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Synthesis and antimicrobial activity of Cobalt (II), Nickel (II), and Copper(II) complexes of some 2'- hydroxychalcones

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ABSTRACT

The complexes of the type ML_2 [where M=Cu (II), Ni (II) and Co (II)] L= 1-(2'-Hydroxy phenyl)-3-(1- Hydroxy, 2, 4- Dibromo phenyl)-2- propen-1-one and 1-(2'-Hydroxy-3'-Iodo-5'-methyl phenyl)-3-(1- Hydroxy 2, 4-dibromo phenyl)-2-propen-1-one. These ligands were prepared by the condensation of substituted 2'- Hydroxyacetophenones and 3, 5 dibromosalicylaldehyde. The structures of the complexes have been proposed by the analytical data, conductivity measurement, magnetic moment, IR, electronic spectral data and thermal studies. Analytical data confirmed 1:2 stoichiometry and the electronic spectral data suggest that all Co (II), Ni (II) complexes have octahedral geometry whereas Cu (II) complexes have square planar geometry. Presence of coordinated water molecules in Co (II) and Ni (II) complexes is confirmed by TGA studies. The conductivity data show that all these complexes are non electrolytes. The ligands and their metal complexes were screened for antibacterial activity against various bacteria like E.coli, S. typhi, S. aureus, B. subtilis and fungicidal activity against various fungi like P.chrysogenum, A. niger, F. moniliformae, and C.albicans.

Keywords: Chalcones, ESR spectra, TGA, Antibacterial activity, antifungal activity Transition metal complexes.

INTRODUCTION

A number of β-dicarbonyl compounds in which the carbonyl function (s) is bonded to C=C linkage (s) have gained considerable importance[1], mainly because such compounds are associated with many biological activities due to the presence of the α, β-unsaturated system, as evidenced from their antimalarial[2], antituberculosis[3], antiplasmodial[4], antitrichomonal[5],

antioxidant[6] and analgesic[7] activities as well as their use as anti-inflammatory and cancer chemo preventive agents[8].

Therefore the synthesis and characterization of such unsaturated carbonyl system and their metal complexes are of tremendous importance. The literature survey reveals that the metal complexes of 2'-Hydroxychalcones demonstrated more potent bactericidal and fungicidal properties than their corresponding ligands.

MATERIALS AND METHODS

All the melting points were determined in an open capillary tube and are uncorrected. Completion of the reaction was monitored by thin layer chromatography on pre-coated sheets of silica gel-G. All the reagents used were chemically pure and are of AR grade. Solvents were dried and distilled before use according to standard procedure[9]. The ligands selected in the preparation of metal complexes are 1-(2'-Hydroxy phenyl)-3-(1- Hydroxy, 2, 4- Dibromo phenyl)-2- propen-1-one and 1-(2'-Hydroxy-3'-Iodo-5'- methyl phenyl)-3-(1- Hydroxy 2, 4-dibromo phenyl)-2-propen-1-one.

General procedure for the synthesis of 2'-hydroxychalcone:-
A mixture of substituted acetophenone (0.01mol), aromatic carboxaldehyde (0.01mol) and NaOH (0.02mol) were dissolved in methanol solution. The reaction mixture was heated for 2-3 hr. The progress of the reaction was monitored by TLC. After completion of the reaction the contents were poured in ice water and then acidified by dil.HCl. The solid obtained was filtered, washed with cold water. Then crude product was crystallized from ethanol to give the corresponding product.

Synthesis of metal complexes
The ligand (0.002 mole) and the metal salt (0.01 mole) in 50 ml methanol was reflux for 2 hour. In all the cases the ligand concentration was in slight excess of the 1:2 metal ligand molar ratio. The solid mass separated was filtered through a sintered glass crucible (G4) and the residue was washed several times with hot methanol until the washings were free of the excess of ligand. These complexes were finally dried under vaccum desicator over fused $CaCl_2$. Analytical and physical data is given in TABLE-1. Molar conductance measurements were carried out in 10^{-3} M in DMF solution using an Elico digital conductometer model-180. The magnetic susceptibility measurements of the complexes in the solid state were made on Guoy balance at room temperature using Hg [Co (NCS) $_4$] as standard. Diamagnetic corrections were applied using pascals constant. The IR spectra of the metal in KBr pallets in the range of 4000-350 cm^{-1} were recorded making use FTIR-SHIMADZU8400S spectrometer.

