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STRUCTURAL CHARACTERIZATION, ELECTROCHEMICAL AND FLUORESCENCE BEHAVIOR OF METAL (II) COMPLEXES OF SCHIFF BASE DERIVED FROM 5-BROMOVANILLIN

Chemistry

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ABSTRACT

Co(II), Ni(II), Cu(II) and Zn(II) complexes of a Schiff base derived from condensation of 3-bromo-4-hydroxy-5-methoxybenzaldehyde (5-bromovanillin) with 4-amino-3-mercapto-5-oxo-1,2,4-triazine were synthesized and their structural features were investigated by IR, 1H NMR, electronic spectroscopy, fluorescence, thermal, conductivity and magnetic measurements. Based on spectral and thermal techniques, octahedral geometry has been proposed for Co(II), Ni(II) and Zn(II) complexes and square planar for Cu(II) complexes.

KEYWORDS

Metal complexes, Schiff base, triazine, fluorescence, electrochemistry.

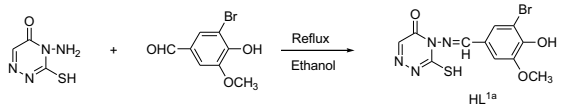
1. INTRODUCTION

In recent years, the progress of Coordination compounds has helped to blur the traditional borders between inorganic and organic chemistry through the isolation of numerous compounds consisting of metal ions and organic ligands. Transition metal complexes of Schiff bases find diverse applications [1-2] owing to structural similarities with natural biological substances, relatively simple preparation procedures and synthetic flexibility. Schiff bases appear to be important intermediates in a number of enzymatic reactions [3] and their complexes with transition metals are widely used in catalytic reactions due to their electronic and structural properties [4-7]. Hence metal complexes of Schiff bases are of valuable interest and play significant role in the development of coordination chemistry. As a part of our continuing work [8-10], we now report the synthesis and characterization of Co(II), Ni(II), Cu(II) and Zn(II) complexes of a Schiff base derived from condensation of 4-amino-3-mercapto-5-oxo-1,2,4-triazine with 5-bromovanillin.

2. Experimental

2.1 Synthesis of *4-[(3-bromo-4-hydroxy-5-methoxybenzylidene)-amino]-3-mercapto-5-oxo-1,2,4-triazine* (HL^{1a})

To a solution of 4-amino-3-mercapto-5-oxo-1,2,4-triazine in 10 ml of absolute alcohol, a solution of 3-bromo-4-hydroxy-5-methoxybenzaldehyde in 10 ml of absolute alcohol was added and the reaction mixture was heated under reflux for eight hours. The Schiff base (Scheme 1) obtained was filtered, washed several times with cold ethanol, dried and then recrystallized from absolute alcohol.
Yellow; Yield: 84%; m.p. 222-224˚C.



Scheme 1

2.1.1 Metal complexes of HL^{1a}

The Co(II), Ni(II), Cu(II) and Zn(II) complexes were synthesized by mixing hot ethanolic solutions of the Schiff bases with the hot ethanolic solutions of respective metal acetates in 1:1 and 1:2 molar ratios. The precipitates formed immediately were filtered off, washed successively with warm water, ethanol, acetone and finally dried on water bath.

3. RESULTS AND DISCUSSION

3.1 IR Spectra

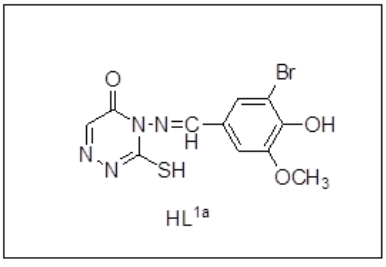
The mode of binding of the free ligand to the metal ion has been elucidated by comparing the IR spectrum of the Schiff base (HL^{1a}) with the spectra of the metal complexes. The characteristic absorption bands of the Schiff base and its metal complexes are given in Table 1.

