

Synthetic, Spectral and Antibacterial Studies on Complexes of Co(II), Ni(II) and Cu(II) with 2,2'-Imino Bis-4,4'-Diphenylthiazole

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A series of complexes of the type ML_2X_2 where $M = \text{Co(II)}$, Ni(II) and Cu(II) , $L = 2,2'$ -iminobis-4,4'-diphenyl thiazole and $X = \text{Cl}^-$, Br^- , NO_3^- and ClO_4^- , have been synthesized and characterized on the basis of elemental analysis, molecular weight measurements, molar conductance, room temperature, magnetic moment, infrared and electronic spectral data. Elemental analysis confirms the stereochemistry of the complexes. The complexes are monomeric and nonelectrolytic in nature. Magnetic moment values indicate paramagnetic nature of the complexes. IR spectra reveal the coordination of the ligands and anions. The electronic spectral data suggest octahedral geometry for the complexes. The complexes show feeble to moderate antibacterial and antifungal activities.

INTRODUCTION

It is reported that 2,2'-iminobisthiazole nucleus plays a vital role in physiological activity of a number of antibiotics^{1,2}. Further it is also known that compounds having sulphur or nitrogen donor atom can enhance the antibacterial activities. Keeping in view the above facts, present investigations were undertaken to synthesize and characterise the complexes of Co(II), Ni(II) and Cu(II) with 2,2'-iminobis-4,4'-diphenylthiazole (IBPT) to establish their structures. The complexes were screened for the antimicrobial activities.

EXPERIMENTAL

All the chemicals used were of AnalaR grade. Elemental analysis for C, H, N, S were carried out by CE-440 elemental analyser. Metals were estimated by standard methods. Molecular weights were determined by Rast's camphor method. Room temperature magnetic susceptibility was determined by using Guoy's balance and diamagnetic corrections were made using Pascal's constants. Molar conductance values were determined by CL-301 Systronics conductivity bridge.

The ligand was prepared by the procedure reported below. A mixture of N'-(4-phenylthiazole-2-yl) thiourea (2.34 g, 0.01 mol) and phenacyl bromide

(1.98 g, 0.01 mol) in ethanol were refluxed for 0.5 h. It was cooled and neutralised with ammonium hydroxide solution. The resulting solid was washed and crystallised from ethanol : acetone (2 : 1) mixture to obtain pale yellow crystals (m.p. 224°C).

Preparation of the metal complexes

Metal salts were dissolved in ethanol and the ligand in dry acetone and were mixed in 1 : 2 molar ratio and refluxed for 2–3 h in perfectly dry condition. Coloured complexes were separated on standing. The separated complexes were filtered, washed with alcohol and acetone mixture, then with petroleum ether and dried over fused calcium chloride under *vacuo*.

RESULTS AND DISCUSSION

The complexes were insoluble in water but readily soluble in organic solvents like DMF and dioxane. The elemental analysis (Table-1) indicates 1 : 2 metal : ligand stoichiometry for all the complexes. The low molar conductance values of all the complexes ($60\text{--}100 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$) (10^{-3}M solution in DMF) indicate their nonelectrolytic nature. Cu(II) complexes are stable up to 300°C. Decomposition occurs above this temperature. The molecular weight (Rast's camphor method) values of the complexes indicate monomeric nature.

The broad and strong band in the region $3400\text{--}3060 \text{cm}^{-1}$ represents a series of overlapping stretching vibrations corresponding to NH groups³. The C—H stretching vibration of aromatic ring seems to have been enveloped by NH stretching vibrations. The other bands observed in the spectra of the ligands are at *ca.* 1610, 1585, 1510 and 1430cm^{-1} . These bands arise due to $\nu(\text{NH})$, cyclic $\nu(\text{C}=\text{N})$, $\nu(\text{C}-\text{N})$ vibrations and $\nu(\text{C}-\text{S})$ vibrations^{4,5}. The other bands observed are at *ca.* 1320, 1270, 1135 and 1050cm^{-1} which may be due to out of plane CH bending of the substituted aromatic ring. The above data clearly established the structure of the ligand which is given in Fig. 1.

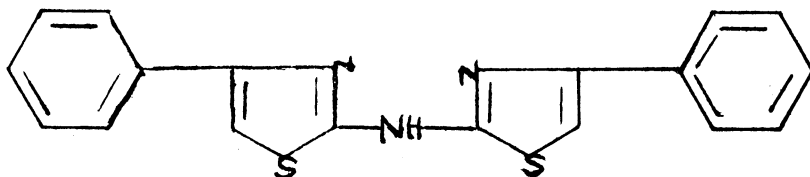


Fig. 1.

In the spectra of the metal complexes the twin bands at *ca.* 1585 and *ca.* 1510cm^{-1} disappeared and a new sharp band appeared at *ca.* 1700cm^{-1} indicating metal-ligand interaction⁶. The band at *ca.* 840cm^{-1} due to $\nu(\text{C}-\text{S})$ of thiazole ring is shifted to lower frequency by $40\text{--}50 \text{cm}^{-1}$ indicating that sulphur atom of

thiazole is involved in the bonding. The new bands appearing at *ca.* 470–430 cm^{-1} and 420–340 cm^{-1} of the complexes were assigned to $\nu(\text{M—N})^7$ and $\nu(\text{M—S})^8$ respectively. Bands at *ca.* 1500, 1300 and 930 cm^{-1} and bands at *ca.* 1260, 1130 and 1000 cm^{-1} suggest the presence of coordinated NO_3^- group⁹ and ClO_4^- group.¹⁰

The magnetic moment values of Co(II), Ni(II) and Cu(II) complexes indicate^{11,12} the presence of three, two and one unpaired electrons respectively (Table-1).

