

SYNTHESIS, MAGNETIC AND SPECTROSCOPIC STUDIES of Ni(II), Cu(II), Zn(II) and Cd(II) COMPLEXES OF A NEWLY SCHIFF BASE DERIVED FROM 5-BROMO-2-HYDROXYBEZYLIDENE)-3,4,5-TRIHYDROXYBENZOHYDRAZIDE)

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ABSTRACT. A new hydrazide Schiff base ligand GHL1 (5-bromo-2-hydroxybenzylidene)-3,4,5-trihydroxybenzohydrazide) was prepared by refluxing of trihydroxybenzhydrazide with an ethanolic of 5-bromo-2-hydroxybenzaldehyde. The ligand reacted with Ni(II), Cu(II), Zn(II) and Cd(II) (acetate salts). All the complexes were characterized by elemental analysis, molar conductivity, TGA, UV-Vis and FT-IR spectral studies. All the complexes have octahedral geometry except Ni(II) complex which has tetrahedral geometry.

KEY WORDS: Hydrazone complexes, Schiff base ligand, Spectral studies

INTRODUCTION

The tridentate of benzhydrazone derivatives ligand containing ONO donor atoms can be synthesized easily by reacting benzhydrazide with any aldehyde or ketone [1]. The presence of donor atoms in the ligand will play an important role in the formation of a stable chelate ring and this situation facilitates the complexation process [2]. Moreover, the synthesis, spectroscopic characterization and reaction of transition metal with hydrazone ligands have shown wide spectra of biological and pharmaceutical activities such as possess antimicrobial, antibacterial, antifungal, anti-inflammatory, anticonvulsant, antitubercular, antiviral, antioxidative effects and inhibition of tumor growth [3-5]. The bioinorganic chemistry paid great attention to the Schiff base complexes because many of these complexes have biologically important species [6]. So, the synthesis of new ligands and complexes would be an important step in the development of coordination chemistry which exhibit novel properties and reactivity [5]. In searching for complexes of transition metals with novel coordination spheres, it was found that the tridentate coordination is made of the hydrazone ligands. This makes them suitable chelating agents for metal ions and preferring the octahedral geometry [7, 8]. Thus in this paper the synthesis and characterization of Ni(II), Cu(II), Zn(II) and Cd(II) complexes with hydrazide derivative are described.

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.

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

Synthesis of gallic hydrazide

3,4,5-Trihydroxybenzoate (1.84 g) and (0.01 M) $\text{C}_8\text{H}_8\text{O}_5$ were added, 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 vacuum [9].

Synthesis of the ligand GHL1

5-Bromo-2-hydroxybenzylidene)-3,4,5-trihydroxybenzohydrazide was prepared by adding trihydroxybenzhydrazide (0.65 g, 3.5 mmol) to an ethanolic solution of 5-bromo-2-hydroxybenzaldehyde (0.70 g, 3.5 mmol). The mixture was refluxed about 12 hour and left it over night. The colorless crystals were obtained upon slow evaporation, filtered off and dried under vacuum [10].

Synthesis of the metal complexes

An ethanolic solution of 5-bromo-2-hydroxybenzylidene)-3,4,5-trihydroxybenzohydrazide (0.35 g, 0.8 mmol) was added to 50 mL of an aqueous solution of the metal salts with three drops of triethylamine. The mixture was stirred and refluxed for 5 hours. The solid product was precipitate, filtered washed and recrystallized from DMSO and dried in desiccator.

RESULTS AND DISCUSSION

The prepared complexes were found to be solids, soluble in dimethylsulfoxide. The elemental analysis shown in Table 1 indicates that all the complexes were in good agreement with the values calculated from the proposed formula

Table 1. Physical properties and analytical data of the ligand and its complexes.

