

STUDIES ON MIXED-LIGAND COMPLEXES OF SOME TRANSITION METALS OF BIOLOGICAL INTEREST

R. Nagar¹ and G. Mohan^{2*}

¹DEPARTMENT OF CHEMISTRY, INSTITUTE OF BASIC SCIENCES, AGRA UNIVERSITY, KHANDARI, AGRA-282 002, INDIA,

²DEPARTMENT OF PHARMACOLOGY, S. N. MEDICAL COLLEGE, AGRA-282 003, INDIA

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A series of mixed-ligand complexes of Co(II), Ni(II), Cu(II) and Zn(II) with general formula $M(IM)(L)\cdot H_2O$, where H_2IM = iminodiacetic acid; L = 2,2'-bipyridyl and *o*-phenanthroline, have been studied and isolated in pure state. The metal chelates have been characterized by elemental analysis, IR and electronic spectra, conductivity and magnetic measurements. The octahedral environment around the metal ion has been proposed. The thermal properties of metal complexes in solid state have been studied under non-isothermal condition in nitrogen atmosphere by simultaneous TG and DTA. TG and DTA curves show that the decomposition took place in two steps. Thermodynamic parameters such as activation energy, E , order of reaction, n , entropy of activation, ΔS^\ddagger , and free energy of activation, ΔG^\ddagger , have been determined by standard methods. All the complexes are non-electrolytic in nature. The antimicrobial activity against fungi is critically examined. The difference in their site of action against various fungi has been explained on the basis of formation constants and liposolubility.

Keywords: mixed-ligand complexes, metal-chelate, ternary complexes

Introduction

The mixed-ligand complexes involving aminoacids and 2,2'-bipyridyl or *o*-phenanthroline as potential ligands have been studied [1, 2]. Heterocyclic ligands have been widely used in the study of metal complexes [3-7] due to their strong chelating behaviour both at low as well as in higher *pH* range. It is well estab-

* Mailing address: Superintendent of Salt, Uran Circle, Uran, New Bombay-400702, INDIA

lished that ternary complexes play a decisive role in the activation of enzymes and also in the storage and transport of active substances through biological membranes [8, 9]. The knowledge of the stability of mixed-ligand complexes is of great importance as many metabolic and toxicological functions depend on it. Attempts have been made to correlate the stability of the complexes with their biocidal activity [10, 11].

The N-heterocyclics, for example, 2,2'-bipyridyl (bipy) or *o*-phenanthroline (phen), usually being less basic than most of the amines, are more useful as nitrogen donors for the metals. Metal complexes involving these heterocyclics were extensively studied [12, 13]. The study of these complexes leads one to conclude that aromaticity enhances the chelating ability of the heterocyclic ligands. Martell [14] studied the mixed-ligand complexes of the type where two ligands form complex with the metal in a wide *pH* range and the first metal ligand complex does not get dissociated even at high *pH*. The stability constants and thermodynamic parameters of 1:1:1, $M(II)(IM)(L)\cdot H_2O$ mixed-ligand species have been reported earlier [15]. In the present paper an attempt has been made to characterize the mixed-ligand complexes to study their thermal behaviour. The stability constants are critically compared with their antimicrobial activity.

Materials and methods

All the chemicals used were of AR grade. The solid metal chelates were synthesized by refluxing of metal acetates (0.01 *m* in 30 ml alcohol) with two different ligands (IM and bipy/phen) (0.01*M* in 70 ml alcohol) for two hours at the *pH* of their formation as given in Table 1. On concentration the reaction mixture, a coloured compound was obtained. This coloured compound was filtered under suction, washed first with water, alcohol and finally with ether and dried over P_4O_{10} in vacuum.

Metal contents in the complexes were estimated by standard methods [16]. The molar conductance was measured in dried DMF on a Toshniwal conductivity bridge. IR spectra were recorded on Perkin Elmer-521 spectro-photometer. The electronic spectra of the complexes were recorded in DMF solution on Shimadzu Double beam spectrophotometer UV 150-02. The magnetic measurements of the complexes were carried out at room temperature by Guoy's method using $CuSO_4\cdot 5H_2O$ as a calibrant. Molecular weight of the complexes was determined by cryoscopic method.

Simultaneous thermal gravimetric (TG) and differential thermal analysis (DTA) of the complexes were carried out at Regional Sophisticated Instrumentation Centre, Nagpur in a constant flow of nitrogen, keeping the heating rate $12.5\text{ deg}\cdot\text{min}^{-1}$ for each run. Activation energy (*E*) and order of reaction were calculated from TG and DTA curves using standard methods. Frequency factor (*Z*),

Table 1 Analytical, molar conductance, magnetic susceptibility data, stability constant and molecular weight of mixed chelates

