

Spectro-magnetic and Antimicrobial Studies on Some 3d metal Complexes with Ethylenedianil of ortho-hydroxyphenylglyoxal

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Abstract: The Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes with a novel tetradentate ligand obtained by condensation of ethylenediamine with ortho-hydroxyphenylglyoxal have been synthesized and characterized by elemental analysis, molar conductance and magnetic susceptibility measurements, IR, UV-Visible and atomic absorption studies. The Cr(III), Fe(III) and Co(II) complexes possess six coordinate octahedral geometry whereas Ni(II), Cu(II) and Zn(II) complexes are square planar and tetrahedral respectively. Bactericidal and fungicidal activities of the compounds were evaluated in vitro by disc diffusion method. The perusal of antimicrobial activities of the compounds reveals that the complexes possess greater bactericidal and fungicidal activities against all the microbes in comparison to ligand which is due to their higher lipophilicity.

Keywords: Bactericidal and Fungicidal Activities, Ortho-Hydroxyphenylglyoxal, Thin-Layer Chromatography, Structural Geometry, Lipophilicity, Tetradentate Ligand

1. Introduction

Polydentate ligands in the field of coordination chemistry and their metal complexes (chelates) are of great interest since many years. It is well known that N, S and O atoms play a key role in the coordination of metals at the active sites of numerous metallo-biomolecules [1]. Chelating ligands containing O, N and S donor atoms show broad spectrum of biological activities and are of special interest because of the variety of ways in which they are bonded to metal ions [1,2]. Most complexes of Schiff's bases act as perfect chelating agents and, are highly biologically active [3].

Ketone Schiff's bases with ON donor binding sites have attracted considerable attention because of their preparative accessibility, potential biological properties [2,4] applications in industries as dyes [4] and versatile coordination properties leading to formation of stable complexes with transition metal ions in unusual coordination numbers and isomeric structures [5-8]. The multifarious biological including antipathogenic behavior

of these metal-Schiff's base complexes is of paramount importance for designing metal-based drugs. In view of mentioned distinguished features of these compounds we report here the synthesis, magnetic, spectral and antimicrobial studies of Cr(III), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) complexes with ethylenedianil of ortho-hydroxyphenylglyoxal.

2. Experimental

The ligand ethylenedianil of ortho-hydroxyphenylglyoxal (L) was synthesized by the condensation of ethylenediamine and ortho-hydroxyphenylglyoxal [4]. The reaction mixture containing ethylenediamine (0.25 mol) and ortho-hydroxyphenylglyoxal (0.5 mol) in ether was stirred at room temperature (~20 °C). The yellow brown precipitate obtained was crystallized from acetone and product was finally washed with ether and dried in air.

The complexes of Fe(III), Co(II), Ni(II) and Zn(II) were synthesized by refluxing their reaction mixtures containing metal chloride (0.01 mol) and ligand (0.01 mol) in

acetone/methanol for 1h at $\sim 75^\circ\text{C}$. Concentrated reaction mixtures on cooling in ice bath yielded solid powders which were washed with cold water and acetone/methanol successively and dried in air. The Cr(III) and monoligand Cu(II) complexes precipitated from their reaction mixtures immediately were filtered out, washed with acetone and dried in air. To the filtrate of monoligand Cu(II) complex on further adding the ligand Cu(II)-bis-ligand complex precipitated was filtered out, washed with acetone and dried in air.

The purity of the compounds was tested by TLC on silica gel layers using chloroform, acetone and butanol solvents.

For the bacterial and fungicidal activities, compounds were screened *in vitro* by Disc Diffusion method [8] against animal pathogens, viz. *Escherichia coli*, *Staphylococcus aureus* and *Xanthomonas holcicola* (bacteria) and *Aspergillus niger*, *Colletotrichum gloeosporioides* and *Fusarium oxysporum* (fungi).

Melting points were determined in open glass capillaries with Stuart SMP-10 melting point apparatus and are uncorrected. Microanalyses were performed on a Vario EL-III analyzer. IR spectra were recorded on Shimadzu Prestige-21 FT-IR spectrophotometer in 4000-200 cm^{-1} region in KBr medium. The electronic spectra were recorded on SP65 UV-Vis. spectrophotometer in methanol solvent. Magnetic susceptibility was measured at room temperature (295°C) on MSB-Auto (Sherwood Scientific Ltd) balance. The molar conductance of complexes was measured in methanol at room temperature on Jenway digital conductivity bridge. Metal contents of the complexes were determined by atomic absorption spectroscopy using BUCK Scientific spectrophotometer.