Compound	Elemental analysis, calculated (found) %			Color	Yield (%)	M.p. ($^{\circ}\text{C}$)
	C	H	N			
GHL1	41.12 (41.47)	4.99 (5.14)	5.99 (6.76)	White	70	255
$[\text{Ni}(\text{GHL1})_2](\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	46.7 (45.6)	4.18 (3.8)	6.2 (6.8)	Yellow	65	260
$[\text{Cu}(\text{GHL1})_2] \cdot 3\text{H}_2\text{O}$	47.65 (45.37)	3.68 (3.34)	7.94 (6.41)	Green	70	240
$[\text{Zn}(\text{GHL1})_2] \cdot 3\text{H}_2\text{O}$	48.5 (47.7)	3.79 (4.03)	8.09(7.53)	White	70	335
$[\text{Cd}(\text{GHL1})(\text{CH}_3\text{COO})_2] \cdot 2\text{H}_2\text{O}$	30.50 (32.85)	2.99 (2.95)	4.88 (4.98)	White	60	150

Electronic spectra and magnetic studies

The electronic spectrum of the ligand GHL1 shows two bands at 307 and 340 nm due to the $n \rightarrow \pi^*$ transition of the chromophore ($-\text{C}=\text{N}-\text{NH}-\text{CO}$). In the spectra of the complexes, these bands were shifted to the lower frequencies which indicate that the imin nitrogen atom and the oxygen atom were involved in coordination with the metal ions [3, 7].

The electronic spectrum of Ni(II) complex displayed two bands in the visible region observed at 422 and 626 nm which are assigned to the electronic transitions ${}^3T_{1(F)} \rightarrow {}^3T_{1(P)}$ (ν_3) and ${}^3T_{1(F)} \rightarrow {}^3T_{2(F)}$ (ν_1), respectively. The band (ν_2) is attributed to the transition ${}^3T_{1(F)} \rightarrow {}^3A_{2(F)}$ which corresponds to the charge transfer (C.T.) at 385 nm [11]. The calculated value of the ligand field parameter $10Dq$ is 19967 cm^{-1} for (ν_1). Thus, the interelectronic repulsion parameter B was calculated and found to be 116 cm^{-1} for Ni(II) complex, this value is less than the free Ni^{2+} ion value of 1040 cm^{-1} which was due to overlapping and delocalization of electrons over the molecular orbital that encompasses both the metal and ligands. Moreover, the nephelauxetic ratio $\beta = B/B^0 = 0.11$ indicates appreciable covalent character in this complex [3-6, 8, 12]. So, the magnetic moment value is 3.4 B.M., which demonstrates that the Ni(II) complex is paramagnetic and has a high spin tetrahedral configuration with ${}^3T_{1(F)}$ ground state [3, 6, 13, 14]. Furthermore, the molar conductivity of 10^{-3} M in DMSO at room temperature is $73\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ indicates that the Ni(II) complex is electrolyte [15].

The electronic spectrum of the Cu(II) complex displayed strong bands in the range of 324-340 nm which can be assigned to $n \rightarrow \pi^*$, charge transfer LMCT band exhibited in the range of 400-415 nm. Thus, the spectrum showed d-d electronic transition at 607 nm which assigned to ${}^2E_g(D) \rightarrow {}^2T_{2g(D)}$. The broadness of the band is due to the ligand field and the Jahn-Teller effect. These absorption prefer the distorted octahedral geometry for the Cu(II) ion. Moreover, the magnetic moment for the Cu(II) complex is 1.9 B.M. which within the expected value for one electron. Furthermore, the complex is non-electrolyte as the molar conductance was found to be at $0.87\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ in 10^{-3} M in DMSO [5, 11, 16-18].

Finally, the diamagnetic Zn(II) and Cd(II) complexes show absorption bands at 325 and 285, 320 nm, respectively. These bands are attributed to the charge transfer MLCT as the electronic configuration of these complexes confirmed the absence of any d-d transition [16, 19, 20]. All data and remarks are found in Table 2.

Table 2. The electronic spectra of free ligands and their complexes.

Compound	λ_{max} nm	Wavenumber cm^{-1}	ϵ_{max} $\text{Lmol}^{-1}\text{cm}^{-1}$	Assignment	μ_{eff} calc.(found) B.M.
GHL1	307	32573	1845	$n \rightarrow \pi^*$	-
	340	29411	2118	$n \rightarrow \pi^*$	
[Ni(GHL1) ₂](CH ₃ COO) ₂ .4H ₂ O	385	25974	1097	${}^3T_{1(F)} \rightarrow {}^3A_{2(F)}$	2.828 (3.4)
	422	23696	16	${}^3T_{1(F)} \rightarrow {}^3T_{1(P)}$	
	626	15974	11	${}^3T_{1(F)} \rightarrow {}^3T_{2(F)}$	
[Cu(GHL1) ₂].3H ₂ O	324	30864	391	$n \rightarrow \pi^*$	1.732 (1.9)
	340	29411	441	$n \rightarrow \pi^*$	
	400	25000	564	C.T	
	415	24096	563	C.T	
	607	16474	31	${}^2E_g(D) \rightarrow {}^2T_{2g(D)}$	
[Zn(GHL1) ₂].3H ₂ O	325	30769	113	C.T (M → L)	diamagnetic
[Cd(GHL1)(CH ₃ COO) ₂].2H ₂ O	285	35087	1200	$\pi \rightarrow \pi^*$	diamagnetic
	320	31250	324	C.T (M → L)	