UV-Visible spectra in DMF were recorded on a SHIMADZU multipurpose recording spectrophotometer model 1601 and TGA and DTA analysis of metal complexes were carried out in nitrogen atmosphere in the range 25-1200 ˚C on schimadzu DTG-50 with a heating rate 10 ˚C min^{-1} using alumina as a standard.

RESULTS AND DISCUSSION

All the complexes are stable at room temperature insoluble in water and most of the common organic solvents but soluble in DMF and DMSO. The analytical data of the complexes (TABLE-1) indicates that their stoichiometry may be represented as 1:2 metal to ligand ratio. The molar conductance values of the complexes in DMF solvents are in the range of 6.45-26.25 ohm^{-1} cm^2 mol^{-1} suggesting their non-electrolytic nature[10].

IR spectra

The ligand showed a weak broad band around 2890-3068 cm^{-1}, but the IR spectra of Ni (II) and Co (II) complexes exhibited intense broad band near 3300-3400 cm^{-1} due to υ OH of coordinated water molecule[11]. In the IR spectra of all the ligands an intense band appearing around 1647 cm^{-1} is attributed to υ(C=O) [12]. This band is shifted to lower wave number in the spectra of the complexes indicating coordination through oxygen of (C=O) group. The medium intensity band appearing around 1533-1569 in the ligands and the complexes are assigned to υ (C=C) (aromatic). The υ (M-O) band was observed in the complexes around 445cm^{-1}[1, 13].

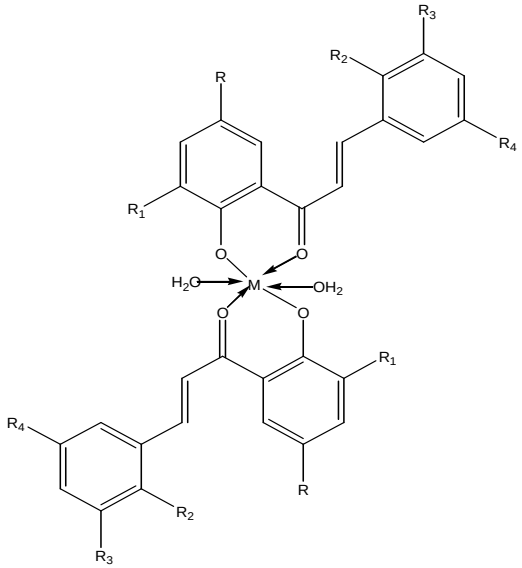
Thermal analysis

The thermogram of Ni (II) and co (II) complexes shows the coordination of two moles of hydrated water where as there is absence of coordination of such hydrated water molecule in case of Cu (II) complexes.

Hence from TGA, it is clear that the complex under study contains two water molecules which are coordinated to central metal ion[14].

Table-1:-*Magnetic moment, Conductivity and analytical data of Co (II), Ni (II) and Cu (II) complexes*

Sr. No.	Comp.	Molecular Formula	Colour	M.P/D.P. ˚C	Elemental Analysis Halogen Found (Calcd)	Elemental Analysis Metal Found (Calcd)	Molar Conductivity Ohm-1 Cm2 Mol-1×10-3	µeff B.M.
1.	S_1	$C_{30}H_{22}O_8Br_4Ni$	Yellow	276	37.48 (37.16)	6.88 (6.54)	25.27	2.41
2.	S_2	$C_{30}H_{22}O_8Br_4Co$	Green	236	37.25 (37.86)	6.97 (6.18)	18.64	4.36
3.	S_3	$C_{30}H_{18}O_6Br_4Cu$	Bluish Green	278	37.27 (37.92)	7.41 (7.86)	21.48	1.67
4.	S_4	$C_{32}H_{24}O_8I_2Br_4Ni$	Dark Yellow	264	26.21 (26.78)	5.18 (5.69)	12.16	2.96
5.	S_5	$C_{32}H_{24}O_8I_2Br_4Co$	Green	234	25.80 (25.16)	5.20 (5.38)	11.32	4.92
6.	S_6	$C_{32}H_{20}O_6I_2Br_4Cu$	Bluish Green	268	27.22 (27.58)	5.59 (5.62)	7.48	1.89



M= Ni (II), Co (II)

Complex No.	R	R_1	R_2	R_3	R_4
1.	H	H	OH	Br	Br
2.	H	H	OH	Br	Br
3.	H	H	OH	Br	Br
4.	CH_3	I	OH	Br	Br
5.	CH_3	I	OH	Br	Br
6.	CH_3	I	OH	Br	Br

Magnetic moment

The μ_{eff} values at room temperature for Cu (II) complexes are in the range of 1.78-1.84 B.M. usually observed for square planar Cu (II) complexes [15, 16]. Ni (II) and Co (II) complexes have magnetic moment values in the range of 2.92-3.14 and 4.38-4.90 B.M. respectively. These values are expected for octahedral geometry of Ni (II) [17, 18], and Co (II) complexes at 25˚C.

