

Synthesis and Biocidal Studies of Some Cu(II) Macrocyclic Complexes

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Two new macrocyclic complexes have been synthesized by condensing dithio-dipropionic acid dihydrazone with 2,6-diacetyl pyridine/2,6-pyridine dicarbonyl dichloride in presence of Cu(II) ions. The complexes have the formulae $\text{Cu}[\text{DPDTDPH}](\text{BF}_4)_2$ and $\text{Cu}[\text{DCDTDPH}](\text{BF}_4)_2$ (where $[\text{DPDTDPH}] = 2,6\text{-diacetyl pyridine dithio dipropionic acid dihydrazone}$ and $[\text{DCDTDPH}] = 2,6\text{-pyridine dicarbonyl dichloride-dithio-dipropionic acid dihydrazone}$. The *in vitro* antimicrobial studies revealed that the macrocyclic complexes are potentially active against a few bacteria and fungi and exhibit greater biocidal effect as compared to the ligand fragments. The synthesized complexes have been characterized by elemental studies, conductivity measurements and spectral (IR and electronic) studies.

INTRODUCTION

Metal ions play an important role in biological systems. Synthetic macrocyclic ligands may serve as models for biologically important ligands formed by self-condensation of four molecules of *o*-amino benzaldehyde have been prepared using a variety of organic salts of Cu(II).¹⁻⁴ Earlier work with similar complexes containing inorganic salts of transition metals has been carried out to determine their relative donor strengths with respect to the macrocyclic ligands prepared⁵⁻⁷. A series of fluoro boro bridged Cu(II) macrocyclic complexes have already been reported⁸⁻¹⁰.

An exhaustive survey of literature shows that macrocyclic polyamines, their salts and chelates with transition metal ions are useful chemical sensitizers¹¹ for photographic silver halide emulsions. The crown-ethers are potential ligands¹²⁻¹⁴ for the transport of alkali and alkaline earth metal ions across natural and artificial membranes. It was also used as an extracting agent for different metal ions. These complexes were found to have octahedral geometry and exhibited antimicrobial activity against bacterial and fungal species¹⁵.

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EXPERIMENTAL

All the chemicals used were of AR grade. Dithio-dipropionic acid dihydrazone and 2,6-diacetyl pyridine/2,6-dipyridine dicarbonyl dichloride were synthesized from their corresponding dimethyl esters of the acids and hydrazine hydrate by the reported procedure¹⁵.

Synthesis of metal complexes

Equimolar amounts of dithio-dipropionic acid dihydrazide (0.01 M), copper acetate (0.01 M) and 2,6-diacetyl pyridine/2,6-pyridine dicarbonyl dichloride (0.01 M) were mixed in ethanol with continuous stirring. The solution thus obtained was refluxed over a water-bath for *ca.* 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 crystals separated out. The crystals were filtered, washed with alcohol, ether and then dried in vacuum over anhydrous CaCl₂ in a desiccator.

RESULTS AND DISCUSSION

All the complexes are coloured solids and stable at room temperature. The analytical data of the complexes suggest that the general composition of the complexes is [Cu[DPDTPH](BF₄)₂] and [Cu[DCDTPH](BF₄)₂]. The complexes are insoluble in water and in common organic solvents. The molar conductance values (104.6–105.8 ohm⁻¹ cm⁻¹ mol⁻¹) reveal the electrolytic nature of the complexes.

The analytical data of the ligands and their copper(II) complexes are presented in Table-1.