Infrared spectra studies

The infrared spectrum of the ligand GHL1 showed strong bands at 3569 and 3223 cm^{-1} which are due to the $\nu(\text{OH})$ and $\nu(\text{NH})$, respectively. Thus, the $\nu(\text{C}=\text{N})$ band of the ligand was observed at 1637 cm^{-1} and this band was shifted to the lower frequencies by 48-19 cm^{-1} in the spectra of the complexes. Furthermore, the complexes exhibited weak bands between 550-575 cm^{-1} which are attributed to $\nu(\text{M}-\text{N})$. This indicates that the ligand was coordinated with the metal ions through the N atom. However, the spectrum of the ligand showed strong band at 1545 cm^{-1} which attributed to $\nu(\text{C}=\text{O})$. Actually, this band was shifted to the lower frequencies by 20-4 cm^{-1} in the spectra of the complexes. While, the $\nu(\text{C}-\text{O})$ appeared at 1089 cm^{-1} in the spectra of the free ligand which was shifted to the higher frequencies by 85-104 cm^{-1} . Moreover, the spectra of the complexes exhibited weak bands between 440-481 cm^{-1} which is attributed to the $\nu(\text{M}-\text{O})$. This indicates that the GHL1 is tridentate ligand which is coordinated with the metal ions through ONO atoms.

The asymmetrical and symmetrical vibration of $\nu(\text{COO}^-)$ were noticed at 1450 and 1346 cm^{-1} , respectively in the spectrum of the Cd(II) complex. So, the complex was also exhibited weak band at 481 cm^{-1} which is due to $\nu(\text{M}-\text{O})$. This indicates that the acetate group is coordinated with Cd(II) ion through the two of O atoms [21-23]. Characteristic vibrations and assignments of free ligand and its complexes as KBr pellets are listed in Table 3.

Table 3. Characteristic IR bands (cm^{-1}) of the ligand and its metal complexes.

Compound	$\nu(\text{OH})$	$\nu(\text{NH})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}-\text{O})$	$\nu(\text{N}-\text{N})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$
GHL1	3569	3223	1637	1545	1089	1049	-	-
$[\text{Ni}(\text{GHL1})_2](\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	3445	3222	1599	1525	1177	1028	575	452
$[\text{Cu}(\text{GHL1})_2] \cdot 3\text{H}_2\text{O}$	3377	3220	1618	1541	1193	1045	556	440
$[\text{Zn}(\text{GHL1})_2] \cdot 3\text{H}_2\text{O}$	3475	3247	1589	1530	1179	1023	559	453
$[\text{Cd}(\text{GHL1})(\text{CH}_3\text{COO})_2] \cdot 2\text{H}_2\text{O}$	3414	3241	1609	1540	1174	1055	550	481

Thermal studies

The weight loss was measured from 40 to 950 $^\circ\text{C}$. The weight losses for each chelate were calculated for the corresponding temperature ranges are shown in Table 4. The metal percentages calculated from metal oxide or metal residues were compared with those determined by the analytical metal content determination [24].

The Ni(II) complex was stable up to 40 $^\circ\text{C}$ and its decomposition started at this temperature and was completed at 952 $^\circ\text{C}$. A mass loss occurred within the temperature range (40-200) $^\circ\text{C}$ corresponding to the loss of four hydrated water molecules. The Ni(II) complex decomposed and produced NiO as residue [found(calculated)%: 8.945(8.28)] in four steps in the temperature range 40-200, 200-350, 350-500 and 500-795 $^\circ\text{C}$, respectively. In the decomposition process of Ni(II) complex, the mass losses corresponded to 4(H_2O), 2(CH_3CO_2), 2($\text{BrPh}-\text{CH}$) and 2[(OH)₃Ph-CON₂H], respectively [24].

