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Biocidal and Characterization Studies of Some Newly Synthesized Co(II) Macrocyclic Complexes

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Two new macrocylic complexes of Co(II) possessing the general formulae M[DPADTAH]$(BF_4)_2$ and M[DPTDPH]$(BF_4)_2$ [where M = Co(II) and [DPADTAH] = diphenyl diacetic acid-N, N′-dithio diacetic acid dihydrazone and [DPTDPH] = 2,6-diacetyl dipyridine-N,N′-thio dipropionic acid dihydrazone and $(BF_4)_2$ = tetraflouroborate. The complexes were characterized with conductance values, elemental studies, IR and electronic spectral analyses and have been assigned octahedral geometries. The *in-vitro* antimicrobial studies revealed that the macrocylic complexes are potentially active against bacteria *S. aureus* and *E. coli* and fungi *A. flavus* and *C. albicans*. Both the complexes exhibit greater biocidal effect as compared to the ligand fragments probably due to the greater penetration of the metal ion into cellular system of microbial strains.

Key Words: Macrocyclic complexes, Co(II), Antibacterial and antifungal activities.

INTRODUCTION

The field of macrocylic compounds has made a tremendous progress in the latter half of twentieth century[1–3]. Macrocycles that are saturated or have double bond in only one part of the ring can be made independently by template synthesis[4]. The study of tetraazomacrocyclic complexes catalyzed Belousov-Zhabotinkii (B-Z) oscillating reaction have been reported in literature[5]. The new B-Z oscillating reaction systems are catalysed by transition metal complexes with tetraazamacrocylic ligand[6–9]. Drewes *et al.*[10] studied the various steric factors which control the formation of medium and large size rings and prepared a number of macrocylic di and tetra-ester phthalic and maleic acids using *o*-xylene as one of the moieties.

EXPERIMENTAL

Reagents of AR grade (BDH/E. Merck) were used as supplied. All the solvents were purified by distillation.

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Preparation of the metal complexes

Equimolar quantities of dithiodiacetic acid dihydrazide (TDPDH) (2.10 g, 0.01 M), cobalt acetate (2.53 g, 0.01 M) and diphenyl diacetic acid (2.72 g, 0.01 M) were mixed in 15 mL ethanol with continuous stirring. The solution thus obtained was refluxed over a water bath for *ca.* 8 h. Subsequently, it was concentrated to one-third of its original volume. Then a little of sodium tetraflouroborate was added and the solution was cooled overnight when yellowish-brown crystals, separated out. These crystals were filtered, washed with alcohol and then dried in vacuum over anhydrous $CaCl_2$ in a desiccator.

The other complex was also synthesized by similar procedure, where dark-yellow crystals were obtained.

RESULTS AND DISCUSSION

Both the coloured solid complexes are 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 104.50 ohm^{-1} cm^2 mol^{-1} which indicate their electrolytic nature. Analytical data suggest 1 : 1 : 1 stoichiometry for the complexes. The ligand fragment, *i.e.*, dithio diacetic acid dihydrazide exhibits 1 : 2 stoichiometry. The analytical data of the ligand fragment is shown in Table-1.

IR spectrum of the ligand revealed sharp and prominent bands at 3340 ν_{sym} (NH_2). 1730 ν(C=O) and 1450 cm^{-1} for $\nu_{sym}(NH_2)$. A sharp band was observed at 2850 cm^{-1} $\nu(CH_2)$ in the spectrum of dithio diacetic acid dihydrazide.

The phenyl ring deformation bands were also observed around 960 cm^{-1}. The peak due to ν(NH) (3340 cm^{-1}) did not undergo any shift in the complexes, thus ruling out the coordination of nitrogen of ligand with the central metal atom.

The peak due to ν(C—S) band underwent a lowering. It appeared at 1195 cm^{-1} in the spectra of complexes, indicating the co-ordination of sulphur of C—S with central metal atom, thus supporting the formation of M—N, M—O M—S bands in the complexes [Table-2].

Electronic Spectra

Electronic spectra of Co(II) complexes exhibit broad bands at 24540–16590 cm^{-1} and are observed in the electronic spectra of the Co(II) complexes. The former band may be assigned to $^2F_g \rightarrow {}^2T_{2g}$ transitions suggesting an octahedral geometry of the complexes. The latter band can be attributed to $L \rightarrow M$ (Table-3).

