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Synthetic, Structural and Antimicrobial Studies of Some Transition Metals Heterocyclic Complexes of Bio-inorganic Relevance

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1 : 1 : 1, M(II)-dipy-multidentate ligand, mixed ligand complexes were synthesised and characterized by elemental analysis, IR and UV spectral studies, magnetic and conductivity measurements [where, M=Co(II), Ni(II) and Cu(II); dipy=4,4′-dipyridyl and multidentate ligand=2-mercaptobenzoic acid (MBA) and 3,5-dinitrosalicylic acid (DNSA)]. The compounds have been screened for their antimicrobial activity on gram +ve bacteria (*Staphylococcus aureus*) and gram −ve bacteria (*Escherichia coli*) at 32°C for 48 hrs and fungi (*Aspergillus niger* and *fumigatus*) by serial dilution method at 32°C for 7 days.

INTRODUCTION

In the recent years immense interest has developed in metal complexes with ligands containing a carboxylic group and a neutral base[1,2] due to the great chelating ability of the biologically active neutral bases. In the light of our earlier observations[3,4], we have extended work on the synthesis and characterization of heterocyclic complexes of Co(II), Ni(II) and Cu(II) with 4,4′-dipyridyl and some powerful chelating agents such as: 2-mercaptobenzoic acid (MBA) and 3,5-dinitrosalicylic acid (DNSA). In order to evaluate the microbiological significance, their antifungal and antibacterial activity has also been carried out.

EXPERIMENTAL

The metal complexes were synthesized by the method of Musumece *et al.*[5] Equimolar alcoholic solutions (2×10^{-3}M) of the two ligands were mixed together with vigorous stirring. To the mixture an alcoholic solution of metal acetate (2×10^{-3} M) was added slowly. The pH of the mixture was adjusted 5–6 and the product was heated over water-bath to crystalline. The precipitate was filtered, washed with ether. Compounds were dried over P_4O_{10} under reduced pressure. The complexes were analysed for C–, H– and N– by microanalytical techniques. Sulphur content was determined by standard method[6]. Toxicity of the complexes was examined in propylene glycol by serial dilution method. Screening of metal chelates

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was carried out at 500 ppm concentration. The complexes found potentially active at this concentration were studied at different lower concentrations to find out their minimum inhibitory concentrations (MIC) values.

RESULTS AND DISCUSSION

Study of magnetic data is quite informative in characterizing the geometry of the complexes. The μ_{eff} values (Table 1) of paramagnetic Co(II) complexes are clearly indicating their tetrahedral stereochemistry around the metal ion. In Ni(II) complexes the small paramagnetism may be due to their tendency towards polymerisation in solid state leading to weak coordination in axial direction resulting in the formation of spin paired square planar distortion. Lower values of magnetic moment in Cu(II) complexes are close to spin only magnetic moment indicating their paramagnetic nature and square planar geometry.

TABLE 1

PHYSICAL AND MAGNETIC DATA OF METAL COMPLEXES

Compound	Molecular formula	Colour	Decomp. Temp. (°C)	Molar Cond. $(\Omega^{-1}\ cm^2\ mol^{-})$	μ_{eff} (BM)
Co(dipy) MBA	$Co(C_{17}H_{12}O_2N_2S)$	Light pink	280	16.22	4.15
Co(dipy) DNSA	$Co(C_{17}H_{10}O_7N_4)$	Dark yellow	215	5.06	4.93
Ni(dipy) MBA	$Ni(C_{17}H_{12}O_2N_2S)$	Grey	242	2.91	0.99
Ni(dipy) DNSA	$Ni(C_{17}H_{10}O_7N_4)$	Parrot green	255	16.30	1.09
Cu(dipy) MBA	$Cu(C_{17}H_{12}O_2N_2S)$	Grey	342	18.90	1.78
Cu(dlpy) DNSA	$Cu(C_{17}H_{10}O_7N_4)$	Green	272	19.95	1.79

IR and electronic spectral data of the metal complexes are listed in Table 2. -OH (Phenolic) stretching and bending vibrations of free DNSA ligand have disappeared in the IR spectra of respective dipy-metal complexes, which conclude that the coordination of the ligand to metal ion has taken place through the deprotonation of phenolic group. Both ν_{asym} (CO) and ν_{sym} (CO) frequencies are lowered by 20–60 cm^{-1} in the spectra of all the related metal complexes. These facts indicate that in metal complexes coordination of acid ligands to the metal ions has taken place through carboxylic group. Negative shifting of $\nu(C{=}N)$ vibration (py) by 20–50 cm^{-1} in related complexes indicates the involvement of pyridine/nitrogen in coordination. ν(C–S) vibration of free MBA ligand at 570 cm^{-1} has shifted towards lower frequency region by 10–20 cm^{-1} in related metal complexes. This shifting of frequency is indicative of the involvement of S in the complexation. The presence of M–O, M–N and

