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Studies on Cobalt(II) Complexes of 2,9-Dimethyl-1,10-phenanthroline with Ligands Containing O-, N- and S- Donor-Atoms

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Co^{2+}-phen-multidentate ligand, mixed ligand complexes have been isolated in pure state and characterized by elemental, magnetic conductance UV and IR spectral data [where phen = 2,9-dimethyl-1,10-phenanthroline and multidentate ligand = 2-mercaptobenzoic acid (MBA), dithiodipropionic acid (DTPA), 3-5-dinitrosalicylic acid (DNSA) or 3,5-dibromosalicylic acid (DBSA). Complexes have been screened for antibacterial and antifungal activity. The compounds found potentially active at 500 ppm were studied at lower concentrations to find out their minimum inhibitory concentration (MIC) values.

INTRODUCTION

Effective complexing ability and biological activity is found in metal chelates of N-containing ligands[1–2], like 1,10-phenanthroline. However, no attempt has been made to study the antimicrobial activity of 2,9-dimethyl-1,10-phenanthroline metal(II) complexes. In an attempt to explore this possibility and to obtain compounds of enhanced antifungal and antibacterial properties, we report here in the Co(II) complexes of 2,9-dimethyl-1,10-phenanthroline with some powerful chelating agents.

EXPERIMENTAL

All the reagents used were either of AnalaR or G.R. (E. Merck) grade. The complexes were synthesized by the method of Musumece *et al.*[3] Equimolar (1 : 1) alcoholic/acetonic solutions (2×10^{-3} M) of the two ligands were mixed together with vigorous stirring. To the mixture an alcoholic solution of cobalt acetate (2×10^{-3}M) was added slowly and with constant stirring. The pH of the solution was adjusted 5–6 and the product was heated over water bath. The resulting coloured precipitate was filtered, thoroughly washed with a mixture of acetone and water (80 : 20) and finally with ether. The complexes were dried over P_4O_{10} under reduced pressure. The complexes were analysed for C, H and N by micro-analytical techniques. Sulphur content was determined by standard method[4].

Antimicrobial activity of the complexes was examined by serial dilution

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method in propylene glycol. Toxicity was determined by measuring bacterial growth after two days and fungal growth after seven days of incubation at 32°C. The complexes found potentially active at 500 ppm were studied at 400 ppm, 300 ppm, 200 ppm, and 100 ppm concentrations to find out their minimum inhibitory concentration (MIC) values.

RESULTS AND DISCUSSION

Analyses and conductance data indicate that the complexes have the composition $Co(A)(B)\cdot nH_2O$ (where A = phen, B = MBA, DTPA, DNSA or DBSA and n = 0 or 2). The μ_{eff} values (Table 1) of the complexes are 4.02–5.13 BM, corresponding to three unpaired electrons[5,6], indicate their spin free octahedral environment around the metal ion. Higher values than the calculated spin only value (3.87 BM) are attributed to an orbital contribution to the paramagnetism. These proposed structures are further substantiated by spectral studies.

IR and electronic spectral data of the complexes are listed in Table 2. Presence of a moderate IR band at 3490 cm^{-1} and 3240 cm^{-1} and a band at 1370 cm^{-1} and 1380 cm^{-1} in DNSA and DBSA ligands respectively are due to phenolic and bending vibrations respectively. These bands have disappeared in the spectra of their respective phen-metal complexes. It concludes that the coordination of the ligand to the metal ion has taken place through deprotonation of phenolic group forming M–O–C–bond[7]. Remarkable shifting in $\nu_{asym}(CO)$ and $\nu_{sym}(CO)$ frequencies towards lower region as compared to respective free acid ligands is observed in all the Co(II) complexes, which suggest the coordination of ligands to metal ion through carboxylic group. Pronounced shifting of $\nu(C{=}N)$ frequency by 30–85 cm^{-1} towards lower region in Co(II) complexes as compared to free ligands suggests the involvement of pyridine-nitrogen in coordination. Lowering of $\nu(C{-}S)$ vibration by 5–30 cm^{-1} in related Co(II) complexes is a strong evidence for the involvement of S in the complexation. Shifting of $\nu(S{-}S)$ vibration by *ca.* 25 cm^{-1} in the DTPA-metal complexes as compared to free DTPA is indicative of the presence of M–S band in these complexes which is further confirmed by the appearance of new $\nu(M{-}S)$ vibration in for IR region. The coordination of metal ion through the O and N-donors of free ligand is also confirmed by the appearance of some new bands in the region 400–480 cm^{-1} and 310–405 cm^{-1}, which are assigned to $\nu(M{-}O)$ and $\nu(M{-}N)$ vibrations respectively in all the complexes[8].

