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Spectrochimica Acta Part A 69 (2008) 816–821
SPECTROCHIMICA ACTA PART A
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Spectroscopic and biological approach of Ni(II) and Cu(II) complexes of 2-pyridinecarboxaldehyde thiosemicarbazone

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Received 19 February 2007; received in revised form 23 April 2007; accepted 7 May 2007

Abstract

Ni(II) and Cu(II) complexes having the general composition $[M(L)_2X_2]$ [where L = 2-pyridinecarboxaldehyde thiosemicarbazone, M = Ni(II) and Cu(II), X = Cl^-, NO_3^- and 1/2 SO_4^{2-}] have been synthesized. All the metal complexes were characterized by elemental analysis, molar conductance, magnetic moment, mass, IR, EPR and electronic spectral studies. The magnetic moment measurements of the complexes indicate that all the complexes are of high-spin type. On the basis of spectral studies an octahedral geometry has been assigned for Ni(II) complexes whereas tetragonal geometry for Cu(II) except $[Cu(L)_2SO_4]$ which posseses five coordinated geometry. The ligand and its metal complexes were screened against phytopathogenic fungi and bacteria in vitro.
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Keywords: Thiosemicarbazone; Nickel(II); Copper(II); Biological activities

1. Introduction

Thiosemicarbazones and their metal complexes have considerable interest because of their biological activities, such as antitumour [1,2], antiviral [3,4], anticancer [5,6], antifungal [7,8], antibacterial [9,10] and antimalarial [11,12]. The beneficial biological activities of heterocyclic thiosemicarbazones in mammalian cells is thought to be due to their ability to inhibit a key enzyme, ribonucleotide diphosphate reductase (RDR), which catalyzes the synthesis of DNA precursors [13]. Nickel is the most toxic metal, which shows the toxicity even in low doses to both plants and animals [14]. It is found that nickel transport involves ATP dependent Mg(II) transport system and toxicity of nickel can be prevented by increasing the concentration of Mg(II) relative to nickel. Copper plays a vital role in the development and performance of the human nervous and cardiovascular systemsas well as the skin, bone, immune and reproductive systems including gene transcription [15,16].

In view of the above applications, in this paper, we report the synthesis, spectral characterization and antimicrobial screening of 2-pyridinecarboxaldehyde thiosemicarbazone(L) and its Ni(II) and Cu(II) complexes. The structure of ligand and scheme for synthesis is shown in Fig. 1.

2. Experimental

All the chemicals used were of AnalaR grade and procured from Sigma–Adlrich and Fluka. Metal salts were purchased from E. Merck and were used as received.

2.1. Synthesis of ligand

Hot ethanolic solution of thiosemicarbazide (4.55 g, 0.05 mol) and 2-pyridinecarboxaldehyde (4.75 mL, 0.05 mol) were mixed slowly with constant stirring. This mixture was refluxed at 70–80 °C for 2 h. On cooling a cream coloured compound is precipitated out. It was filtered washed with cold EtOH and dried under vaccum over P_4O_{10}. Yield, 68%, mp 180 °C. Elemental analysis found (%) C 46.62; H 4.49; N 31.20. Calculated for $C_7H_8N_4S$ (atomic mass 180) was C 46.67; H 4.45; N 31.11%.

2.2. Synthesis of complexes

Hot ethanolic (20 mL) solution of ligand (0.36 g, 0.002 mol) and hot ethanolic (20 mL) solution of the corresponding metal

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doi:10.1016/j.saa.2007.05.033

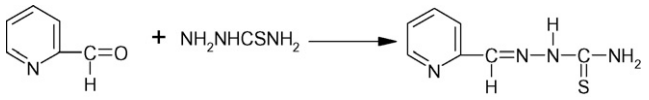

Fig. 1. Synthesis and structure of the ligand (L).

salts (0.001 mL) were mixed together with constant stirring. The mixture was refluxed for 3–4 h at 70–80 °C. On cooling, colored complexes were precipitated out. They were filtered, washed with 50% ethanol and dried under vaccum over P_4O_{10}.