Metal complex	Analysis: found/(calculated)				Molar* conductance/ $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$	μ_{eff} B. M. at 303 K	$\log K_{\text{MLL}}$ at 25°C	pH of isolation	Molecular weight found / calc.
	C	H	N	M					
Co(IM)(bipy)·H ₂ O	45.82 (46.16)	3.92 (4.15)	11.05 (11.54)	15.83 (16.18)	3.59	4.98	11.87	6.50	352 (364)
Ni(IM)(bipy)·H ₂ O	45.74 (46.19)	3.87 (4.15)	10.58 (11.54)	16.07 (16.13)	3.33	2.92	12.13	6.28	347 (364)
Cu(IM)(bipy)·H ₂ O	44.35 (45.59)	4.23 (4.10)	10.83 (11.39)	16.54 (17.23)	3.19	1.83	12.55	5.65	357 (368)
Zn(IM)(bipy)·H ₂ O	44.48 (45.36)	4.18 (4.08)	10.93 (11.34)	16.83 (17.64)	3.82	-	11.46	6.40	361 (370)
Co(IM)(phen)·H ₂ O	50.05 (49.49)	3.72 (3.89)	11.05 (10.82)	14.85 (15.18)	2.59	5.01	11.48	6.68	366 (388)
Ni(IM)(phen)·H ₂ O	48.74 (49.53)	3.63 (3.89)	9.86 (10.83)	14.46 (15.13)	2.08	3.03	11.63	6.10	362 (388)
Cu(IM)(phen)·H ₂ O	46.38 (48.92)	3.72 (3.85)	9.87 (10.69)	15.49 (16.17)	1.23	2.02	12.17	5.45	378 (392)
Zn(IM)(phen)·H ₂ O	48.10 (48.69)	3.95 (3.83)	10.23 (10.65)	15.87 (16.56)	2.09	-	11.19	6.30	383 (394)

* at 25 °C of 10⁻³ M solution in dimethyl formamide (DMF)

entropy of activation (ΔS^\ddagger) and free energy of activation (ΔG^\ddagger) were calculated from DTA.

Results and discussion

Elemental analyses data and molecular weight determination of the metal complexes (Table 1) indicate 1:1:1 (*MLL'*) type stoichiometry. These data also show the presence of one water molecule in all the complexes. The presence of water molecule is further confirmed by thermal dehydration and IR spectra of the complexes. The low values of molar conductance ($1-4 \text{ ohm}^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$) were observed which indicate the non ionic nature of the complexes [17].

IR studies

The free ligand (H_2IM) shows a band around $3300-3100 \text{ cm}^{-1}$ which is shifted to the lower frequency region in the case of their complex, suggesting the coordination through N of NH group. This ligand shows another band at 1680 cm^{-1} which is shifted to the lower frequency region in the metal complex, confirm the coordination of the ligand to the metal ion through carboxylic acid moiety [18]. The coordination of heterocyclics (bipy/phen) is indicated by the positive shifts of C=C, C=N and ring stretching modes [15, 16]. The coordinated water molecule is indicated by the appearance of a broad band in the region of $3400-3200 \text{ cm}^{-1}$ in all the complexes. However, some new bands are observed in the region of $860-700$, $510-490$ and $415-410 \text{ cm}^{-1}$ which are probably due to the coordinated water molecule [20] and the formation of M-O and M-N bond, respectively [21, 22].

Electronic spectra and magnetic studies

The magnetic moment of Co(II), Ni(II) and Cu(II) complexes and electronic spectral data are given in Tables 1 and 2.

Co(II) complexes

All the cobalt complexes were proposed to have octahedral geometry [23] as confirmed by their magnetic moment values. Three bands observed in the electronic spectra of cobalt complexes around 7600 , $16400-16300$ and $20400-20100 \text{ cm}^{-1}$ may be assigned to ${}^4T_{1g} \rightarrow {}^4T_{2g}$ (F), ${}^4T_{1g} \rightarrow {}^4A_{2g}$ (F) and ${}^4T_{1g} \rightarrow {}^4T_{1g}$ (P) transitions, respectively. The value of ν_2/ν_1 ratio is within the range of theoretical values, suggesting a considerable covalent character of the bond.

Table 2 Electronic spectral data of Co(II), Ni(II) and Cu(II) complexes at 25°C of 10^{-4} M solution in dimethyl formamid (DMF)

Complex	Band maxima / cm^{-1}	Assignment	Dq. / cm^{-1}	B	β	v_2 / v_1	LFSE / kcal mol^{-1}	$\delta / \%$
Co(II)(bipy).H ₂ O	7610	$4T_{1g} \rightarrow 4T_{2g}$ (F)	8730	908	0.935	2.14	14.966	6.95
	16340	$\rightarrow 4A_{2g}$ (F)						
Ni(II)(bipy).H ₂ O	20120	$\rightarrow 4T_{1g}$ (P)						
	9360	$3A_{2g} \rightarrow 3T_{2g}$ (F)	9360	793	0.761	1.64	32.091	31.23
Cu(II)(bipy).H ₂ O	15385	$\rightarrow 3T_{1g}$ (F)						
	24600	$\rightarrow 3T_{1g}$ (P)						
Co(II)(phen).H ₂ O	15550	$2E_g \rightarrow 2T_{2g}$	15550				26.657	
	7625	$4T_{1g} \rightarrow 4T_{2g}$ (F)	8775	930	0.958	2.15	15.043	4.38
Ni(II)(phen).H ₂ O	16400	$\rightarrow 4A_{2g}$ (F)						
	20430	$\rightarrow 4T_{1g}$ (P)						
Cu(II)(phen).H ₂ O	9250	$3A_{2g} \rightarrow 3T_{2g}$ (F)	9250	812	0.780	1.66	31.714	28.20
	15380	$\rightarrow 3T_{1g}$ (F)						
Cu(II)(phen).H ₂ O	24550	$\rightarrow 3T_{1g}$ (P)						
	15625	$2E_g \rightarrow 2T_{2g}$	15625				26.786	

