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Structrual and Biological Studies of Some Bivalent Metal Macrocyclic Compounds of Biochemical Significance

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Two new macrocyclic complexes of formulae M(DCODH) $(BF_4)_2$ (where M = Cu(II) and Ni(II) and (DCODH = 2,6-pyridine dicarbonyl dichloride-oxydiacetic acid dihydrazone) have been synthesized and characterized with the help of elemental studies, IR spectral analysis and electronic spectra. These have been further screened antimicrobially for their biological studies against bacterial species, *E. coli* (gram negative) and *S. aureus* (gram positive) and fungi *C. albicans*, and found to possess greater biological effect as compared to the ligand fragments and the metal salts.

INTRODUCTION

Macrocyclic compounds are applicable as complexing agents and ion chelating resins. For example synthetic cyclic polyethers, cyclic polythiaethers, cyclic polyazaethers and bicyclic amines. The selectivity of cyclic antibiotics towards cations has commercial applications, *e.g.*, valinomycin in ion-selective electrodes[1, 2]. Although ligands having oxygen and nitrogen as the donor atoms are by far the most studied[3]. The interest in complexes of these ligand systems now covers the full areas ranging from general considerations to metal-sulphur bonding and electronic delocalisation in transition metal complexes to potential biological activity and practical application[4] and their complexes with Ni(II), Cu(II), Zn(II), Co(II) metal ions. Metal ions play an important role in biological system. Many complexes containing synthetic macrocyclic ligands may serve as models for biologically important species. The presence of Ni and Cu in the enzyme hydrogenase is an example of the catalytic role of metal ions in redox reactions of biological importance when coordinated with macrocyclic environments[5–8].

Studies on electrical properties of phthalocyanines date back to 1948 when Eley and Vartanyan discovered the ususal temperature dependence of the resistivities of the phthalocyanines and their metal derivatives[1–4]. Phthalocyanines have the advantage of the possibility of changing their properties by structural modification through peripheral substitution in the macrocycles.

The nickel(II) fluoro-boro macrocyclic complexes combine apically with exogenous nitrogen bases which possess quite unusual structural and spectro-

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scopic properties[9]. The Cu(II) macrocyclic complexes with 2,9-dimethyl-3,10-diphenyl-(14)-1,3,8,10 tetraene N_4(MePhTIM)[10–12]. The interaction between metal ions and ligands may lead to the formation of poly chelates in which the chelated metal ions are bridged by ligand molecules[13].

EXPERIMENTAL

All chemicals were pure grade. The electronic spectra (ethanol or methanol) were recorded on a Perkin-Elmer Lambda-14 spectrophotometer. Infrared spectra were scanned on an IR spectral spectrophotometer. Complexes have been further screened for their biological studies against bacterial and fungal species by serial dilution method.

Synthesis of Metal Complexes

Equimolar amounts of oxy-acetic acid dihydrazide (0.01 M), Ni acetate (0.01 M), and 2,6-pyridine dicarboyl dichloride (0.01 M) were mixed in ethanol with continuous stirring. The solution thus obtained was refluxed over a water bath for around 6 h. Subsequently, it was concentrated to one-third of its original volume. Then, a little of sodium tetrafluoroborate was added and the solution was cooled overnight, when black crystals separated out. The crystals were filtered, washed with alcohol, ether and then dried in vacuum over anhydrous $CaCl_2$ in a desiccator. The other complexes were also synthesized by similar procedure.

RESULTS AND DISCUSSION

All the synthesized complexes are coloured solids and insoluble in water and common organic solvents. The elemental analysis suggests 1 : 1 metal : ligand stoichiometry for the complexes. The ligand fragment, *i.e.*, oxy-diacetic acid dihydrazide, exhibits 1 : 2 stoichiometry. The analytical data of the ligand fragment is shown in Table-1.

