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Biological Studies of some Ni(II) Macrocyclic Complexes

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Two new macrocyclic complexes of formulae Ni[DCDTADH] $(BF_4)_2$ and Ni[DPDTADH]$(BF_4)_2$ (where (DCDTADH) = 2,6-pyridine-dicarbonyl-dichloride-di-thio-diacetic acid dihydrazone and (DPDTADH) = 2,6-diacetyl pyridine di-thio-diacetic acid dihydrazone have been synthesized and characterized with the help of conductivity measurements, molecular weight determination, elemental studies and IR spectral analysis. The complexes have been found to possess octahedral geometry and have been found to be potentially active against a few bacteria and fungi and exhibit greater biocidal effect as compared to the ligand fragments and isolated metal ion.

INTRODUCTION

The complexes of metal ions with macrocyclic ligands are significant because of their resemblance with many natural systems, such as porphyrins[1] and cobalamines[2]. Many of the transition metal ions in the living systems work as enzymes or carriers in macrocyclic ligand-field environment. These ligands are also of theoretical interest as they are capable of furnishing an environment of controlled geometry and lignd field strength[3–6].

Shankir and coworkers have reported[7, 8] transition metal complexes of polyamide macrocycles prepared through metal ion controlled condensation reactions. A 16-membered tetradentate N_6-macrocyclic ligand and its Ni(II) complexes have been prepared by template method[9]. The Ni(II) fluoro-boro macrocyclic complexes combine apically with exogenous nitrogen bases which possess quite ususual structural and spectroscopic properties[10]. It seems that stabilization of the formal states Ni^0 and Ni^{1+}, in case the reduction is ligand-based anion radical formation, arises on account of a high degree of unsaturation due to in corporation of a pair of electrophilic BF_4 group at the bridge heads coupled with α-diamine groups that favour the dative M—Nπ bonding interactions[11–15].

EXPERIMENTAL

All the chemicals used for synthesis were of AR grade.

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Synthesis of metal complexes: Equimolar amounts of dithio-diacetic acid dihydrazide (0.01 M), Ni(II) acetate (0.01 M) and 2,6-pyridine-di-caronyl-dichloride (0.01 M)/2,6-diacetyl pyridine (0.01 M) were mixed in methanol with continuous stirring. The solution thus obtained was refluxed over a water-bath for 6 h; subsequently it was concentrated to one-third of its original volume. Then a little tetra-fluoroborate was added and the solution was cooled overnight when dark green/brownish-black crystals separated out. The crystals were filtered, washed with alcohol and ether and then dried in vacuum over anhydrous $CaCl_2$ in a desiccator.

RESULTS AND DISCUSSION

All the coloured solid complexes are stable at room temperature. The molar conductance values for the complexes (103.6–110.0 ohm^{-1} cm^2 mol^{-1}) in DMF indicate their electrolytic nature[16]. The analytical data show that these macrocyclic complexes can be represented as $[Ni(C_{11}H_9N_5O_4S_2Cl_2)](BF_4)_2$ and $[Ni(C_{13}H_{15}N_5O_2S_2)](BF_4)_2$ (Table-1).

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

Compound (colour) [m.f.]	m.p. (°C)	% Analysis, found (calcd.)			
		C	H	N	Ni
[DCDTADH] (Yellowish white) $[C_{11}H_9N_5O_4S_2Cl_2]$	210	31.75 (32.27)	2.15 (2.20)	16.90 (17.11)	–
[DPDTADH] (White) $[C_{13}H_{15}N_5O_2S_2]$	220	45.87 (46.29)	4.38 (4.45)	19.95 (20.77)	–
$Ni[DCDTADH](BF_4)_2$ (Dark green) $Ni[C_{11}H_9N_5O_4S_2Cl_2](BF_4)_2$	250	19.92 (20.63)	1.38 (1.40)	10.54 (10.94)	9.10 (9.17)
$Ni[DPDTADH](BF_4)_2$ (Brownish black) $Ni[C_{13}H_{15}N_5O_2S_2](BF_4)_2$	243	26.95 (27.47)	2.54 (2.64)	11.80 (12.33)	10.24 (10.33)

The IR spectra of the macrocyclic ligand fragments show a weak band at *ca.* 3250 cm^{-1} which is associated with the N—H stretching mode observed as in metal free porphyrins[17]. The —CH_2 groups present in the ligand are indicated by the presence of bands at 1375 and 1435–1425 cm^{-1}. All the complexes show a band around *ca.* 1620 cm^{-1} (C=N). At the same time, no band is observed around 1780–1700 cm^{-1} which indicates the coordination of nitrogen of NH_2 groups with the metal. The bands appearing around 450 cm^{-1} in all the complexes indicate ν(Ni—N) vibration which further confirms the coordination of these groups with the metal ions (Table-2).

Both the complexes show bands at 34000–33000 cm^{-1} which may be due to charge transfer transitions. The observed magnetic moment values of the Ni(II) macrocyclic complexes and a weak intensity band at 11900–11200 cm^{-1} region may be assigned to $^5T_{2g} \rightarrow {}^5E_g$ transitions which are consistent with the octahedral geometry around Ni(II) ion.

TABLE-2

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

Functional groups	[DCDTADH]	[DPDTADH]	Ni[DCDTADH]$(BF_4)_2$	Ni[DPDTADH]$(BF_4)_2$
$—CH_2$	2975	2770	2975	2770
—NH	3250	3150	3250	3150
>C=O	1750	1610	1690	1595
$—NH_2$	1780	1800	1730	1760
>C=N	1620	1625	1610	1615
(Ni—N)	–	–	450	448

Both the ligand fragments and their nickel(II) complexes were screened *in vitro* for their antimicrobial activity 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 DCDTADH and DPDTADH were prepared in propylene glycol and those of their metal complexes in DMSO diluted with culture media to give the required drug conentration in 2.5% DMSO. The MIC values of all the compounds are presented in Table-3.

TABLE-3

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

Compounds	Bacteria		Fungi	
	E. coli	*S. aureus*	*A. niger*	*C. albicans*
$Ni(CH_3COO)_2·4H_2O$	0.880	0.880	0.880	0.880
[DCDTADH]	2.785	2.785	2.785	2.785
[DPDTADH]	3.275	4.250	4.250	4.250
Ni[DCDTADH]$(BF_4)_2$	0.729	0.729	0.890	0.890
Ni[DPDTADH]$(BF_4)_2$	0.610	0.725	0.725	0.725

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