3. Results and Discussion

All the metal complexes are stable in air. Microanalytical data (Table 1) are consistent with the molecular formulae of the compounds. The molar conductance values account for

[10] non-electrolytic nature of Cr(III), Fe(III), Co(II) and Ni(II) complexes, and 1:2 and 1:1 electrolytic nature of the two Cu(II) and Zn(II) complexes respectively.

In order to identify the binding modes of the ligand in the complexes, IR spectrum of the free ligand was compared with that of complexes. The free ligand displayed νOH and $\nu\text{C-O}$ bands at 3458 cm^{-1} and 1066 & 1129 cm^{-1} of phenolic/enolic groups. In the spectra of the complexes the absence of νOH band, lowering in frequency of $\nu\text{C-O}$ bands (ca. 1045 & ca. 1103 cm^{-1}) and appearance of a new band in $488\text{--}561\text{ cm}^{-1}$ attributed to $\nu\text{M-O}$ reveal coordination of deprotonated phenolic/enolic group of the ligand; an additional band appeared in $453\text{--}473\text{ cm}^{-1}$ region in the spectra of Cu(II) and Zn(II) complexes could be attributed to $\nu\text{M-O-M}$ vibrations. The azomethine group stretching vibration, displayed in ligand spectrum at 1613 cm^{-1} , appeared at low value ($1457\text{--}1538\text{ cm}^{-1}$) in complexes indicates coordination of azomethane nitrogen with metals. The appearance of new band in $465\text{--}489\text{ cm}^{-1}$ range in complex spectra attributed to $\nu\text{M-N}$ supported the presence of azomethane group in the coordination zone of the metals. The shifting of $\nu\text{C=O}$ band of ligand (1646 cm^{-1}) on complexation in $1602\text{--}1642\text{ cm}^{-1}$ range is a strong evidence in support of the view regarding coordination of deprotonated enolic group of quinonoid structure of the ligand [2].

A band at 375 cm^{-1} , 303 cm^{-1} and 247 cm^{-1} in Fe(III), Zn(II) and mono-ligand trinuclear Cu(II) are assigned to $\nu\text{M-Cl}$ and $\nu\text{Cu-Cl-Cu}$ vibrations of monodentate and bidentate chloride respectively. Two infrared active $\nu\text{Cr-Cl}$ bands at 248 cm^{-1} and 377 cm^{-1} of monodentate chloride in Cr(III) complex indicates its C_{2v} (trans symmetry) [10,11].

Lattice water exhibited symmetric and antisymmetric stretching and bending vibrations in $3209\text{--}3493\text{ cm}^{-1}$ and $1601\text{--}1630\text{ cm}^{-1}$ regions respectively, whereas coordinated water displayed wagging (ρ_w), twisting (ρ_t), rockling (ρ_r) vibrations and $\nu\text{M-OH}_2$ peak in $832\text{--}1044\text{ cm}^{-1}$ and $252\text{--}399\text{ cm}^{-1}$ regions respectively of complex spectra.

