



Preparation and Spectroscopic Investigation of Newly Schiff Base of 5-chloro-2-hydroxybenzylidene)-3,4,5-Trihydroxybenzohydrazone with Some Metal Ions

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ABSTRACT

An ethanolic solution of metal salts was added slowly to an ethanolic solution of 5-chloro-2-hydroxybenzylidene)-3,4,5-trihydroxybenzohydrazone with few drops of triethylamin to give complexes with the general formula $[M(\text{GHL}2)_2] \cdot 2\text{H}_2\text{O}$, $[\text{Cu}_2(\text{GHL}2)_2] \cdot 4\text{H}_2\text{O}$ and $[\text{Cd}(\text{GHL}2)(\text{CH}_3\text{COO})_2] \cdot 2\text{H}_2\text{O}$ where M is Ni(II) and Zn(II), GHL2 is 5-chloro-2-hydroxybenzylidene)-3,4,5-trihydroxybenzohydrazone. The resulting complexes were characterized by elemental analysis, magnetic measurements and spectral studies. The Schiff base GHL2 ligand acts as tridentate ligand was coordinated with the metal ions through O, N, O except with Cd(II) as the ligand behaves as bidentate ligand coordinated with Cd(II) ion through O, N atoms. However, $[\text{M}(\text{GHL}2)_2] \cdot 2\text{H}_2\text{O}$ and $[\text{Cd}(\text{GHL}2)(\text{CH}_3\text{COO})_2] \cdot 2\text{H}_2\text{O}$ were proposed to possess Octahedral geometry while $[\text{Cu}_2(\text{GHL}2)_2] \cdot 4\text{H}_2\text{O}$ was proposed to possess tetrahedral geometry.

Key words: Hydrazone complexes, 5-chloro-2hydroxybenzylidene)-3,4,5-trihydroxybenzohydrazone complexes, spectral studies, Schiff base complexes.

INTRODUCTION

Schiff bases are able to coordinate with many different metals to stabilize them in various oxidation states, enabling the use of Schiff base metal complexes for a large variety of useful catalytic transformation¹. As model of biological systems, it has been reported that the structure of the substituent bonded to the imino nitrogen affects the

coordination geometry of the complexes^{2,3}. They are described advanced organic chemistry, structure and mechanism as any of a class of derivatives of the condensation of aldehydes or ketones with primary amines. Most of the Schiff bases are used as chemical intermediates, perfume bases, dyes, rubber accelerators and liquid crystals for electronics. During the past two decades, considerable attention has been paid to the

chemistry of the metal complexes of Schiff bases containing nitrogen and other donors (Tarafer *et al.*, 2000). This may be attributed to their stability and biological activities⁵. It is well known that some drugs have higher activity when administered as metal complexes than free ligands⁶. For example Cu(II) complex of salicylaldehyde benzoylhydrazone was shown to be a potent inhibitor of DNA synthesis and cell growth⁷. There are also some reports on the antitumor agents and potential antifungal agents by using gallic hydrazones and their complexes^{8,9}. Keeping this in view, the coordination of Schiff base of 5-chloro-2-hydroxybenzylidene)-3,4,5-trihydroxybenzohydrazone with metal ions Ni(II), Cu(II), Zn(II) and Cd(II) is investigated in this work.

EXPERIMENTAL

Materials and techniques

The chemicals used in this study were all pure grade (Ni(II) acetate, Cu(II) acetate, ZnCl₂, Cd(II) acetate, gallic hydrazide, 2-acetylpyridine, ethanol, DMSO, DMF, Triethylamine and KBr) from Merck.

Infrared spectra were obtained using KBr discs (4000-400 cm⁻¹) on Perkin –Elmer FT-IR spectrometer. The electronic spectra were carried out using a Cary 50Conc. UV-visible was recorded using spectrophotometer in DMSO solution 10⁻³M. Thermal analysis studies of the complex were performed on Perkin-Elmer Pyris Diamond DTG/TA Thermal System under nitrogen atmosphere at a heating rate of 10°C/min from 30-900°C. Elemental analysis (C, H, N) were performed by using a Flash EA 1112 Series elemental analyzer.