TABLE-1
ANALYTICAL DATA OF LIGAND FRAGMENT AND Cu(II) AND Ni(II) MACROCYCLIC COMPLEXES

Compound (Colour)	m.p. (°C)	% Analysis, Found (Calcd.)			M	Λ_m ohm^{-1} cm^2 mol^{-1}
		C	H	N		
DCODH (Yellowish white)	216	28.93 (29.60)	6.05 (6.17)	33.93 (34.56)	– –	–
Cu[DCODH]$(BF_4)_2$ (Brownish black)	260	23.03 (23.38)	1.49 (1.59)	11.34 (12.40)	10.21 (11.24)	106.60
Ni[DCODH]$(BF_4)_2$ (Black)	243	22.56 (23.58)	1.50 (1.60)	11.40 (12.50)	9.45 (10.48)	109.50

Infrared Spectra

The IR spectra of all the ligand fragements have sharp and prominent bands at 3050 ν(NH), 1550 ν(C═O) and 1450 cm^{-1} δ(NH_2). A sharp band was observed at 2175 cm^{-1} (CH_2) in the spectrum of oxy-diacetic acid hydrazide. The pyridine ring deformation bands were also observed around 850 cm^{-1}.

In the IR spectra of metal complexes the peaks due to ν(NH) did not undergo any shift (3050 cm^{-1}) ruling out the coordination of nitrogen of (NH) with the central metal atom (Table-2).

However the band due to ν(C=O) experienced a negative shift by 30–40 cm^{-1} appearing at 1510 cm^{-1} while the position of ν(N—N) band shifted to higher wave numbers (1050 cm^{-1}). These observations led to the conclusion that the amide oxygen of ν(C=O) and the nitrogen of ν(N—N) band are involved in coordination.

Electronic Spectra

Both the Cu(II) and Ni(II) complexes exhibit two broad bands and in the region of 14330–14260 cm^{-1} and another in the range 28460–27805 cm^{-1}. The former band may be assigned to $^2E_g \rightarrow {}^2T_{2g}$ transition, suggesting an octahedral geometry of the complexes. The latter band can be attributed to L → M charge tansfer spectrum (Table-3).

TABLE-2

IR SPECTRAL DATA (cm^{-1}) OF THE COMPOUNDS

Functional group	DCODH	$Cu(DCODH)(BF_4)_2$	$Ni(DCODH)(BF_4)_2$
ν(—CH_2)	2975	2975	2975
ν(—NH)	3050	3050	3050
ν(>C=O)	1750	1710	1705
$\delta(NH_2)$	1450	–	–
ν(N—N)	1510	1530	1535
ν(C=N—)	–	1615	1645
ν(M—O)	–	325	330
ν(M—N)	–	255	245

TABLE-3

ELECTRONIC SPECTRAL DATA (cm^{-1}) OF THE COMPLEXES

S. No.	Compounds	Trasitions (cm^{-1})	
		$^2E_g \rightarrow {}^2T_{2g}$	L → M
1	$Cu(DCODH)(BF_4)_2$	14,330	28,460
2	$Ni(DCODH)(BF_4)_2$	14,260	27,805

Antimicrobial Study: The ligand and its metal complexes have been screened for antibacterial and antifungal activities by serial dilution method. The antimicrobial activity of the compounds has been tested against *Esherichia coli* (gram negative) and *Staphylococcus aureus* (gram positive). The antifungal activity of the compounds has been tested against *Aspergillus niger* and *Candida albicans*. The results indicate that the ligand DCODH has been found to be moderately active against both bacteria and fungi used as compared to its metal complex except the complexes Cu[DCODH] $(BF_4)_2$ which are more potent towards the fungal cells than the bacterial cells.

The results of these activities show that the screened complexes have been found to possess greater biological effects as compared to the ligand fragments and the metal salts. The 'MIC' values for the compounds have been represented in Table-4.

TABLE-4
'MIC' VALUES OF THE COMPOUNDS IN MOLAR CONCENTRATION ($\times 10^{-4}$)

S. No.	Compounds	Bacteria		Fungi	
		E. coli	*S. aureus*	*A. niger*	*C. albicans*
1.	DCODH	5.120	5.110	5.084	5.130
2.	$Cu(DCODH)(BF_4)_2$	0.230	0.230	0.120	1.120
3.	$Ni(DCODH)(BF_4)_2$	0.120	0.240	0.236	0.236

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