Table 1. Analytical data, magnetic moment and physical properties of compounds

S.No.	Compounds	Color	Yield (%)	M.P ($^\circ\text{C}$)	Molar Cond. ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)	μ_{eff} (B.M.)	Elemental analysis (%)			
							Calculated.	(Found)		
							C	H	N	M
1	$\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_4$	Yellow	41	152 ± 2	-	-	66.67 (67.01)	4.94 (4.62)	8.64 (8.43)	-
2	$[\text{Cr}_2\text{L}(\text{H}_2\text{O})_2\text{Cl}_4]\cdot 6\text{H}_2\text{O}$	Gray	63	>300	7.8	3.83	30.33 (30.77)	4.21 (4.45)	3.93 (3.76)	14.57 (13.67)
3	$[\text{FeL}(\text{H}_2\text{O})\text{Cl}]\cdot 6\text{H}_2\text{O}$	Black	65	195 ± 2	5.6	3.64	40.04 (40.5)	5.19 (4.98)	5.19 (5.28)	10.38 (9.83)
4	$[\text{CoL}(\text{H}_2\text{O})_2]\cdot 4\text{H}_2\text{O}$	Gray	83	185 ± 2	11.0	3.73	44.17 (44.58)	5.32 (5.80)	5.72 (5.54)	12.07 (11.48)
5	$[\text{NiL}]\cdot \text{H}_2\text{O}$	Brown yellow	64	245 ± 2	39.7	1.25	54.18 (54.42)	4.01 (4.86)	7.59 (8.06)	14.72 (15.56)
6	$[\text{Cu}_3\text{L}_2]^{+2}\cdot 2\text{Cl}^-\cdot 4\text{H}_2\text{O}$	Black green	58	278 ± 2	159.7	1.23	44.20 (43.55)	3.30 (3.44)	7.59 (8.02)	19.50 (20.27)
7	$[\text{Cu}_3\text{LCl}_2(\text{H}_2\text{O})_2]\cdot 2\text{Cl}^-$	Green brown	42	283 ± 2	154.2	1.19	31.28 (32.13)	2.32 (2.49)	4.05 (4.42)	28.99 (30.10)
8	$[\text{Zn}_2\text{LCl}(\text{H}_2\text{O})]^{+}\cdot \text{Cl}^-\cdot 4\text{H}_2\text{O}$	Light yellow	82	>300	86.5	Diamag.	35.19 (34.83)	3.58 (3.89)	4.59 (5.06)	14.25 (14.93)

$\text{L} = \text{C}_{18}\text{H}_{14}\text{N}_2\text{O}_4$

Magnetic moment of Cr(III) complex (3.83 BM) is typical of spin-free d^3 octahedral geometry. Among the four peaks displayed in the absorption spectrum at 14286 cm^{-1} , 24390 cm^{-1} , 30303 cm^{-1} and 34482 cm^{-1} first three band are characteristic of ${}^4A_{2g} \rightarrow {}^4T_{2g}(F)$, ${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$, ${}^4A_{2g} \rightarrow {}^4T_{1g}(P)$ d-d transitions respectively [13,14] and fourth band attributed to ligand to metal charge transfer [13].

Although in absence of antiferromagnetic interactions low magnetic moment, 3.64 BM, of Fe(III) complex indicates high spin ($S = 5/2$) to low spin ($S = 1/2$) crossover phenomenon [10] but electronic spectral bands splitting pattern is characteristic of high-spin octahedral geometry. Absorption bands at 20833 cm^{-1} , 24390 cm^{-1} , 27027 cm^{-1} , 28571 cm^{-1} and 37037 cm^{-1} may be assigned to the spin-forbidden electronic transitions from ground sextet term ${}^6A_{1g}$ to ${}^4T_{1g}(G)$, ${}^4T_{2g}(G)$, ${}^4A_{1g}(G)$, ${}^4E_g(G)$ and ${}^4E_g(D)$ respectively; other two bands at 40000 cm^{-1} and 47619 cm^{-1} correspond to charge transfer transitions [12,13].

Observed magnetic moment of Co(II) complex, 3.37 BM, and absorption bands at 14925 cm^{-1} , 17544 cm^{-1} and 24390 cm^{-1} attributed to ${}^4T_{1g} \rightarrow {}^4T_{2g}(F)$, ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$ and ${}^4T_{1g} \rightarrow {}^4T_{2g}(F)$ respectively are consistent with spin free octahedral geometry [14,15] of this paramagnetic. Additional bands displayed in $30303\text{--}47619\text{ cm}^{-1}$ region of spectrum are due to charge transfer transitions.

The lower magnetic moment of Ni(II) complex, 1.25 BM, than spin-only value of spin free d^8 configuration (2.83 BM) indicates the presence of both spin paired and spin free,

states in equilibrium in the solid. However spectral bands occurring at 23529 cm^{-1} and 28572 cm^{-1} are characteristic of ${}^1A_{1g} \rightarrow {}^1B_{1g}$ and ${}^1A_{1g} \rightarrow {}^1A_{2g}$ d-d transitions respectively of square planar spin paired geometry [12, 16] of this complex. High frequency bands spreading over $33898\text{--}45456\text{ cm}^{-1}$ region correspond to charge transfer transitions.

