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Structural Characterization and Biocidal Studies of Some Nickel(II) Macrocyclic Complexes

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Two new macrocyclic complexes with formulae Ni[IDADH]$(BF_4)_2$ amd Ni[TDPDH]$(BF_4)_2$ {wherc [IDADH] = di-phenyl-diacetic acid-N-imino diacetyl dihydrazone and (TDPDH) = diphenyl diacetic acid-N-thio dipropionic acid dihydrazone have been synthesized. These complexes have been screened for their antibacterial and antifungal activities against certain specified microbial strains, *viz.*, bacterial strains *S. auerus* and *E. coli* and fungal strains *A. niger* and *C. albicans*. These complexes have been characterized using molar conductances, magnetic studies, elemental analysis and spectral (IR and electronic) studies. The complexes have been found to have octahedral structures. Both the complexes show greater biological activity than the ligand fragments, the activity effect being more against bacterial species and slightly less against fungal strains.

INTRODUCTION

Lindoy *et al.* have reported[1–4] that crown ethers can form complexes with natural molecules such as CH_3CN, urea and DMSO[5,6]. Recently, it has been published that diaza-18-crown-6 reacted with ethylene chloride to form a new kryptand[7]. The synthesis and characterisation of a series of 14 or 16 membered octaaza 6 : 6 : 6 : 6 annulated macrocyclic complexes[8] have been reported. The $-NH_2$ group in the metal complexes of dihydrazides and dihydrazones[9–11] has been used as an intermediate to prepare macrocyclic and clathrochelate complexes of transition metals by the template reaction with aldehydes and ketones[12,13]. The Ni(II) complexes are found to undergo diffusion control quasi-reversible two step once-reduction process.

Urbach and Busch[14] have reported the synthesis of some Ni(II) complexes with the macrocyclic ligands L^3. They found that the stereochemistry of the metal ion in the complexes based upon $(NiL^3)^{2+}$ varied with the anion. Thus when the anions are Cl^-, Br^- or ClO_4^-, five coordinate species, a square-planar compound has been formed. Hydrazones and their metal complexes have been extensively used in many biological processes[15,16]. Biological screening has been done against two pathogenic bacteria, *i.e.*, *Clapsilla* and *Pseudomonas* and two non-pathogenic bacteria, *i.e.*, *Escherichia coli* and *Staphylococcus aureus* in order

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to explore their vital antimicrobial activities[17, 18]. The complexes have been found to exhibit definite biocidal activities.

EXPERIMENTAL

Chemicals of A.R. grade have been used for synthesizing the compounds. Imino diacetic acid dihydrazide and thiodipropionic acid dihydrazide have been synthesized from their corresponding dimethyl esters of acid and hydrazine hydrate by the reported procedure[19]. The dihydrazides and their complexes have been characterized by single spot analysis and by determination of elemental studies and IR electronic spectral analysis. Cryoscopic method was used for determination of molecular weights of the compounds in DMSO.

The nickel(II) complexes were synthesized by the following general method:

Equimolar amounts of either imino-diacetic acid dihydrazide (0.01 M) or thiodipropionic acid dihydrazide (0.01 M), nickel acetate (0.01 M) and diphenyl diacetic acid (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. The solution was cooled overnight when yellowish-white crystals separated out. The crystals were then washed repeatedly with alcohol and ether and then dried in vacuum over anhydrous calcium chloride in a desiccator.

RESULTS AND DISCUSSION

The coloured solid complexes are stable at room temperature and soluble in DMSO, DMF and propylene glycol but insoluble in common organic solvents. The analytical data are presented in Table-1. The molar conductance values (103.5–105.7 ohm^{-1} cm^2 mol^{-1}) suggest the 1 : 2 electrolytic nature of these complexes.