2.3. Physical measurements

The C, H and N were analyzed on Carlo-Erba 1106 elemental analyzer. The Nitrogen content of the complexes was determined using Kjeldahl's method. Molar conductance was measured on the ELICO (CM82T) conductivity bridge. Magnetic susceptibility was measured at room temperature using $CuSO_4{\cdot}5H_2O$ as callibrant. Electronic impact mass spectrum was recorded on JEOL, JMS, DX-303 mass spectrometer. IR spectra (KBr) were recorded on FTIR spectrum BX-II spectrophotometer. The electronic spectra were recorded in DMSO on Shimadzu UV mini-1240 spectrophotometer. EPR spectra of the Cu(II) complexes were recorded as polycrystalline sample at room temperature on E_4-EPR spectrometer using the DPPH as the *g*-marker.

3. Results and discussion

On the basis of elemental analysis, the complexes were found to have the composition as shown in Table 1. The molar conductance measurements of the complexes in DMSO correspond to non-electrolyte [17]. Thus, the complexes may be formulated as $[M(L)_2X_2]$, where M = Ni(II) and Cu(II) and X = Cl^-, NO_3^- and 1/2 SO_4^{2-}. EI mass spectrum of the ligand (Fig. 2) confirms the proposed formula by showing the final peak at 179 u [($C_7H_8N_4S$), calculated atomic mass 180 u] and other peaks like 44, 60, 78, 88, 91, 119 and 135 u may correspond to various fragments. The intensity of these peaks gives an idea of the stability of these fragements. The highest frequency band of the 2-pyridinecarboxaldehyde thiosemicarbazone at 3433 cm^{-1}can assigned to the asymmetric ν(N–H) vibration of the terminal NH_2 group. The other bands at 3261 and 3156 cm^{-1} may be due to the symmetric ν(N–H) vibrations of the imino and amino

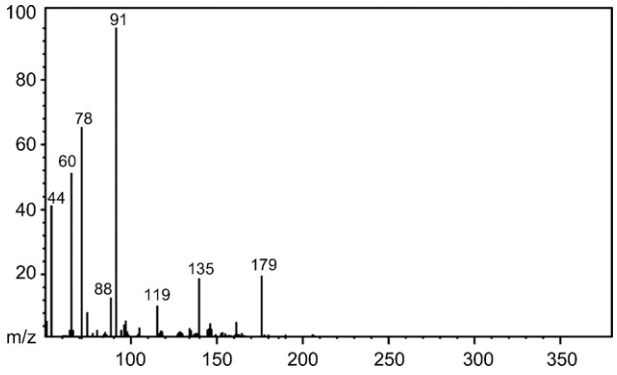

Fig. 2. Electron impact mass spectrum of ligand (L).

groups. A band at ~1610 cm^{-1} in the IR spectrum of the ligand is due to $\nu(C{=}N)_{azomethane}$ group. On complex formation position of this band is shifted toward lower side [18]. Another band in the region ~559 cm^{-1} in the free ligand is due to $\nu(C{=}N)_{pyridine}$ group is also shifted toward higher frequency this indicates that the nitrogen atom of the pyridine group is involved in complex formation [19]. The (C=S) vibration at 742 cm^{-1} of the free ligand is not shifted on complexation which indicate that the non involvement of sulphur in coordination [20].

These results indicate that the presence of the thiosemicarbazone ligand coordinated to the Ni(II) an Cu(II) ions through the $N_{azomethane}$ and $N_{pyridine}$ chelating centres. Thus, it has been concluded that ligand acts as bidentate chelating agent [21].

3.1. IR bands due to anions

In the IR spectra of nitrato complexes three bands are appeared at 1420–1475, 1320–1351 and 1016–1043 cm^{-1}. The position of these bands suggests that both the nitrate groups are coordinated to the metal ion in a unidentate fashion [22].

In the IR spectrum of Ni(II) sulphato complex absorption bands are appeared at ~1106, ~1066 and ~1042 cm^{-1} suggesting bidentate behaviour of the sulphate ion but in the case of Cu(II) complex absorption bands are appeared at ~1179, ~1019 and ~942 cm^{-1} suggesting unidentate behaviour of the sulphate ion [23].