The magnetic moments of both Cu(II) complexes, 1.23 BM and 1.19 BM, are lower than spin-only value of d^9 configuration most probably due to the presence of antiferromagnetic interactions in these trinuclear paramagnetics. Three bands occurring in $24390\text{--}25000\text{ cm}^{-1}$, $26316\text{--}27027\text{ cm}^{-1}$ and $28986\text{--}30303\text{ cm}^{-1}$ regions of electronic spectra attributed to ${}^2B_{1g} \rightarrow {}^2A_{1g}$, ${}^2B_{1g} \rightarrow {}^2B_{2g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ transitions respectively of their square planar geometry [17,18]. As a typical example structure of monoligand trinuclear Cu(II) complex is shown in Figure 1.

The perusal of antimicrobial activities of the compounds (Table 2) reveals that the complexes possess greater bactericidal and fungicidal activities against all the microbes in comparison to ligand which is due to their higher lipophilicity. This modified antimicrobial behavior of the complexes may be accounted for on the basis of Chelation Theory and Overtones Concept [19]. Among all the compounds Zn(II) complex which showed highest antimicrobial activity against both test bacteria and antifungal activity against *A. niger* and greater than standard drugs, could be considered a promising drug against these microbes.

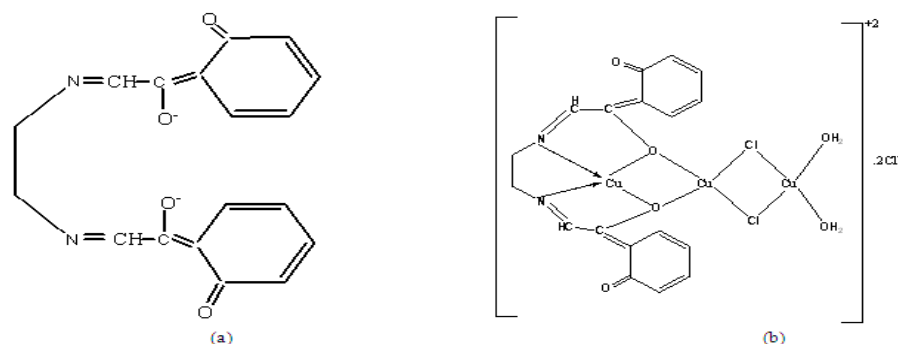


Figure 1. Structures of a) quinonoid Ligand and b) Cu(II) monoligand complex

Table 2. Antimicrobial activity data of Compounds

S.N	Compounds	Inhibition Zone (mm)											
		Bacteria						Fungi					
		<i>S. aureus</i>	<i>X. holcicola</i>	<i>E. coli</i>	<i>C. gloeosporioides</i>	<i>F. oxysporum</i>	<i>A. niger</i>	<i>S. aureus</i>	<i>X. holcicola</i>	<i>E. coli</i>	<i>C. gloeosporioides</i>	<i>F. oxysporum</i>	<i>A. niger</i>
		10μl	20μl	10μl	20μl	10μl	20μl	10μl	20μl	10μl	20μl	10μl	20μl
1	Ligand	7	9	-	-	-	-	9	11	-	-	7	10
2	[Cr ₂ L(H ₂ O) ₂ Cl ₄].6H ₂ O	12	13	x	X	7	8	10	12	x	x	9	12
3	[FeL(H ₂ O)Cl].6H ₂ O	10	11	x	X	6	10	10	11	x	x	8	11
4	[CoL(H ₂ O) ₂].4H ₂ O	8	10	x	X	6	7	9	10	x	x	8	11
5	[NiL].H ₂ O	15	18	13	22	x	x	x	x	15	20	15	22
6	[Cu ₃ L ₂] ²⁺ .2Cl ⁻ .4H ₂ O	17	19	25	31	x	x	x	x	13	20	8	25
7	[Cu ₃ LCu ₂ (H ₂ O) ₂].2Cl ⁻	17	20	22	27	x	x	x	x	8	12	10	15
8	[Zn ₂ LCu(H ₂ O)] ⁺ .Cl ⁻ .4H ₂ O	23	25	25	32	x	x	x	x	12	18	19	27
9	DMSO (Control)	-	-	-	-	-	-	-	-	-	-	-	-
10	Chlroamphinicol	21	23	25	30	27	31	-	-	-	-	-	-
11	Bavistin	-	-	-	-	-	-	30	35	15	20	20	25

x = not attempted

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