The electronic spectra of Co(II) complexes show bands at 8950–9760 cm^{-1} , 18000 cm^{-1} and 20800–21590 cm^{-1} assignable to ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})(\nu_1)$, ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})(\nu_2)$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ respectively. These transitions suggest an octahedral geometry around the metal ion^{13,14}. Dq, B, β , β_0 , ν_2/ν_1 values have been found to be 905–824, 796.7–687.3, 0.82–0.71, 18–29 and 2–1.8 respectively, which agree with the values for octahedral Co(II) complexes¹¹. The electronic spectra of Ni(II) complexes show bands at 9810–10010 cm^{-1} , 16750–17100 cm^{-1} and 26120–26980 cm^{-1} which are assigned to ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})(\nu_1)$, ${}^3\text{T}_{1g}(\text{F})(\nu_2) \rightarrow {}^3\text{T}_{1g}(\text{P})(\nu_3)$ transitions¹⁴ respectively. Dq, B, β , β_0 , ν_2/ν_1 values have been found to be 1001–981, 878–809, 0.832–0.767, 16.7–23.29, 1.67–1.71 respectively which agree with the values of octahedral Ni(II) complexes¹⁵.

The electronic spectra of Cu(II) complexes show broad band at *ca.* 18800–14700 cm^{-1} and 27000 cm^{-1} assignable to ${}^2\text{E}_g \rightarrow {}^2\text{T}_{1g}$ and CT bands respectively¹⁶ suggesting an octahedral geometry around the metal ion.

Antimicrobial activities: The complexes were screened for their antimicrobial and antifungal activity using cup-plate method¹⁷. The testing were carried out at a concentration of 100 mg using gram positive (*staphylococcus aureus*, *S. citris*) and gram negative (*Escherichia coli*, *Salmonella byphosa*) bacteria. The antifungal testing was carried out against *Aspergillus niger* and *Neurospora cressa*. It was observed that some of the compounds exhibited feeble to moderate activity. The chloro-perchlorato complexes are very active as compared to other complexes.

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TABLE-1
ANALYTICAL AND PHYSICAL DATA OF METAL COMPLEXES

Compound (colour)	μ_{eff} (B.M.)	Analysis %, found (calcd.)				
		M	C	H	N	S
IBPT (Pale yellow)	—	—	64.3 (64.5)	3.8 (3.9)	12.1 (12.5)	18.9 (19.1)
Co(IBPT) ₂ Cl ₂ (Orange)	4.19	7.3 (7.4)	53.5 (54.0)	3.1 (3.3)	10.1 (10.5)	15.6 (16.0)
Cu(IBPT) ₂ Br ₂ (Light yellow)	4.21	6.2 (6.6)	48.2 (48.6)	2.8 (2.9)	9.4 (9.5)	14.1 (14.4)
Co(IBPT) ₂ (NO ₃) ₂ (Pale brown)	4.23	6.5 (6.9)	50.1 (50.6)	2.9 (3.1)	12.8 (13.1)	14.7 (15.0)
Co(IBPT) ₂ (ClO ₄) ₂ (Brown)	4.18	6.1 (6.3)	46.3 (46.6)	2.7 (2.8)	9.0 (9.1)	13.4 (13.8)
Ni(IBPT) ₂ Cl ₂ (Golden yellow)	3.12	7.1 (7.3)	53.8 (54.0)	3.1 (3.3)	10.2 (10.5)	15.6 (16.0)
Ni(IBPT) ₂ Br ₂ (Brown)	2.83	6.4 (6.6)	48.2 (48.6)	2.6 (2.9)	9.3 (9.5)	14.0 (14.4)
Ni(IBPT) ₂ (NO ₃) ₂ (Violet)	2.96	6.1 (6.9)	50.3 (50.6)	2.9 (3.1)	12.8 (13.1)	14.8 (15.0)
Ni(IBPT) ₂ (ClO ₄) ₂ (Pale violet)	3.10	6.0 (6.3)	46.2 (46.6)	2.7 (2.8)	8.8 (9.1)	13.5 (13.8)
Cu(IBPT) ₂ Cl ₂ (Blackish red)	1.83	7.6 (7.9)	53.4 (53.7)	3.0 (3.2)	10.0 (10.4)	15.6 (15.9)
Cu(IBPT) ₂ Br ₂ (Yellow)	1.85	6.9 (7.1)	48.1 (48.4)	2.7 (2.9)	9.2 (9.4)	13.9 (14.3)
Cu(IBPT) ₂ (NO ₃) ₂ (Leaf green)	1.86	7.1 (7.4)	50.2 (50.4)	2.8 (3.0)	12.7 (13.1)	14.6 (14.9)
Cu(IBPT) ₂ (ClO ₄) ₂ (Brick red)	1.89	6.5 (6.8)	46.0 (46.3)	2.5 (2.8)	8.7 (9.1)	13.2 (13.7)

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