Table 1: Important IR frequencies (cm^{-1}) of the Schiff bases (HL^{1a-c}) and their metal complexes

Compounds	ν(N=CH)	ν(C-S)	ν(S-H)	ν(OOCCH$_3$)	ν(H$_2$O/OH)	ν(M-S)	ν(M-N)
Schiff base	1591	-	2750	-	-	-	-
Co(L^{1a})(OAc).3H$_2$O	1580	755	-	1744	3366	363	453
Co(L^{1a})$_2$.2H$_2$O	1581	749	-	-	3269	367	452
Ni(L^{1a})(OAc).3H$_2$O	1578	738	-	1745	3291	374	451
Ni(L^{1a})$_2$.2H$_2$O	1576	738	-	-	3359	372	463
Cu(L^{1a})(OAc).H$_2$O	1583	752	-	1744	3377	384	462
Cu(L^{1a})$_2$	1581	753	-	-	-	383	474
Zn(L^{1a})(OAc).3H$_2$O	1583	761	-	1746	3421	387	466
Zn(L^{1a})$_2$.2H$_2$O	1582	764	-	-	3214	384	469

3.2 ^{1}H NMR Spectra

^{1}H NMR spectra(DMSO-d_6, δ, ppm) of HL^{1a} and its metal complexes:



^{1}H NMR(HL^{1a}): δ = 7.46 (s, 1H, Ar-H); 7.64 (s, 1H, Ar-H); 9.77 (s, 1H, OH); 3.90 (s, 3H, OCH_3); 8.44 (s,1H, -N=CH-); 13.70 (s, 1H, -SH)

^{1}H NMR (Zn(L^{1a})(OAc).3H$_2$O): δ = 7.49 (s, 1H, Ar-H); 7.55 (s, 1H, Ar-H); 9.76 (s, 1H, OH), 3.97 (s, 3H, OCH_3); 8.86 (s, 1H, -N=CH)

^{1}H NMR (Zn(L^{1a})$_2$.2H$_2$O): δ = 7.46 (s, 2H, Ar-H), 7.63 (s, 2H, Ar-H), 9.77 (s, 2H, OH), 3.95 (s, 6H, OCH_3), 8.85 (s, 2H, -N=CH-)

The ^{1}H NMR spectra of the 1:1 and 1:2 Zn(II) complexes showed absence of SH proton signal indicating the deprotonation of thiol group and coordination of sulphur with metal [11]. However, the resonance signal obtained for azomethine proton deshielded as compared to the Schiff base suggesting the coordination of azomethine nitrogen to the Zn(II) ion [12].

3.3 Electronic Spectra and Magnetic measurements

The electronic spectra provided information regarding the arrangement of ligand around the metal ion.

Cobalt(II) complexes

The electronic absorption spectra of the Co(II) complexes exhibited two intense bands around 10152-10363 cm^{-1} (ν_1) and 19617-19723 cm^{-1} (ν_3) respectively, which are attributed to $^4T_{1g}$ (F) → $^4T_{2g}$ (F) (ν_1) and $^4T_{1g}$ (F) → $^4T_{1g}$ (P) (ν_3) transitions [13]. These bands are characteristic of high spin octahedral Co(II) complexes.

The 1:1 and 1:2 Co(II) complexes of HL^{1a} have magnetic moments of 4.64 and 4.79 BM respectively at room temperature which are in good agreement with those reported for octahedral Co(II) complexes.

Nickel(II) complexes

In case of Ni(II) complexes reported in thesis, the electronic spectra showed three absorption bands in the region 9970-10162 cm^{-1}, 17311-17351 cm^{-1} and 24762-24885 cm^{-1} corresponding to $^3A_{2g}$ (F) → $^3T_{2g}$ (F) (ν_1), $^3A_{2g}$ (F) → $^3T_{1g}$ (F) (ν_2) and $^3A_{2g}$(F) → $^3T_{1g}$ (P) (ν_3) transitions, respectively, suggesting octahedral geometry for the Ni(II) ion [11]. The observed magnetic moment values for the 1:1 and 1:2 Ni(II) complexes are 3.10 and 3.23 BM respectively corresponding to two unpaired electrons and consistent with the octahedral geometry around the Ni(II) ion [12].

Copper(II) complexes

The electronic spectra of the 1:1 and 1:2 Cu(II) complexes exhibited single absorption band at 18170 and 18254 cm^{-1} respectively assigned to $^2B_{1g}$ → $^2A_{1g}$ (ν_1) transition indicative of square planar geometry around the Cu(II) ion [9]. The effective magnetic moment values measured at room temperature are 1.80 and 1.81 B.M for 1:1 and 1:2 Cu(II) complexes respectively further confirming square planar geometry around the Cu(II) ion [13].