Electron spin resonance study

The ESR spectra of Cu (II) complexes in the polycrystalline state shows two peaks, one of intense absorption at high field and the other of less intensity at low field. From these spectra the values of $g_{\parallel}$ and $g_{\perp}$ have been calculated by Kneubehls method [19]. The observed g-values point to the presence of the unpaired electron in the dx^2-y^2 orbital with $g_{\parallel} > g_{\perp}$ characteristic of square planar of elongated tetragonal geometry. The $g_{\parallel}$ obtained for the Cu (II) complexes is less than 2.3 indicating covalent character of the metal-ligand bond[20]. The axial symmetry parameter (G) for the complexes is found to be greater than 4. This shows absence of interaction between copper centers in the solid state[21].

Antimicrobial activity:

The antibacterial activity of the compounds was determined by agar diffusion method against various bacteria like *E.coli, S. typhi, S. aureus, and B. subtilis* at various concentrations such as 20, 50and 100 µg /ml. The zone of inhibition was measured in mm and DMSO was used as solvent. Sterile nutrient agar was seeded with test organism and layered in sterile petri plate.

After solidification, agar cups were borered with cork borer 0.1 ml of the compound solution was added to the cup with the help of micropipettes, one cup in the plates was filled with solvent. Standard penicillin (10v/ml) was used as reference drug. The plates were kept at low temperature (4 °C) for 20minute to allow diffusion of the compound. Then the plates were incubated at 37 °C for 24 hr. After proper incubation the plates were observed for zone of no growth (zone of inhibition of growth) around the cup. Similarly the same compounds were screened for the antifungal activity against different organisms like *P.chrysogenum, A. niger, F. moniliformae,* and *C.albicans* by using poison plate method. The compound was mixed with sterile potato dextrose agar medium so as to get final concentration 2%. It was then poured in sterile petri plate and allowed to solidify. Spots of test organisms were placed on the agar surface. A plate without compound was prepared for control. The plates were incubated at room temperature for 48 hr. After proper incubation plates were observed for growth of the test organisms. The growth indicates that the compound is not antifungal while inhibition of growth of test organism indicates antifungal activity. The antifungal activities of the compounds were compared with standard grysofulvin.

Table-2 Antimicrobial activity of synthesized compounds

Product	Bacterial Strain				Fungal Strain			
	Ec	St	Sa	Bs	An	Pc	Fm	Ca
1) S_1	11	14	12	21	+ve	-ve	-ve	-ve
2) S_2	--	11	29	18	-ve	-ve	-ve	-ve
3) S_3	--	--	22	23	-ve	+ve	RG	-ve
4) S_4	9	--	8	16	+ve	-ve	-ve	-ve
5) S_5	6	8	13	25	+ve	RG	-ve	-ve
6) S_6	--	--	17	19	-ve	+ve	-ve	+ve
Penicillin	18	20	32	28	NA	NA	NA	NA
Grysofulvin	NA	NA	NA	NA	-ve	-ve	-ve	-ve

Ec-E.coli, St-S.typhi, Sa- S.aureus, Bs-B.subtilis; An-A.niger, Pc-P.chrysogenum, Fm-F.moneliformae, Ca-C.albicans; *-ve: No growth of fungi,+ve: Growth of fungi, RG-Reduced growth, NA-Not Applicable, Zone of inhibition was measured in mm.*

The results of antimicrobial data are given in Table-2.The data revealed that all the compounds were found to be active against S. aureus and B. subtilis. Only Compound S_2 was showed inhibition of growth against all the tested fungi. Compound S_3 and S_5 were showed reduced growth against one or more pathogens.

CONCLUSION

It is clear from the present results that preliminary studies showed their good inhibitory properties. In general Ni (II), Co (II) and Cu (II) complexes are more active than their parent ligand and hence may serve as vehicles for activation of the ligand as principle cytotoxic species.

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