The Cu(II) complex was stable up to 35 $^\circ\text{C}$ and its decomposition started at this temperature and was completed at 608 $^\circ\text{C}$. A mass loss occurred within the temperature range 36-266 $^\circ\text{C}$ corresponding to the loss of three hydrated water molecules [24]. The Cu(II) complex decomposed and produced Cu as a residue [found(calculated)%: 7.21(8.4)] in three steps in the temperature range of 36-266, 271-446, and 452-608 $^\circ\text{C}$, respectively. In the decomposition process of Cu(II) complex, the mass losses corresponded to 3(H_2O), 2($\text{C}_7\text{H}_5\text{N}_2\text{OBr}$) and 2($\text{C}_6\text{H}_5\text{O}_3$), respectively.

The Zn(II) complex was stable up to 35.00 °C and its decomposition started at 35.04 °C and was completed at 710.61 °C. A mass loss occurred within the temperature range 35.04-315.21 °C corresponding to the loss of three hydrated water molecules [24]. The Zn(II) complex decomposed and produced Zn as a residue [found(calculated)%: 8.85(9.43)] in four steps in the temperature range 35.04-315.21, 318.53-341.79, 347.33-592.10 and 596.53-710.61 °C, respectively. In the decomposition process of Zn(II) complex, the mass losses corresponded to 3H₂O, (C₆H₅O₃)₂CO and (BrPhCHNNH)₂CO, respectively.

The Cd(II) complex was stable up to 40.00 °C and its decomposition started at this temperature and was completed at 950 °C. A mass loss has occurred within the temperature range of 40.00-140.0 °C corresponding to the loss of two hydrated water molecules. The Cd(II) complex decomposed and produced CdO residue [found(calculated)%: 12.2 (19.2)] in four steps in the temperature range of 40.00-140.0, 145.0-250.0, 300.0-470 and 470.0-950.0 °C, respectively. In the decomposition process of Cd(II) complex, the mass losses corresponded to 2H₂O, 2H₂O, (2CH₃CO₂, N₂) and (BrPhCH₂ + C₇H₆O₄), respectively. The TGA curves of these complexes, 6.411%, 6.322%, 8.147% and 6.060%, respectively, indicate weight loss. This shows that the complexes contain 4, 4, 3 and 3 moles of water per complex molecule, respectively. The IR spectra of the complexes are characterized by appearance of a broad band in the region of 3416-3377 cm⁻¹, due to the ν(-OH) of the water [25]. This water was not identified by the elemental analyses, therefore location of the water molecules were outside the complex structure. The curves of TGA concerning the solid complexes reflected the experimental results for the residual amount of loss of mass which were in good agreement with the calculated results. The intermediate and the final products of the thermal decomposition of the complexes were identified by IR spectra as well. The thermal decomposition processes of the complex were summarized in Table 4.

Table 4. Thermal analysis data for some metal complexes of GHL1.

Complex	Stage	Temperature (°C)	Weight loss (%) found (calc.)	Assignment	Residue (%) found(calc.)
[Ni(GHL1) ₂](CH ₃ COO) ₂ .H ₂ O	1	40.0-200.0	8.15(7.98)	4H ₂ O	NiO 8.9 (8.3)
	2	200.0-350.0	11.98(13.09)	2(CH ₃ CO ₂)	
	3	350.0-500.0	36.95(37.20)	(Br-Ph-CH) ₂	
	4	500.0-795.0	33.97(33.95)	[3(OH)Ph-CONHNH] ₂	
[Cu(GHL1) ₂].3H ₂ O	1	36.1-266.2	5.82 (7.01)	3H ₂ O	Cu 7.21 (8.03)
	2	270.6-446.4	65.12(64.82)	2(C ₇ H ₅ N ₂ OBr)	
	3	452.0-607.9	21.85(20.62)	2(C ₆ H ₅ O ₃)	
[Zn(GHL1) ₂].3H ₂ O	1	35.0-315.2	6.05(7.10)	3H ₂ O	Zn 8.8(9.4)
	2	318.5-341.7	19.17(20.23)	BrPhCHNNH	
	3	347.3-592.1	30.85(32.25)	(BrPhCHNNH)CO	
[Cd(GHL1)(CH ₃ COO) ₂].H ₂ O	1	40.00 -140.0	6.40(5.38)	2H ₂ O	CdO 12.2(19.2)
	2	145.0-250.0	11.10(10.76)	2H ₂ O	
	3	300.0-470.0	22.76(21.83)	(2CH ₃ CO ₂ + N ₂)	
	4	470.0-950.0	47.58(47.98)	BrPhCH ₂ + C ₇ H ₅ O ₄	