3.4 Thermal Studies

TG and DTA of $Co(L^{1a})_2.2H_2O$ and $Ni(L^{1a})_2.2H_2O$ were carried out at 10°C min^{-1} under air atmosphere from ambient to 800°C temperature. The thermograms of both the complexes showed three decomposition steps. The calculated and experimental % weight losses of the complexes at different temperatures and the nature of peaks are given in Table 2.

Table 2: TG and DTA data of metal complexes in air atmosphere

Compounds	Temp (°C)	Decomposed moiety	Weight Loss (%)		Nature of Peak
			Calcd.	Found	
Co (L1a)2.2H2O	110-180	H2O	4.34	4.40	Endo
	180-455	Organic moiety	51.53	51.70	Exo, small
	455-780	Triazine	28.94	30.30	Exo, small
Ni (L1a)2.2H2O	120-230	H2O	4.35	4.50	Endo
	230-520	Organic moiety	51.36	52.34	Exo, sharp
	520-700	Triazine	35.34	33.80	Exo, sharp

TG and DTA curves of selected samples are shown in Figure 1. The calculated and experimental % weight losses of the complexes at different temperatures and the nature of peaks are given in Table 2.

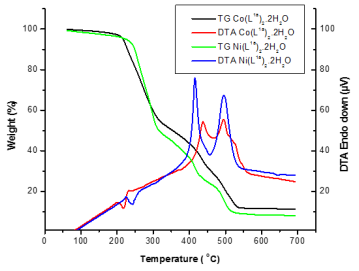


Figure 1: TG and DTA curves of $Co(L^{1a})_2.2H_2O$ and $Ni(L^{1a})_2.2H_2O$

3.5 Fluorescence Spectra

In order to investigate the effect of M(II) ions on the fluorescence of the ligand, the fluorescence spectra of the ligand and its metal complexes were recorded in DMF at room temperature with excitation wavelength 265 nm (Figure 2). The fluorescence spectrum of the ligand exhibited weak fluorescence emission [14, 15] at 343 and 538 nm. On complexation, enhancement of fluorescence was observed with strong fluorescence emission at ~342 and ~539 nm. The decrease in fluorescence emission of HL^{1a} and its complexes was in the order of Zn(II) > Cu(II) > Co(II) > Ni(II) > Hl^{1a}.

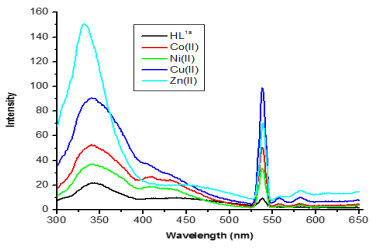


Figure 2: Fluorescence spectra of Schiff base and its metal complexes

3.6 Cyclic Voltammetry

The redox behavior of the Cu (II) complexes has been investigated by cyclic voltammetry in DMF using tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. The cyclic voltammogram in 10^{-3}M solution was recorded at room temperature in the potential range, 1.6 V to 0.6 V with a scan rate of 0.1V/s. The complex, $Cu(L^{1a})OAc.H_2O$ displayed a reduction peak at E_{pc} = -0.488 V, characteristic of the Cu(II) → Cu(I) couple and corresponding oxidation peak at E_{pa} = -0.221 V indicating Cu(I) → Cu(II) couple. The peak separation between the cathodic and anodic potential is very high indicating one electron, quasi-reversible process [16].

4. CONCLUSIONS

Metal complexes with Schiff base derived from 4-amino-3-mercapto-5-oxo-1,2,4-triazine with 3-bromo-4-hydroxy-5-methoxybenzaldehyde were synthesized. On the basis of different techniques, Co(II), Ni(II) and Zn(II) complexes were assigned octahedral geometries and square planar geometry was proposed for Cu (II) complexes. The enhanced fluorescence exhibited by the metal complexes especially the Zn(II) complexes establishes possibility of these complexes to be used in fluorescent sensors and light emitting devices.

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