Synthesis of gallic hydrazide

3,4,5-trihydroxybenzohydrazone was synthesized by adding 3,4,5-trihydroxybenzoate (1.84 g) and (0.01 M) C₈H₈O₅ respectively to 9 ml of hydrazine hydrate, after stirred 30 min. The product was immediately precipitate, filtered off, washed and recrystallized with ethanol and dried under vacuum¹⁰.

Synthesis of the ligand GHL2

5-chloro-2-hydroxybenzylidene)-3,4,5-trihydroxybenzohydrazone was prepared by adding drop wise of 3,4,5-trihydroxybenzohydrazone (0.40 g, 2.1 mmol) into an ethanolic solution of 5-chloro-2-hydroxybenzaldehyde (0.033 g, 2.1 mmol). The mixture was refluxed for about 12 hour and left to stand overnight. Yellow crystals separated out, filtered off and washed with chloroform and dried under vacuum¹¹.

Synthesis of the metal complexes

An ethanolic solution (20 ml) of metal salt (0.029- 0.08 g) was added slowly to an ethanolic solution (25 ml) of 5-chloro-2-hydroxybenzylidene)-3,4,5-trihydroxybenzohydrazone with few drops of triethylamine. The mixture was stirred and refluxed for 5 hours. The solid product was precipitate, filtered and recrystallized from dimethylsulfoxide.

RESULT AND DISCUSSION

On the basis of elemental analysis the complexes were assigned to possess the compositions shown in Table 1. Thus, all the complexes are solid and completely soluble in DMSO.

Table 1: Physical characteristics and analytical data of the ligand and its complexes

Compound	Color	Yield%	M. p. (°C)	Elemental analysis, calculated (Found)%		
				C	H	N
GHL2	Yellow	75	270	52.11(51.83)	3.44(4.33)	8.68(8.50)
[Ni(GHL2) ₂]. 2H ₂ O	Brown	70	280	45.43(44.22)	3.54(3.37)	7.57(7.50)
[Cu ₂ (GHL2) ₂]. 4H ₂ O	Green	70	310	40.48(40.08)	1.94(2.05)	6.74(6.85)
[Zn(GHL2) ₂]. 2H ₂ O	White	75	265	43.06(42.35)	3.62(3.42)	7.17(7.07)
[Cd(GHL2)(CH ₃ COO) ₂]. 2H ₂ O	Yellow	75	230	42.89 (42.56)	1.80(1.75)	6.25(5.95)

The electronic spectra and magnetic studies

The electronic spectra of the free ligand GHL2 shows electronic transitions $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$

at 290 and 307, 340 nm respectively. The electronic spectrum of the $[\text{Ni}(\text{GHL2})_2] \cdot 2\text{H}_2\text{O}$ showed three absorption bands in the visible region at 315, 424

Table 2: The electronic spectra data and magnetic moments of the compounds

Compound	λ_{max} n.m	Wave number cm^{-1}	Assignment	μ_{eff} Calc.(found) B.M
GHL2	290	34482	$\pi \rightarrow \pi^*$	-
	307	32573	$n \rightarrow \pi^*$	
	340	29411	$n \rightarrow \pi^*$	
$[\text{Ni}(\text{GHL2})_2] \cdot 2\text{H}_2\text{O}$	295	33898	$\pi \rightarrow \pi^*$	2.828(2.513)
	315	31746	${}^3\text{A}_{2g(\text{F})} \rightarrow {}^3\text{T}_{1g(\text{P})}$	
	424	23584	${}^3\text{A}_{2g(\text{F})} \rightarrow {}^3\text{T}_{1g(\text{F})}$	
	440	22727	${}^3\text{A}_{2g(\text{F})} \rightarrow {}^3\text{T}_{2g(\text{F})}$	
$[\text{Cu}_2(\text{GHL2})_2] \cdot 4\text{H}_2\text{O}$	274	36496	$\pi \rightarrow \pi^*$	diamagnetic
	324	30864	$n \rightarrow \pi^*$	
	340	29411		
	401	24937		
$[\text{Zn}(\text{GHL2})_2] \cdot 2\text{H}_2\text{O}$	287	34843	$\pi \rightarrow \pi^*$	diamagnetic
	295	33898	C.T (M \rightarrow L)	
	323	30959	C.T (M \rightarrow L)	
$[\text{Cd}(\text{GHL2})(\text{CH}_3\text{COO})_2] \cdot 2\text{H}_2\text{O}$	295	33898	$\pi \rightarrow \pi^*$	diamagnetic
	384	26041	C.T (M \rightarrow L)	
	397	25188	C.T (M \rightarrow L)	