Table 1
Elemental analysis data of the complexes

Complex	Colour	Yield (%)	mp (°C)	M.W.	Elemental analysis found (calculated) (%)			
					M	C	H	N
Ligand ($C_7H_8N_4S$)	Shiny cream	68	176	180	–	46.67 (46.62)	4.45 (4.49)	31.11 (31.20)
$[Ni(L)_2Cl_2]$ $NiC_{14}H_{16}N_8S_2Cl_2$	Green	62	237	490	11.98 (11.95)	34.28 (34.25)	3.26 (3.22)	22.86 (22.82)
$[Ni(L)_2(NO_3)_2]$ $NiC_{14}H_{16}N_{10}S_2O_6$	Light brown	63	258	543	11.81 (11.83)	30.93 (30.91)	2.95 (2.93)	25.78 (25.76)
$[Ni(L)_2SO_4]$ $NiC_{14}H_{16}N_8S_3O_4$	Dark brown	69	230	515	11.39 (11.36)	32.62 (32.65)	3.10 (3.08)	21.74 (21.72)
$[Cu(L)_2Cl_2]$ $CuC_{14}H_{16}N_8S_2Cl_2$	Light green	69	195	491	13.03 (13.02)	39.10 (39.12)	3.26 (3.27)	17.11 (17.12)
$[Cu(L)_2(NO_3)_2]$ $CuC_{14}H_{16}N_{10}S_2O_6$	Green	72	197	544	11.76 (11.74)	35.29 (35.26)	2.94 (2.92)	20.59 (20.57)
$[Cu(L)_2SO_4]$ $CuC_{14}H_{16}N_8S_3O_4$	Shiny green	70	205	516	12.40 (12.38)	37.20 (37.22)	3.10 (3.12)	16.28 (16.24)

4. Nickel(II) complexes

At room temperature these complexes show magnetic moment in the range 2.91–2.95 BM (Table 2). These values are in tune with a high spin configuration [24].

Table 2
Magnetic moments and electronic spectral data of the complexes

Complex	μ_{eff} (BM)	λ_{max} (cm^{-1})
$[Ni(L)_2Cl_2]$	2.92	11185, 14084, 25575
$[Ni(L)_2(NO_3)_2]$	2.91	11235, 14049, 23364
$[Ni(L)_2SO_4]$	2.95	11185, 14925, 24096
$[Cu(L)_2Cl_2]$	1.85	10080, 15898, 24038
$[Cu(L)_2(NO_3)_2]$	1.83	11098, 15948, 24096
$[Cu(L)_2SO_4]$	1.89	10162, 15847, 24154

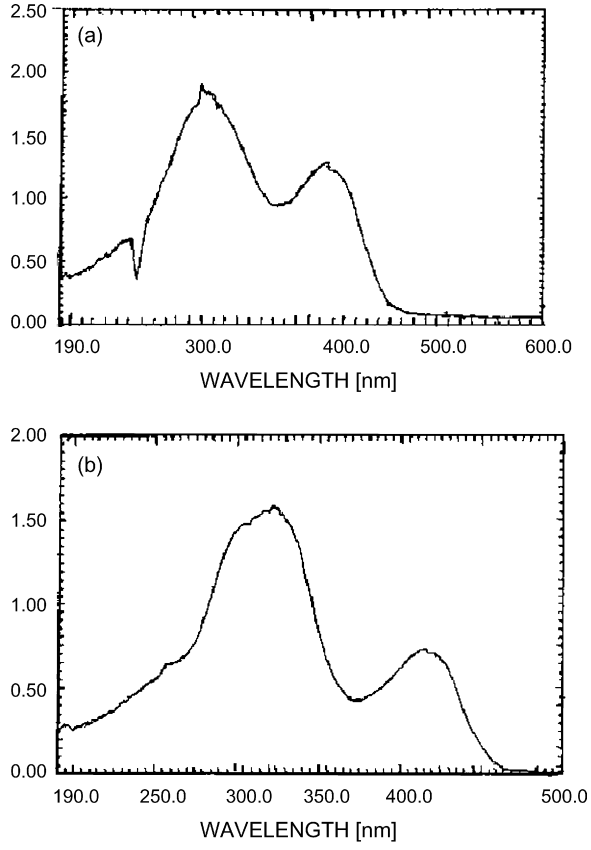

Fig. 3. Electronic spectra of the complexes. (a) $[Ni(L)_2Cl_2]$ and (b) $[Cu(L)_2Cl_2]$.