CONCLUSIONS

In this paper synthesis and spectroscopic characterization of hydrazone derivative ligand and their Ni(II), Cu(II), Zn(II) and Cd(II) complexes were presented. The elemental analysis, magnetic susceptibility, FT-IR, UV-Vis, TGA spectral observation suggest the tetrahedral geometry around Ni(II) complex as shown in Figure 1 and octahedral geometry around Cu(II),

Zn(II) and Cd(II) complexes as shown in Figure 2. The conductance measurement of Ni(II) complex is electrolyte. The Cd(II), Ni(II), Zn(II) and Cu(II) complexes are thermally stable up to 35 °C. Moreover, in these complexes the ligand GHL1 acts as a mononegative charge tridentate ligand and it is coordinated with the metal ions through O, N, O except with Ni(II) and Cd(II) complexes. The ligand behaves as a neutral bidentate which is coordinated with the metal ions through O, N atoms.

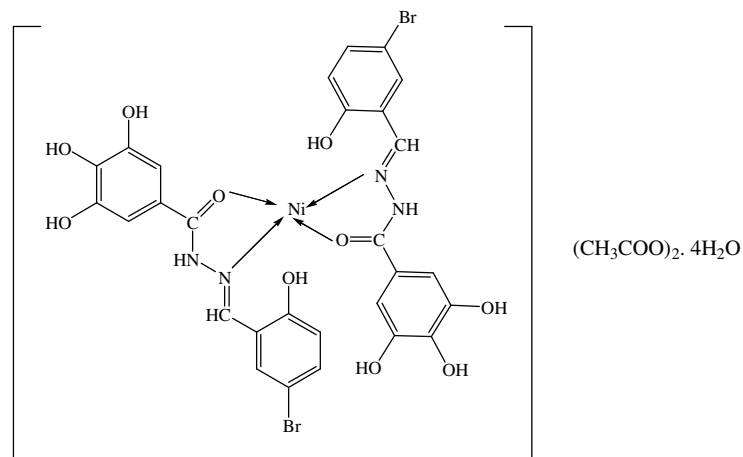


Figure 1. Proposed structure of [Ni(GHL1)₂](CH₃COO)₂.H₂O.

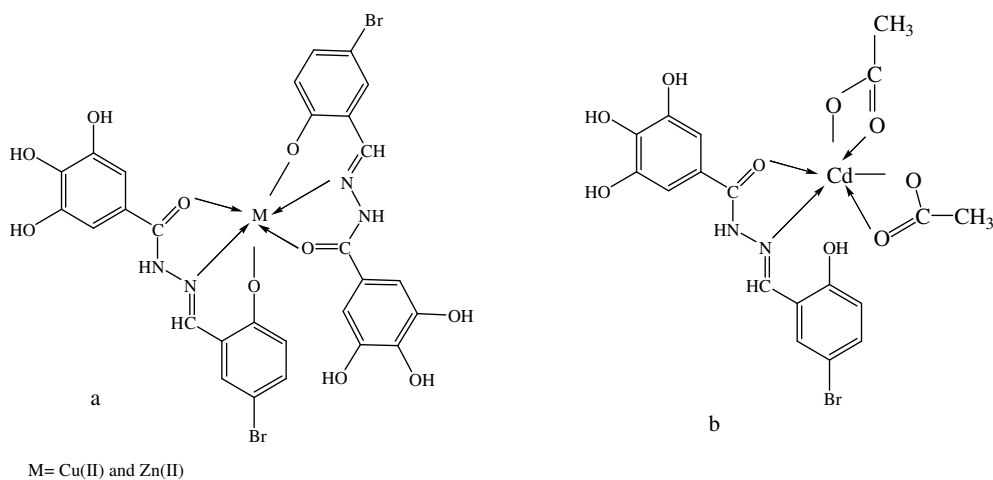


Figure 2. (a) Structure of [M(GHL1)₂] and (b) structure of [Cd(GHL1)(CH₃COO)₂].H₂O.

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