Table 3: Thermal analysis data of some metal complexes of GHL2

Complex	Step	Temperature (°C)	Weight loss (%) Found (Calculated)	Assignment	Residue (%) Found (calculated)
$[\text{Ni}(\text{GHL2})_2] \cdot 2\text{H}_2\text{O}$	1	50.08-249.6	5.280 (4.86)	$2\text{H}_2\text{O}$	NiO 11.917
	2	249.60-389.54	27.516 (26.54)	$\text{C}_8\text{H}_5\text{N}_2\text{O}_2\text{Cl}$	(10.08)
	3	389.54-461.81	15.87 (16.88)	$\text{C}_6\text{H}_5\text{O}_3$	
	4	460.66-800.20	39.415 (41.20)	$\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}$	
$[\text{Cu}_2(\text{GHL2})_2] \cdot 4\text{H}_2\text{O}$	1	38.08-89.88	8.638 (8.66)	$4\text{H}_2\text{O}$	2CuO
	2	256.48-424.66	68.070 (67.84)	$\text{C}_{28}\text{H}_2\text{ON}_2\text{O}_7\text{Cl}_2$	
	3	429.33-577.65	4.834 (5.20)	N_2O	
$[\text{Zn}(\text{GHL2})_2] \cdot 2\text{H}_2\text{O}$	1	35.29-180.19	5.367 (4.61)	$2\text{H}_2\text{O}$	ZnO 9.38
	2	180.19-343.78	24.36 (25.16)	$\text{C}_8\text{H}_5\text{N}_2\text{OCl}$	(10.42)
	3	392.86-527.24	17.58 (16)	$\text{C}_6\text{H}_5\text{O}_3$	
	4	530.75-784.32	38.06 (39.12)	$\text{C}_{14}\text{H}_{10}\text{N}_2\text{OCl}$	
$[\text{Cd}(\text{GHL2})(\text{CH}_3\text{COO})_2] \cdot 2\text{H}_2\text{O}$	1	39.5-130	4.032 (4.01)	$2\text{H}_2\text{O}$	CdO
	2	130-280	14.26 (13.16)	$2(\text{CH}_3\text{COO})$	11.03
	3	280-410	28.536 (27.9)	$(\text{C}_6\text{H}_6\text{O}_3)$	(12.54)
	4	410-680		$(\text{C}_7\text{H}_4\text{OCl})$	
	5	770-1003	5.89 (6.2)	2CO	

and 440 nm which may be assigned to ${}^3A_2g_{(F)}$, ${}^3T_1g_{(F)}$, ${}^3A_2g_{(F)}$ ${}^3T_1g_{(F)}$ and ${}^3A_2g_{(F)}$ ${}^3T_2g_{(F)}$ respectively. The position of the observed d-d transition permits to calculate the ligand field parameters. Energy of the first spin allowed transition ${}^3A_2g_{(F)}$ ${}^3T_2g_{(F)}$ which directly gives the value of 10 Dq which is equal to 2272 cm^{-1} . Racha parameter B was calculated and found to be 856 cm^{-1} which is less than the free ion value (1040 cm^{-1}) which indicates a greater degree of covalence. Thus, the nephelauxetic parameter α is obtained by using the formula $\beta = B_{complex}/B_{free ion} = 0.823$. Actually, decrease of β value indicates that the complex has prefer covalent character in metal ligand bond¹²⁻¹⁵. The magnetic moment of the Ni(II) complex is 2.513 B. M, which agrees with the presence of Ni(II) ion in octahedral geometry^{13, 16-18}. The spectrum of $[Cu_2(GHL2)_2] \cdot 4H_2O$ exhibited a high intensity bands at 274 and 324 nm in the UV region which is attributed to the $\pi \rightarrow \pi^*$ and $n\pi^*$ respectively. Thus, the spectrum shows band at 340 nm which is