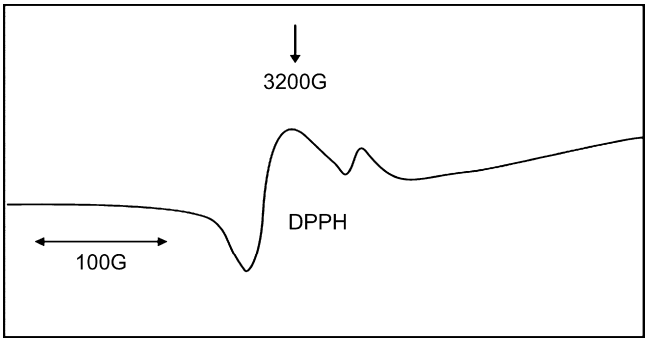

Fig. 4. EPR spectrum of $Cu(L)_2SO_4$ as polycrystalline state.

Table 3
EPR spectral data of the Cu(II) complexes

Complex	Temperature	Data as polycrystalline sample			G
		$g\|\|$	$g_\perp$	g_{iso}	
$[Cu(L)_2Cl_2]$	RT	2.0641	2.0255	2.0383	2.5137
$[Cu(L)_2(NO_3)_2]$	RT	2.0773	2.0318	2.0469	2.4308
$[Cu(L)_2SO_4]$	RT	2.2115	2.1673	2.1820	1.2641

The electronic spectra of the complexes display three absorption (Fig. 3a) bands in the range 11185–11235, 14049–14925 and 23364–25574 cm^{-1}. The ground state of Ni(II) in an octahedral coordination is $^3A_{2g}$. Thus, these bands may be assigned to three spin allowed transitions $^3A_{2g}(F) \rightarrow {}^3T_{2g}$ (F) (ν_1), $^3A_{2g}(F) \rightarrow 3T_{1g}$ (F) (ν_2) and $^3A_{2g}$ (F) $\rightarrow {}^3T_{1g}$ (P) (ν_3), respectively. The position of bands indicates that the complexes have six-coordinated octahedral geometry [25,26] (Fig. 5).

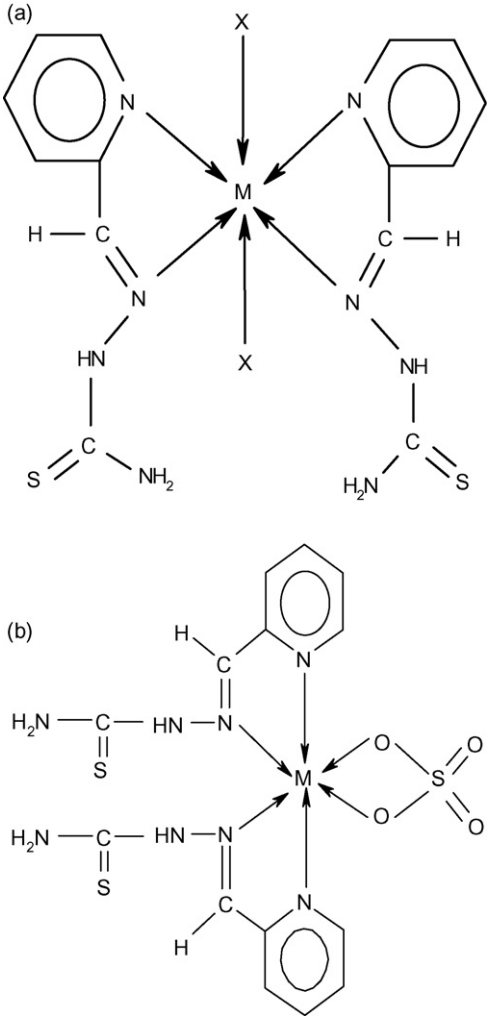

Fig. 5. Suggested structure of the complexes. (a) $[M(L)_2X_2]$, where M = Ni(II) and Cu(II) and X = Cl^- and NO_3^- and $[Cu(L)_2SO_4]$. (b) $[M(L)_2SO_4]$, where M = Ni(II).

5. Copper(II) complexes

The magnetic moments of Cu(II) complexes were recorded at room temperature. The complexes show magnetic moments in the range 1.83–1.89 BM corresponding to one unpaired electron.

