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Synthetic, Structural and Antimicrobial Studies of Some Ni(II) and Cu(II) Macrocyclic Complexes

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Two new macrocyclic complexes of formulae M(DPODH)$(OAc)_2$, (Where M = Ni(II) and Cu(II) and (DPODH)$(OAc)_2$ = 2,6-diacetyl pyridine oxy diacetic 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 posses greater biological effect as compared to the ligand fragments and the metal salts.

INTRODUCTION

There has been tremendous research work on macrocyclic chemistry during the last two to three decades. Such an activity has gained momentum due to the realization that metal ions play an important role in biological system. The biological system contains naturally occurring chelates[1] of metals such as Co^{2+}, Cu^{2+}, Zn^{2+} and Ni^{2+} with amines and related compounds. The presence of Ni in the enzyme hydrogenase is an example of the catalytic role of metal ions in redox reactions of biological importance when coordinated with macrocyclic environment.

Macrocyclics, due to their intriguing ligating properties have opened up a new area of coordination chemistry. Macrocyclic compounds are ideally applicable as complexing agents and ion-chelating resins. The selectivity of cyclic antibiotics towards cations has commercial applications, *e.g.*, valinomycin in ion-selective electrodes[2].

A series of fluoro-boro bridged Ni(II), Co(II), Cu(II) and Co(III) macrocyclic complexes have been reported[3–5]. Transition metal complexes involving vicinal dihydrazones[6–12] have been used as intermediates to prepare macrocyclic and clathro chelate metal complexes by template condensation with aldehydes and ketones[13–15].

Recently, synthesis of esters of some di-carboxylic acids *viz* (imino-di acetic

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acid), di-thio di propionic acid and thio di-propionic acid have been carried out. Extending our earlier work, we have again synthesized two more new macrocyclic complexes of Cu(II) and Ni(II) by condensing 2,6-diacetyl pyridine with oxy-acetic acid dihydrazide which have been reported here.

In the series of macrocyclic compounds research investigation have been done with the complexes of porphyrines, corrins and phthalocyanines and their relation with prominent species containing macrocyclics occurring in nature such as cytochromes, haemoglobin, chlorophyll complexes containing macrocyclics are simple models found in metallo proteins.

EXPERIMENTAL

Chemicals of AR grade have been used for synthesizing the compounds. Oxy-diacetic acid dihydrazide has been synthesized from their corresponding dimethyl ester of the acid and hydrazine hydrate by the reported procedure[16]. Their purity was ascertained by preliminary investigation *viz*., repeated melting point determination, TLC for single spot analysis, determination of elemental studies, IR spectral analysis and electronic spectral analysis. These have been further screened antimicrobially for their biological studies against bacterial species and fungal species.

Synthesis of metal complexes

Equimolor amounts of oxyacetic acid dihydrazide (0.01 M), copper acetate (0.01 M) and 2.6 diacetyl pyridine (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, solution was cooled overnight when brownish-black crystals separated out. The crystals were filtered, washed with alcohol and ether and then dried in vacuum over anhydrous calcium chloride in a desicator.

Nickel(II) complex was also synthesized by similar procedure.

RESULTS AND DISCUSSION

Both the synthesized complexes are coloured solids and stable at room temperature and soluble in DMSO, DMF and propylene glycol but insoluble in common organic solvents. These complexes have molar conductance values in the range of 106.60–109.50 ohm^{-1} cm^2 mol^{-1}, indicate their electrolytic nature. Analytical data suggest 1 : 1 : 1 stoichiometry for the complexes. The ligand fragment, *i.e.*, oxydiacetic acid dihydrazide, exhibits 1 : 2 stoichiometry. The analytical data of the ligand fragment and metal complexes are presented in Table-1.

Infrared Spectra

The IR spectra of all the ligand fragments reveal sharp and prominent bands at 3080 ν(NH), 1660 ν(C═O) and 1570 cm^{-1} $\delta(NH_2)$. A sharp band was observed at 2280 cm^{-1} $\nu(CH_2)$ in the spectrum of oxy-di-acetic acid dihydrazide. The pyridine ring deformation bands were also observed around 960 cm^{-1}.

TABLE-1
ELEMENTAL ANALYSIS AND MOLAR CONDUCTANCE DATA OF THE COMPOUNDS

Compound (colour)	(m.p.) °C	% Analysis, found (Calcd.)				Λ_m (ohm^{-1} cm^2 mol^{-1})
		C	H	N	M	
DPODH (yellowish white)	220	28.93 (29.60)	6.05 (6.17)	33.93 (34.50)	–	–
Cu[DPODH](OAc)$_2$ (brownish black)	263	33.03 (33.15)	3.09 (3.18)	13.20 (14.80)	12.10 (13.40)	106.60
Ni[DPODH](OAc)$_2$ (black)	245	32.60 (33.50)	3.11 (3.22)	14.85 (15.00)	11.65 (12.50)	109.50

In the IR spectra of metal complexes, the peak due to ν(NH) did not undergo any shift (3080 cm^{-1}) ruling out the coordination of nitrogen of (NH) with the central metal atom. However, the band due to ν(C=O) experienced a negative shift by 40–50 cm^{-1}, appearing at 1610 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 (N—N) bond have involved in coordination (Table-2).

TABLE-2
IR SPECTRAL DATA (cm^{-1}) OF THE COMPOUNDS

Functional Group	DPODH	Cu[DPODH](OAc)$_2$	Ni[DPODH](OAc)$_2$
ν(CH$_2$)	2280	2280	2280
ν(—NH)	3080	3080	3080
ν(>C=O)	1760	1715	1710
δ(—NH$_2$)	1570	–	–
ν(N—N)	1050	1070	1075
ν(>C=N—)	–	1620	1655
ν(M—O)	–	425	430
ν(M—N)	–	355	345

TABLE-3
ELECTRONIC SPECTRAL DATA (cm^{-1}) OF THE COMPLEXES

Compounds	Transitions (cm^{-1})	
	$^2E_g \longrightarrow {}^2T_{2g}$	L ⟶ M
Cu[DPODH](OAc)$_2$	15,440	29,570
Ni[DPODH](OAc)$_2$	15,370	28,910

Electronic Spectra

Both the Cu(II) and Ni(II) complexes exhibit two broad bands one in the region of 15440–15370 cm^{-1} and another in the range of 29570–28910 cm^{-1}. The former band may be assigned to $^2E_g \rightarrow {}^2T_{2g}$ transitions, suggesting an octahedral geometry of the complexes[16]. The latter band can be attributed to L → M charge transfer spectrum (Table-3).

Antimicrobial Study: Both the ligand fragments and their respective metal chelates have been screened *in vitro* for their antimicrobial activity using serial dilution method against bacterial species *viz., Escherichia coli* (gram negative) and *Staphylococcus aureus* (gram positive) and two fungal strains, *viz., Aspergillus niger* and *Candida albicans*. The results of these activities show that the complexes have been found to possess greater biological effect 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 (× 10^{-4})

S. No.	Compounds	Bactria		Fungi	
		E. coli	*S. aureus*	*A. niger*	*C. albicans*
1.	$Cu(CH_3COO)_2 \cdot 4H_2O$	0.980	0.972	0.980	0.986
2.	$Ni(CH_3COO)_2 \cdot 4H_2O$	0.975	0.975	0.965	0.965
3.	DPODH	5.110	5.100	5.082	5.120
4.	$Cu[DPODH](OAc)_2$	0.228	0.228	0.116	0.116
5.	$Ni[DPODH](OAc)_2$	0.119	0.238	0.234	0.238

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