	280(4.92), 345(5.19)
CuL	280(5.28), 381(5.5), 487(sh)
NiL	269(5.1), 398(5.2), 462(sh)
MnL	257(5.6), 384(5.7), 499(sh)
CoL	280(5.28), 384(5.5),
ZnL	286(5.3), 359(5.6), 480 (sh)
CdL	280(5.6), 354(5.7), 456 (sh)

=mol⁻¹ L cm⁻¹ in CH₂Cl₂

Table 5. Photophysical data for the ligand and complexes.

Compound	Absorption, (nm)	Emission, (nm)
H ₂ L	280	382
NiL	398	450, 485, 531, 542
MnL	384	435, 486, 524, 541
CoL	384	434, 486, 525, 541
ZnL	385	435, 487, 527, 541
CdL	280	382

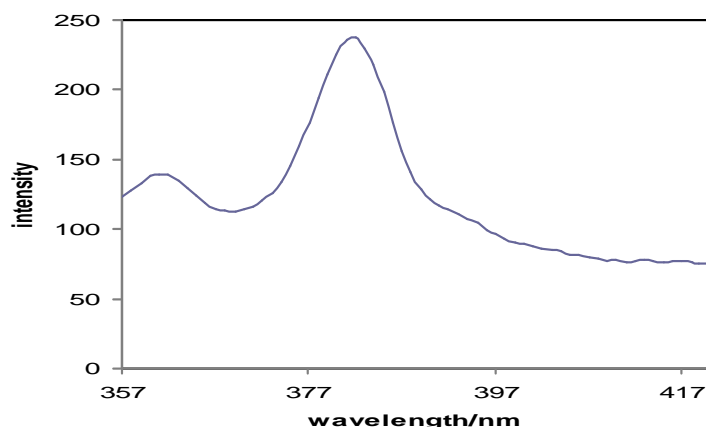
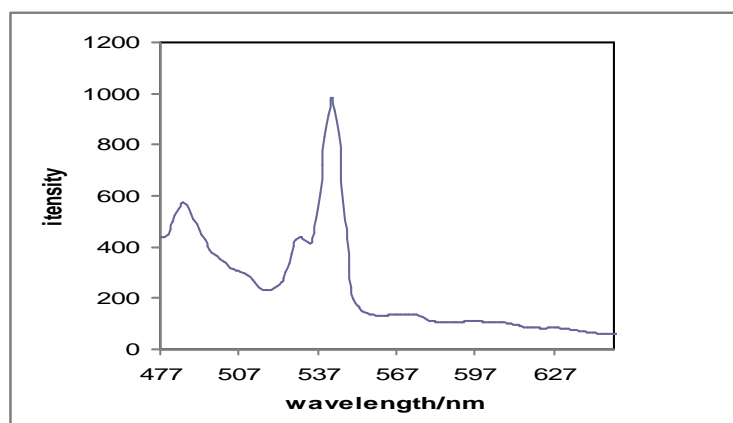
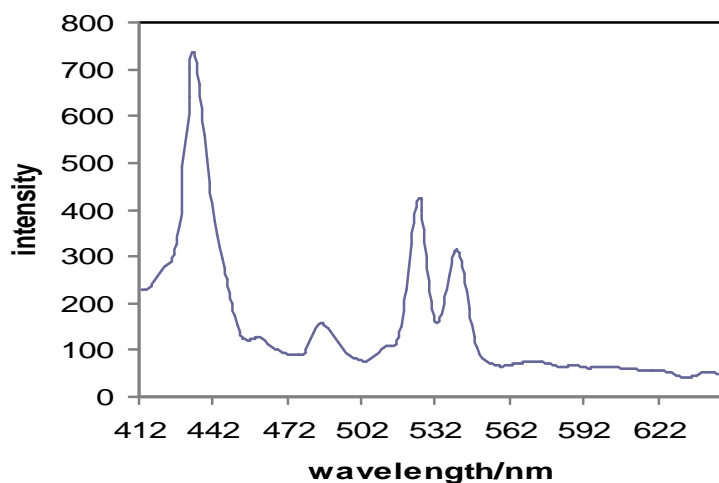
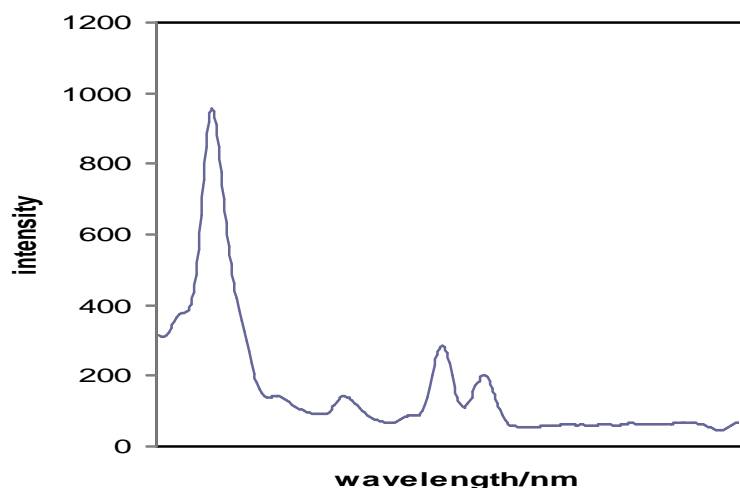
Fig. 1. Luminescence spectra of ligand**Fig. 2.** Luminescence spectra of NiL

Fig. 3. Luminescence spectra of MnL.**Fig. 4.** Luminescence spectra of CoL.

The first peak was assigned to benzene π - π^* . This band was not significantly affected by chelating. The second band in the spectra of Schiff base at 345nm was assigned to n - π^* transition. This band was shifted to a longer wavelength (10-43 nm) along with an increase in its intensity. This shift is attributed to the donation of the lone pairs of the nitrogen atoms of the Schiff base to the metal ion (N-M) (Liu et al., 2006). The diamagnetism of NiL and the lack of absorption above 650 nm in its electronic spectra are indicative of square-planer geometry of NiL complex (Costs et al., 1986). For the CuL complex, d-d transition occurs under at 487nm as a shoulder which is consistent with a planar geometry around the copper ion (Swett and Dudek, 1968).

Luminescence properties

Ligand (H_2L) and all its complexes exhibit fluorescence at 380-542 nm in solid state at room temperature. These are assigned as intra ligand (π - π^*) fluorescence (Pal et al., 2006), (Banthia and Samanta, 2006) (. It is interesting that the Ni(II), Co(II), Mn(II), Zn(II) and Cu(II) complexes show a higher intensity that of free ligand H_2L . The emission peak has a large red shift in contrast to the free ligand H_2L . Metal ions can enhance the fluorescence emission of some Schiff base ligands containing aromatic ring. In the absence of metal ion, the fluorescence of the ligand is probably quenched by a photoinduced electron transfer (PET) process due to the presence of lone pairs of electrons of the donor atoms in the ligand. Such a PET process is prevented by the complexation of H_2L with a metal. Therefore the fluorescence intensity may be greatly enhanced by the coordination of metal ions. Spectral results are set in Table 5 and spectral pattern is shown in Fig. 1-4. CdL complex shows emission behavior such as ligand. The strong fluorescence emissions of complexes make them a potentially useful photoactive material in photophysical chemistry.

Acknowledgement

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