In the complexes three electronic spectral bands fall in the region 8244–8560 cm^{-1}, 14870–15896 cm^{-1} and 19350–19880 cm^{-1} corresponding to $^4T_{1g}\rightarrow{}^4T_{2g}[\nu_1]$, $^4T_{1g}\rightarrow{}^4A_{2g}$ $[\nu_2]$ and $^4T_{1g}\rightarrow{}^4T_{1g}(P)$ $[\nu_3]$ transitions respectively. The values of ν_2/ν_1 (1.73–1.92) indicate their octahedral configuration. Lower values of ν_2/ν_1 in Co(phen) MBA and Co(phen) DBSA may be due to the distortion in their geometries. The calculated Dq, B, β and

TABLE 1
PHYSICAL AND MAGNETIC DATA OF Co(II) COMPLEXES

Compound	Molecular formula	Color	Decomposition temp. (°C)	Molar conductance (Ω^{-1} cm^2 mol^{-1})	μ_{eff} (BM)
Co(phen) MBA.2H_2O	$Co(C_{21}H_{20}O_4N_2S)$	Dark yellow	300	7.40	4.02
Co(phen)DTPA	$Co(C_{20}H_{20}O_4N_2S_2)$	Green	220	14.50	5.06
Co(phen)DNSA.2H_2O	$Co(C_{21}H_{18}O_9N_4)$	Orange	260	36.50	5.13
Co(phen)DBSA.2H_2O	$Co(C_{21}H_{18}O_5N_2Br_2)$	Light pink	210	34.40	4.82

TABLE 2
SPECTRAL DATA AND LIGAND FIELD PARAMETERS OF Co(II) COMPLEXES

Compound	IR Frequencies (cm^{-1})			Electronic Spectral Data and Ligand Field Parameters					
	ν(C=O)	ν(C=N)	ν(C–S)	Observed band position (cm^{-1})	10 Dq (cm^{-1})	Racah parameter (B)	% Covalent character (β%)	LFSE	ν_2/ν_1
Co(phen) MBA	1580(s) 1490(m)	1525(m)	565(m)	8560 14870 19672	6310	590.80	89·57	10.81	1.73
Co(phen) DTPA	1625(s) 1420(m)	1515(m)	630(s)	8470 15336 19540	6866	631.07	77.49	11.77	1.81
Co(phen) DNSA	1600(s) 1544(m)	1540(s)	—	8244 15896 19350	7652	700.93	59.79	13.11	1.92
Co(phen) DBSA	1585(s) 1385(s, br)	1550(s)	—	8425 15775 19880	7350	692.00	61.86	12.60	1.74

LFSE values of the complexes are within the range of the values reported for octahedral Co(II) complexes.

The biocidal activity of the metal chelates is considerably higher as compared to that of the metal ions and ligands[9,10]. The inhibition of fungal and bacterial growth rate increases gradually with the increase of ligands concentration in the complexes.[11] Antimicrobial screening data reveal that the activity of the complexes has increased considerably as compared to free ligands against the test pathogens. The increase in toxicity 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[12] due to breaking the peptide linkage, due to their more liposoluble nature on being coordinated with the metal ion forming a stable metal chelate. Inactivity of Co(phen) DBSA 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 or bacterial cell wall, due to which penetration through the wall by the toxic agent cannot take place and toxic reactions within the spore do not occur. The poor activity or non-toxic nature of DNSA complex of Co(II) against *Aspergillus fumigatus* may be attributed to the involvement with NO_2^- as nutrient.

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