TABLE-1
ANALYTICAL DATA OF Ni(II) MACROCYCLIC COMPLEXES

Compound (Colour) (m.f.)	m.p. (°C)	% Analysis, found (Calcd)			
		C	H	N	Ni
[IDADH] (White) $[C_4H_{11}N_5O_2]$	245	29.72 (29.81)	6.80 (6.83)	43.43 (43.47)	–
[TDPDH] (White) $[C_6H_{14}O_2N_4S]$	110	34.82 (34.95)	6.73 (6.79)	34.71 (34.78)	–
$Ni[IDADH](BF_4)_2$ (Yellowish-white) $Ni[C_{20}H_{21}N_5O_4](BF_4)_2$	270	38.24 (38.35)	3.28 (3.35)	11.10 (11.18)	9.31 (9.38)
$Ni[TDPDH](BF_4)_2$ (Yellowish sky blue) $Ni[C_{22}H_{24}O_2N_4S](BF_4)_2$	280	39.15 (39.36)	3.48 (3.57)	8.28 (8.34)	8.69 (8.75)

Prominent bands were observed in the infrared spectra of imino diacetic acid dihydrazide and thiodipropionic acid dihydrazides at 3150, 3050, 1110 and 1210 and 1600 cm^{-1} due to ν(NH), ν(NH), ν(C=O), ν(C=O) and δ(NH) respectively. A sharp band was observed at 2900 cm^{-1} (CH_2) in spectrum of IDADH and TDPDH. The (N—N) transitions are observed around 1050 cm^{-1}. The aromatic ring deformation bands also appear at 1150 (out-of-plane) and 1030 cm^{-1} (in-plane) in the spectrum of DPDA (diphenyl diacetic acid) dihydrazide. The positions of ν(N—H) shifted to higher wavenumbers (1080 cm^{-1}) and the nitrogen of (N—N) bond is involved in complexation. The spectra of complexes exhibited certain additional bands. An intense band appeared at 1590 cm^{-1} due to the formation of C=N bond in the complexes. The IR spectra of the metal complexes exhibit some new bands which do not exist in the spectra of ligand fragments. The electronic spectra of around 540–530, 450–440 and 340–325 cm^{-1}, supporting the formation of ν(Ni—N), ν(Ni—O) and ν(Ni—S) bonds respectively[21].

The electronic spectra of both the Ni(II) complexes exhibit two broad bands at 17,950–15,880 and 30,600–28,150 cm^{-1} and 15,960–15,800 and 29,160–28,850 cm^{-1}. The former band may be assigned to $^3E_g - {}^2T_{2g}$ transitions suggesting an octahedral geometry for these complexes. The latter band can be attributed to L—M charge transfer band.

The two Ni(II) macrocyclic complexes were screened *in vitro* for their antimicrobial studies using serial dilution method against two bacteria, *viz.*, *Escherichia coli* (gram-negative) and *Staphylococcus aureus* (gram-positive) and two fungal strains, *viz.*, *Aspergillus niger* and *Candida albicans.*

The test solutions of imino diacetic acid dihydrazide (IDADH) and diphenyl diacetic acid dihydrazide (DPADH) were prepared in propylene glycol and those of their metal complexes in DMSO diluted with culture media to give the required drug concentration in 2.5% DMSO. The ligand fragments IDADH and DPADH exhibited equal biocidal effect against *S. aureus* and *E. coli* and against both the fungal strains being more for DPADH as compared to IDADH. Both the complexes showed greater biological activity than the ligand fragments, the activity effect being more against bacterial species and slightly less against fungal strains (Table-2).

TABLE-2
MIC VALUES OF THE COMPOUNDS IN MOLAR CONCENTRATION (× 10^{-4})

S.No.	Compounds	Bacteria		Fungi	
		E. coli	*S. aureus*	*A. niger*	*C. albicans*
1.	$Ni(CH_3COO)_2{\cdot}4H_2O$	0.886	0.886	0.886	0.886
2.	[IDADH]	6.210	6.210	6.210	6.210
3.	[TDPDH]	6.250	6.250	6.250	6.250
4.	$Ni[IDADH](BF_4)_2$	0.235	0.110	0.110	0.110
5.	$Ni[TDPDH](BF_4)_2$	0.230	0.105	0.105	0.105

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