expected to be the charge transfer LMCT. Moreover, the magnetic moment of the complex was found to be diamagnetic which proved the tetrahedral geometry¹⁹⁻²¹. Finally, the diamagnetic of Zn(II) and Cd(II) complexes exhibited absorption bands at 287 and 295 nm due to $\pi \rightarrow \pi^*$. Appearance of these band are due to $\pi \rightarrow \pi^*$ transition associated with azomethine linkage and L-M charge transfer transition. Moreover, the spectrum of the complexes also shows bands at 295, 323 and 384 nm due to the charge transfer as the electronic configuration of these complexes confirmed the absence of any d-d transition²¹⁻²⁴. All the data of the magnetic susceptibility and electronic spectra of the free ligand and its complexes are listed in Table 2.

Thermal studies

The Ni(II) complex was thermally stable up to around 500 °C. In the TGA curve of Ni(II) complex, 5.280% weight loss was observed correlating to 2 mole of water per complex. The IR spectrum of the

Table 4: IR spectra of the free ligand and its complexes

Compound	$\nu(\text{Ar-OH})$	$\nu(\text{NH})$	$\nu(\text{C=N})$	$\nu(\text{C-O})$	$\nu(\text{N-N})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$
GHL2	3555	3224	1615	1090	953	-	-
$[\text{Ni}(\text{GHL2})_2] \cdot 2\text{H}_2\text{O}$	3384	2974	1603	1151	1094	597, 525	415
$[\text{Cu}_2(\text{GHL2})_2] \cdot 4\text{H}_2\text{O}$	3427	2957	1612	1264	1091	480	409
$[\text{Zn}(\text{GHL2})_2] \cdot 2\text{H}_2\text{O}$	3449	2969	1569	1024	1180	553	441
$[\text{Cd}(\text{GHL2})(\text{CH}_3\text{COO})_2] \cdot 2\text{H}_2\text{O}$	3432	2977	1610	1174	1047	555	496

complex was indicated by the appearance of a broad band in the region of 3384 cm^{-1} , due to the $\nu(\text{OH})$ of water. For the $[\text{Cu}_2(\text{GHL2})_2] \cdot 4\text{H}_2\text{O}$ a mass loss occurred within the temperature range of 38.08-89.883 °C corresponding to the loss of four hydrate water molecules and at the temperature range of 265.48-424.66 °C corresponding to loss of $(\text{C}_{28}\text{H}_{20}\text{N}_2\text{O}_7\text{Cl}_2)$ molecule. Finally, at the temperature range of 492.33-577.65 °C a mass loss occurred corresponding to a loss of N_2O molecule. The decomposition continues till a constant weight was obtained where 2CuO residue was formed in 18.45%. The Zn(II) complex was stable up to 34.12 °C and its decomposition started at 35.29 and was completed at 784.32 °C. In the TGA curve of this complex, 5.367% weight loss was observed correlating to 2 mole of water per complex molecule.

The Zn(II) complex decomposed and produced ZnO as residue [found (calculated)%: 9.38(10.42)] in three steps in the temperature range of 35.29-180.19, 392.86-527.24 and 530.75-784.32 °C respectively. In the decomposition process of Zn(II) complex, the mass losses corresponded to $2\text{H}_2\text{O}$, $\text{C}_8\text{H}_5\text{N}_2\text{OCl}$, $\text{C}_6\text{H}_5\text{O}_3$ and $\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_4\text{Cl}$ molecules respectively. The Cd(II) complex was stable up to 39.44 °C and its decomposition started from this temperature onward and was completed at 1003 °C. At the temperature range of 39.47-130.0 °C a mass loss occurred corresponding to a loss of two mole of H_2O . At the temperature range of 130.0-280.0 °C mass losses occurred due to the loss of 2(CH_3COO) molecules. At the temperature range of 280-420 °C mass losses occurred due to the loss of $(\text{C}_6\text{H}_6\text{O}_3)$ molecules. At the temperature range of