The electronic spectra of these complexes display bands (Fig. 3b) in the range 10080–11098, 15847–15948 and 24038–24154 cm^{-1}. These bands correspond to the transitions $^2B_{1g} \rightarrow {}^2A_{1g}(d_{x^2-y^2} \rightarrow d_{z^2})\nu_1$, $^2B_{1g} \rightarrow {}^2B_{2g}(d_{x^2-y^2} \rightarrow d_{zy})\nu_2$ and $^2B_{1g} \rightarrow {}^2E_g(d_{x^2-y^2} \rightarrow d_{zy}d_{yz})\nu_3$, respectively. Therefore, the complexes may be considered to possess a tetragonal geometry [27].

EPR spectra of the Cu(II) complexes were recorded, at room temperature as polycrystalline samples (Fig. 4), on the X-band at 9.1 GHz under the magnetic field range 2800–3000 G. The analysis of spectra give $g\|$ 2.0641–2.2115 and $g_\perp$ 2.0255–2.1673 (Table 3). The trend $g\| > g_\perp > 2.0023$, observed for the complexes, under study, indicate that the unpaired electron is localized in the $d_{x^2-y^2}$ orbital of the Cu(II) ion and the spectral figures are characteristic for the axial symmetry. Tetragonally elongated geometry is thus confirmed for the aforesaid complexes [28].

$G = (g\| - 2)/(g_\perp - 2)$, which measure the exchange interaction between the metal centres in a polycrystalline solid has been calculated. According to Hathaway and Billing [29] if $G > 4$ the exchange interaction is neglisible, but $G < 4$ indicates considerable exchange interaction in the solid complexes. The complexes reported in this paper gives the 'G' value in the range 1.2641–2.5137, which is <4, indicating exchange interaction in the solid complexes.

6. In vitro bioassays of ligand and Ni(II) and Cu(II) complexes

Cultures of phytopathogenic fungi and bacteria such as *Rhizoctonia bataticola*, *Alternaria alternata*, *Fusarium odum*, *Bacillus macerans* and *Pseudomonas striata* were procured from Indian type culture, Division of Plant Pathology, Indian Agricultural Research Institute, New Delhi, India, and maintained on slants of potato dextrose agar (PDA) and nutrient agar (NA) media.

6.1. Antifungal assay

The preliminary fungitoxicity screening of the compounds at different concentrations were performed in vitro against the test fungi, *R. bataticola*, *A. alternata* and *F. odum* by the food poision technique [30,31]. Stock solutions of compounds were prepared by dissolving the compounds (0.064 mg) in DMF. Chlorothalonil used as commercial fungicide and DMFserved as control. Appropriate quantities of the compounds in DMF was added to potato dextrose agar medium in order to get a concentrations of 250, 125, 62.5 μg mL^{-1} of compound in the medium.

Table 4
Antifungal activities of ligand and Ni(II) and Cu(II) complexes

Complex	Fungus tested	Fungal inhibition (%) at concentrations (μg mL^{-1})		
		250	125	63.5
Ligand ($C_7H_8N_4S$)	*R. bataticola*	84.4	72.7	43.3
	A. alternata	90.0	73.4	42.2
	F. odum	80.0	70.0	41.0
$[Ni(L)_2Cl_2]$	*R. bataticola*	33.3	–	–
	A. alternata	61.1	43.3	22.2
	F. odum	49.0	31.0	–
$[Ni(L)_2(NO_3)_2]$	*R. bataticola*	50.0	44.5	16.7
	A. alternata	61.2	48.9	20.0
	F. odum	48.0	34.0	–
$[Ni(L)_2SO_4]$	*R. bataticola*	35.0	–	–
	A. alternata	58.0	39.0	–
	F. odum	33.0	224.0	–
$[Cu(L)_2Cl_2]$	*R. bataticola*	76.6	48.8	20.0
	A.alternata	62.3	47.4	22.2
	F. odum	72.0	45.0	–
	R. bataticola	72.2	45.5	11.1
	A. alternata	67.7	48.9	11.2
	F. odum	64.0	46.0	18.0
$[Cu(L)_2SO_4]$	*R. bataticola*	68.0	48.5	19.0
	A. alternata	60.0	41.0	14.7
	F. odum	58.0	33.0	–
Chlorothalonil (standard)	*R. bataticola*	90.0	76.6	49.0
	A. alternata	98.0	80.0	46.0
	F. odum	89.0	74.0	42.0