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

Compound (m.f.)	Colour	m.p. (°C)	% Analysis, Found (Calcd:)			
			C	H	N	Cu
[DPDTPH] [C ₁₅ H ₁₉ N ₅ O ₂ S ₂]	Yellowish white	109	48.10 (49.30)	5.08 (5.20)	18.90 (19.17)	—
[DCDTPH] [C ₁₃ H ₁₃ N ₅ O ₂ S ₂ Cl ₂]	White	110	37.00 (38.40)	3.13 (3.20)	16.92 (17.24)	—
Cu[DPDTPH](BF ₄) ₂ Cu[C ₁₅ H ₁₉ N ₅ O ₂ S ₂](BF ₄) ₂	Black	177	29.14 (30.34)	3.14 (3.20)	11.51 (11.81)	10.31 (10.71)
Cu[DPDTPH](BF ₄) ₂ Cu[C ₁₃ H ₁₃ N ₅ O ₂ S ₂ Cl ₂](BF ₄) ₂	Blue	183	24.18 (24.62)	1.97 (2.05)	9.95 (10.04)	9.90 (10.02)

The IR spectra of dithio-dipropionic acid dihydrazone show sharp and prominent bands at 3050, 1680 and 1500 cm⁻¹ due to the presence of $\nu(\text{NH})$, $\nu(\text{C}=\text{O})$ and $\nu(\text{NH}_2)$ groups respectively. $\nu(\text{N}-\text{N})$ transitions were observed around 1020 cm⁻¹ (Table-2).

TABLE-2
IR SPECTRAL DATA (cm⁻¹) OF THE COMPOUNDS

Functional group	DPDTPH	DCDTPH	Cu[DPDTPH](BF ₄) ₂	Cu[DCDTPH](BF ₄) ₂
CH ₂	2770	2770	2770	2770
—NH	3010	3010	3010	3010
>C=O	1690	1980	1580	1580
—NH ₂	1610	1610	—	—
N—N	1150	1150	1175	1175
>C=N	—	—	1550	1550
v(M—O)	—	—	550	560
v(M—N)	—	—	475	475
v(M—S)	—	—	300	305

In the IR spectra of the metal complexes, the peak due to v(NH) did not show any shift (3050 cm⁻¹), ruling out the coordination of nitrogen of (NH) with the central metal atom.

The peak due to v(C—S) bond underwent a lowering. It appeared at 1090 cm⁻¹ in the spectra of complexes indicating the coordination of sulphur of (C—S) with central metal atom thus supporting the formation of (M—N) and (M—O) bond in the complexes. The third band appearing around 300 cm⁻¹ confirmed the presence of (M—S) bond in the complexes.

The broad bands at 17,500–15,600 and 29,600–27,150 cm⁻¹ are observed in the electronic spectra of the Cu(II) complexes. The former may be assigned to ²E_g → ²T_{2g} transition, suggesting thereby an octahedral geometry for these complexes¹⁶ and the latter can be attributed to L–M charge transfer band (Table-3).

TABLE-3
ELECTRONIC SPECTRAL DATA (cm⁻¹) OF THE COMPLEXES

Compounds	Transitions (cm ⁻¹)	
	³ E _g → ² T _{2g}	L–M
Cu[DPDTPH](BF ₄) ₂	15,600	29,600
Cu[DCDTPH](BF ₄) ₂	17,500	27,150

Antibacterial activity is carried out against gram +ve bacterium, e.g., *S. aureus* and gram -ve bacterial strain *E. Coli* along with fungi *A. niger* and *C. albicans*.

The biological activity shows that antimicrobial activity of ligand enhances several folds on complexation. This increase in the antimicrobial activity is probably either due to faster diffusion of metal complexes as a whole through the cell membrane or due to the combined activity effect of the metal and ligand¹⁷.

The MIC values of 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	
		<i>E. Coli</i>	<i>S. Aureus</i>	<i>A. Niger</i>	<i>C. Albicans</i>
1.	Cu((CH ₃ COO) ₂ · 4H ₂ O	0.880	0.878	0.880	0.886
2.	[DPDTPH]	4.110	4.100	4.082	4.120
3.	[DCDTPH]	4.100	4.080	4.072	4.110
4.	Cu[DPDTPH](BF ₄) ₂	0.220	0.220	0.110	0.110
5.	Cu[DCDTPH](BF ₄) ₂	0.112	0.232	0.230	0.232

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