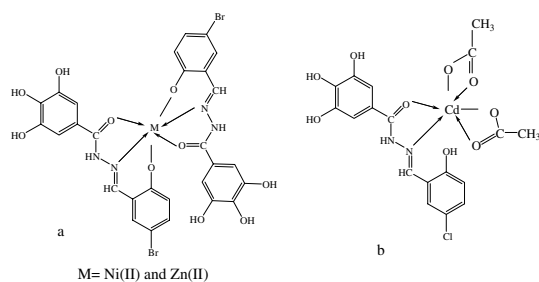


Fig. 1 (a): Proposed structure of $[M(\text{GHL}2)]$ and (b) Proposed structure of $[\text{Cd}(\text{GHL}2)(\text{CH}_3\text{COO})_2]$

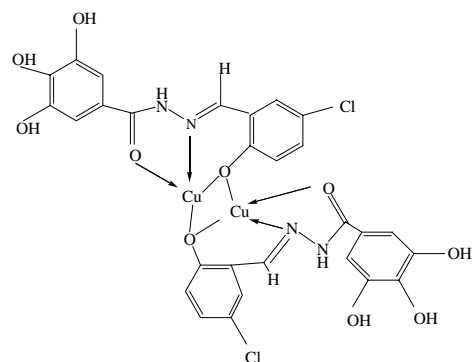


Fig. 2: Proposed structure of $[\text{Cu}_2(\text{GHL}2)_2] \cdot 4\text{H}_2\text{O}$

420-680°C mass losses occurred due to the loss of ($\text{C}_7\text{H}_4\text{OCl}$) molecules. Finally, at the temperature range of 770-1003°C mass loss occurred due to loss of CO molecule and this continues till a constant weight is obtained where a metal residue is CdO formed by 11.03%. All the thermal decomposition processes of the complexes are summarized in Table 3.

Infrared spectra studies

The infrared spectra of the free ligand GHL2 shows absorption bands at 3224 and 953 cm^{-1} which are attributed to $\nu(\text{NH})$ and $\nu(\text{N-N})$ respectively. Moreover, the spectrum of the ligand shows strong bands at 3555 cm^{-1} which is due to $\nu(\text{Ar-OH})$. This band shifted to the lower frequencies in all complexes by 171-106 cm^{-1} which indicated that the OH in hydrazone group is probably involved in complex formation. Moreover, the $\nu(\text{C=N})$ band of the ligand is observed at 1615 cm^{-1} and this band is also shifted to the lower frequencies by 46-3 cm^{-1} in the spectra of the complexes. Thus, the spectra of the complexes shows weak bands at 409-496 cm^{-1} which are attributed to $\nu(\text{M-N})$. The spectrum of the Cd(II) complex shows two bands at 1460 and 1347 cm^{-1} which are attributed to the asymmetrical

and symmetrical vibration of (COO^-). Thus, the complex shows weak band at 555 cm^{-1} which is due to $\nu(\text{M-O})$ ²⁵⁻²⁹. Table 4 shows all the characteristic vibrations and assignments of the free ligand and its complexes.

CONCLUSION

A newly synthesized of hydrazone Schiff base ligand with some metal ions are presented in this article. The analytical, spectral, magnetic and thermal studies confirm the coordination of hydrazone Schiff base with metal ions. Based on the presented results, the following concerning the structure of the prepared complexes can be suggested the octahedral geometry around Ni(II), Zn(II) and Cd(II) ions as shown in Figure 1 and Tetrahedral geometry for $[\text{Cu}_2(\text{GHL}2)_2] \cdot 4\text{H}_2\text{O}$ as shown in Figure 2.

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