Antimicrobial activity of the compounds

These compounds were assayed for their antimicrobial activities against four test organisms, namely *S. aureus*, *E. coli*, *A. flavus* and *C. albicans*.

Further their MIC values against these organisms were determined by "Serial dilution method" using DMF as a solvent. The results are given in Table-4.

TABLE-1
PHYSICAL, ANALYTICAL, MOLECULAR WEIGHT DATA OF Co(II) COMPLEXES

Compound	m.p. (°C)	Colour	m.w. Found (Calcd.)	% Analysis, Found (Calcd.)				Molar conductivity (ohm^{-1} cm^2 mol^{-1})
				C	H	N	M	
Co(II) [DPADTAH] $(BF_4)_2$	282	Brownish black	544.6 (545.6)	24.03 (24.23)	2.28 (2.38)	12.00 (12.30)	—	—
Co(II) [DPTDPH] $(BF_4)_2$	302	Dark brown	562.9 (564.0)	31.34 (31.66)	3.21 (3.34)	12.21 (12.31)	11.01 11.10	108.20 106.50

TABLE-2
INFRARED ABSORPTION FREQUENCIES (cm^{-1}) OF THIO DIPROPIONIC ACID DIHYDRAZIDE AND ITS METAL COMPLEXES

S. No.	Functional group	TDPDH	[Co(II) DPADTAH]$(BF_4)_2$	[Co(II) DPTDPH]$(BF_4)_2$
1	$-CH_2$	2890	2850	2860
2	—NH	3340	3315	3275
3	>C=O	1730	1680	1675
4	$-NH_2$	1450	—	—
5	N—N	1090	1060	1040
6	>C=N	—	1580	1575
7	>C=S	1195	1130	1090
8	M—O	—	445	430
9	M—N	—	540	515
10	M—S	—	340	330

TABLE-3
ELECTRONIC SPECTRAL TRANSITIONS (cm^{-1}) OF Co(II) MACROCYLIC COMPLEXES

S. No.	Compound	Transitions (cm^{-1})	
1.	Co(II)[DPADTAH]$(BF_4)_2$	12,640	24,450
2.	Co(II)[DPTDPH]$(BF_4)_2$	12,530	24,200

TABLE-4
MIC IN MOLAR CONCENTRATION (x 10^4) OF SYNTHESIZED DIHYDRAZIDE AND THEIR MACROCYCLIC COMPLEXES

S. No.	Compound	Bacteria		Fungi	
		E. Coli	*S. Aureus*	*A. Niger*	*C. Albicans*
1.	TDPDH	6.150	6.155	6.150	6.150
2.	Co(II)[DPADTAH]$(BF_4)_2$	0.226	0.228	0.165	0.275
3.	Co(II)[DPTDPH]$(BF_4)_2$	0.215	0.215	0.105	0.105

Order of dihydrazides and metal complexes:

Against bacteria		Against fungi
$Co[DPADTAH](BF_4)_2$	>	$Co[DPDTAH](BF_4)_2$ >
$Co[DPTDPH](BF_4)_2$	>	TDPDH/$Co[DPDTADH](BF_4)_2$ > TDPDH

REFERENCES

1. A.Z. Werner, *Inorg. Chem.*, **3**, 267 (1983).
2. G. Dayakar and P. Lingaiah, *Indian J. Chem.*, **35A**, 614 (1996).
3. G. Dayakar and P. Lingaiah, *Asian J. Chem.*, **9**, 179 (1997).
4. R. Hoss and F. Vogtle, *Angew. Chem. Int. Engl.*, **33**, 375 (1994).
5. Z.Q. Xu, S.S. Ni and J.D. Xu, *Chin. Chem. Lett.*, **2**, 493 (1991).
6. ———, *Acta Chem. Sinica*, **50**, 1085 (1992).
7. J.M. Song, S.S. Ni and J.D. Xu, *Chin. J. Chem. Phys.*, **7**, 192 (1994).
8. C.C. Wu, L. Zhao, Z.Q. Xu, F.X. Xie and S.S. Ni, *J. Inorg. Chem.*, **12**, 121 (1996),
9. G. Hu, Z.Q. Zu, F.X. Xie, L.Hu and S.S. Ni, *Asian J.Chem.*, **12**, 1031 (2001).
10. S.E. Drewes and P.C. Coleman, *J. Chem. Soc., Perkin Trans.*, **1**, 2184 (1972).

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