TABLE 2

SPECTRAL DATA AND LIGAND FIELD PARAMETERS OF METAL COMPLEXES

Compound	IR Frequencies (cm^{-1})			Electronic Spectral Data and Ligand Field Parameters						
	ν(C=N)	ν(C=O)	ν(C–S)	Observed band position (cm^{-1})	10 Dq (cm^{-1})	Racah parameter (B)	Naphelauxetic ratio (β)	% covalent character (β%)	LFSE	ν_2/ν_1
Co(dipy) MBA	1615(sb) 1395(s)	1560(m)	550(wb)	6080 14456 17120	8376	889.06	0.7938	25.97	28.71	2.37
Co(dipy) DNSA	1610(s) 1350(s)	1540(mb)	—	6120 14560 17080	8440	885.33	0.7904	26.51	28.93	2.38
Ni(dipy) MBA	1620(s) 1390(s)	1550(s)	555(m)	18200 29520 34660	18200	638.66	0.5913	69.11	—	1.62
Ni(dipy) DNSA	1620(s) 1360(m)	1540(m)	—	18130 28790 35100	18130	633.33	0.5864	70.53	—	1.58
Cu(dipy) MBA	1630(s) 1400(s)	1580(m)	560(wb)	16970	8485	—	—	—	—	—
Cu(dipy) DNSA	1625(sb) 1355(s)	1550(s)	—	17440	8720	—	—	—	—	—

M–S bonds in dipy-metal complexes are evident from the ν(M–O), ν(M–N) and ν(M–S) bands appearing in the regions 350–510 cm^{-1}, 315–460 cm^{-1} and 300–345 cm^{-1} respectively[7].

Cobalt(II) complexes indicate three electronic spectral bands in the region 6080–17120 cm^{-1} and are assigned to have tetrahedral geometry. The bands may be attributed to $^4A_{2g} \rightarrow {}^4T_{2g}$ (ν_1), $^4A_{2g} \rightarrow {}^4T_{1g}$ (ν_2) and $^4A_{2g} \rightarrow {}^4T_{1g}$ (P) (ν_3) transitions respectively. The ratio ν_2/ν_1 and the values of Dq, B and β are in good agreement with the values reported for tetrahedral complexes of Co(II). Ni(II) complexes show three electronic spectral bands corresponding to $^1A_{1g} \rightarrow {}^1E_u$ (ν_1), $^1A_{1g} \rightarrow {}^1A_{2u}$ (ν_2) and $^1A_{1g} \rightarrow {}^1B_{1u}$ (ν_3) transitions which coincides well with the square planar stereochemistry of these complexes. In Cu(dipy)MBA and Cu(dipy)DNSA a broad electronic spectral band falls at 16970 cm^{-1} and 17440 cm^{-1} respectively corresponding to $^2B_{1g} \rightarrow {}^2A_{1g}$ transition, reported for the complexes with the square planar CuO_2N_2 chromophore[8]. The calculated Dq values also substantiate their square planar configuration around the Cu(II) ion.

Antimicrobial screening data reveal that the activity of metal chelates except Cu(dipy) MBA and Cu(dipy) DNSA has increased considerably as compared to free ligands against the test pathogens. The increase in toxicity in these complexes may be attributed to the combined bioactive effect of metal and both the ligands present in a complex and trace elements present in bacteria and fungi species[9] due to breaking the peptide linkage, due to their more liposoluble nature on being coordinated with the metal ion forming a stable metal chelate. Non-toxic nature of Cu(dipy) MBA and poor activity of Co(dipy) MBA against *A. niger* may be due to the fact that the geometry and charge distribution around the molecule are incompatible with the geometry and charge distribution around the peripheries of the pores of the fungal and bacterial cell wall by the toxic agent cannot take place and toxic reactions with the spores do not occur[10]. Inactivity of Cu(dipy) DNSA against all the test bacteria and fungi species may be attributed to their involvement with NO_2^- as nutrient. From the order of MIC values, it is obvious that the three metal chelates differ in their toxic action. Ni(II) complexes are more toxic than Co(II) and Cu(II) complexes while Cu(II) complexes do not show any significant effect (MIC=>500). In general the order of toxicity is Ni > Co > Cu.

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