Table 5
Antibacterial activities of ligand and Ni(II) and Cu(II) complexes

Complex	Bacteria tested	Diamater (mm) of compounds at concentrations ($\mu g\,mL^{-1}$)		
		250	125	63.5
Ligand ($C_7H_8N_4S$)	*B. macerans*	18	11	–
	P. striata	12	–	–
$[Ni(L)_2Cl_2]$	*B. macerans*	20	16	–
	P. striata	17	11	–
$[Ni(L)_2(NO_3)_2]$	*B. macerans*	22	16	10
	P. striata	15	9	–
$[Ni(L)_2SO_4]$	*B. macerans*	15	8	–
	P. striata	14	7	–
$Cu(L)_2Cl_2]$	*B. macerans*	34	25	11
	P. striata	15	–	–
$[Cu(L)_2(NO_3)_2]$	*B. macerans*	20	11	–
	P. striata	14	7	–
$[Cu(L)_2SO_4]$	*B. macerans*	28	19	12
	P. striata	15	8	–
Streptomycin (standard)	*B. macerans*	30	25	14
	P. striata	40	26	16

The medium was poured into a set of two Petriplates under aseptic conditions in a laminar flow hood. When the medium in the plates was solidified, a mycelial discs of 0.5 cm in diameter cut from the periphery of the 7 days old culture and it was aseptically inoculated upside down in the centre of the Petriplates. These treated Petri dishes were incubated at $26 \pm 1\,^{\circ}C$ until fungal growth in the control Petriplates was almost complete.

The mycelial growth of fungi (mm) in each Petriplates was measured diametrically and growth inhibition (I) were calculated by using the formula:

$$I\,(\%) = \frac{C - T}{C} \times 100, \qquad \mathrm{IC} = \left[\frac{I(\%) - \mathrm{CF}}{100 - \mathrm{CF}}\right] \times 100$$

IC = corrected percent inhibition, CF = is the correction factor obtained the equation; CF = ((90 − Co)/Co) × 100.Where 90 is the diameter (mm) of the Petridish and Co is the growth of fungus.

Results of the fungicidal screening (Table 4) show that, the free ligand (L) was highly active than all the Ni(II) and Cu(II) complexes against all type of fungi [32].

6.2. Antibacterial assay

The antibacterial activities of the ligand and its Cu(II) and Ni(II) complexes against test bacteria *B. macerans* (Gram-positive) and *P. striata* (Gram-negative) at different conc. was checked by disc diffusion technique [33,34]. Twenty-five milliliters of terilized nutrient agar media (NA) was poured in each Petriplates. After solidification 0.1 mL of test bacteria spreads over the medium using a spreader. The test compounds in measured quantities were dissolved in DMF to get concentrations of 250, 125 $\mu g\,mL^{-1}$ of compounds. The disc of Whatmann No. 1 filter paper having the diameter 5.00 mm each containing (1.5 $mg\,cm^{-1}$) of compounds were placed at four equidistant places at a distance of 2 cm from the center in the inoculated Petriplates. Filter paper disc treated with DMF served as control and streptomycin used as a standard drug. All determination were made in duplicate for each of the compounds. Average of two independent readings for each compounds was recorded. These Petriplates were kept in refrigerator for 24 h for pre-diffusion. Finally Petriplates were incubated at 30 °C for 24 h.

The antibacterial results (Table 5) show that all the metal complexes are more active than free ligand [35]. It has also been observed that concentration plays a vital role in increasing the degree of inhibition; as the concentration increases, the activity increases.

7. Conclusions

The proposed study revealed an octahedral geometry for Ni(II) complexes whereas tetragonal geometry for Cu(II) complexes except $[Cu(L)_2SO_4]$ which posseses five coordinated geometry. Ligand acts as bidentate chelating agent through nitrogen of the pyridine ring and ν(C=N) group. The results of antifungal activity show that ligand is highly fungitoxic than the complexes against all type of fungi. On the otherhand, the antibacterial data reveals that that the complexes are superior than the free ligand. This increases the lipophilic character of the metal chelate and favours its permeation through the lipoid layer of the bacterial memberanes. It has also been proposed that concentration plays a vital role in increasing the degree of inhibition; as the concentration increases, the activity increases.

Acknowledgements

We are thankful to the Zakir Husain College, for providing research facilities. ACBR Delhi University, for recording

IR spectra RSIC, IIT Mumbai, for recording EPR spectra and DRDO, New Delhi, for financial assistance.

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