Ni(II) complexes

The magnetic moments of the nickel complexes were found in the range 2.90–3.03 B.M., which indicate the octahedral environmental around the metal ion. This geometry was further confirmed by electronic spectra. Three bands around 9300, 15380 and 24600 cm^{-1} were probably due to three spin allowed transitions from ${}^3A_{2g} \rightarrow {}^3T_{2g}$ (F), ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (F) and ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (P), respectively in the octahedral environment [24]. The ligand field parameters Dq , B , β and LFSE are calculated. The Racah interelectronic repulsion parameter B is less than free ion value.

The calculated values of ν_2/ν_1 ratio is within the range expected for an octahedral geometry.

Cu(II) complexes

The magnetic moment values of copper complexes were found in the range of 1.8–2.1 B.M. indicating spin only value with octahedral geometry [25]. This was further confirmed by the electronic spectra of the complexes, in which only band observed around 16000–14000 cm^{-1} is probably due to the ${}^2E_g \rightarrow {}^2T_{2g}$ transition [26].

Zn(II) complexes

On the basis of elemental analyses, IR spectra, molar conductance and molecular weight determination data, all the zinc complexes were proposed to have an octahedral geometry.

The usefulness of electronic spectra in ascertaining the nature of bonding involved in these complexes are limited. Taking the free ion as standard, the ligand causes a slight red shift (nephelauxetic effect) of the absorption spectral band [27]. The magnitude of this shift is dependent upon the change in the inter electronic repulsion parameter [28]. The value of nephelauxetic ratio (β) which is less than one points towards the very slight incidence of covalency in the metal ligand bond. The % covalency (δ) for all the studied systems have been calculated [29] and given in Table 2. Partial covalent character of the metal ligand bond is noticed.

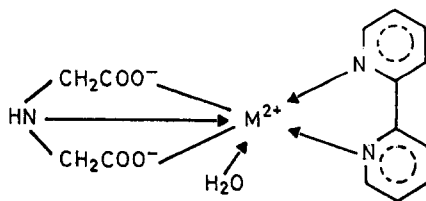


Fig. 1 $M(\text{II})(\text{bipy})\cdot\text{H}_2\text{O}$ ternary complexes $M^{2+}=\text{Co}(\text{II}), \text{Ni}(\text{II}), \text{Cu}(\text{II})$ and $\text{Zn}(\text{II})$

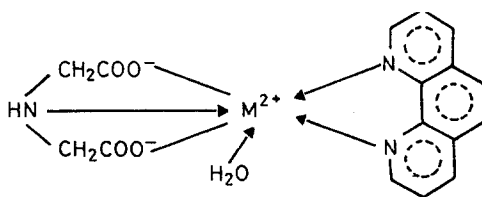


Fig. 2 $M(\text{IM})(\text{phen})\cdot\text{H}_2\text{O}$ ternary complexes $M^{2+}=\text{Co}(\text{II}), \text{Ni}(\text{II}), \text{Cu}(\text{II})$ and $\text{Zn}(\text{II})$

On the basis of analytical analyses and infrared spectral data it appears that the ligands (H_2IM and bipy/phen) act as tridentate and bidentate chelating agents, coordinating via the carboxylic oxygen, imino nitrogen and nitrogen of 2,2'-bipyridyl and *o*-phenanthroline. Therefore, on the basis of above studies, the structures (Figs 1–2) may be proposed for the studied mixed-ligand complexes.

TG and DTA studies

The results of TG and DTA studies are shown in Figs 3–4. On gradual heating from room temperature, the hydrated metal complexes dehydrated within the temperature range $130^\circ\text{--}175^\circ\text{C}$. The corresponding weight loss as resulted by the dehydration and decomposition processes are in good agreement with the calculated values. The complexes were found thermally stable and undergo decomposition within the temperature range $310^\circ\text{--}520^\circ\text{C}$. The resultant final products were the metal oxide in all the cases. The results of thermal decomposition of a compound may be explained in terms of various equations. Freeman and Carrol's rate expression [30] for the thermal decomposition of a compound, where the compound decomposes continuously with time and temperature and one product is gaseous, can be expressed as:

$$\frac{\Delta [\log (dw / dt)]}{\Delta \log W_r} = -\frac{E}{2.303R} \frac{\Delta(1/T)}{\Delta \log W_r} + n$$

where T = Temperature on absolute scale

R = Gas constant

E = Energy of activation

n = Order of reaction

W_r = Difference between the total loss in weight and the loss in weight at time t

$\frac{dw}{dt}$ = Value of rate of weight loss

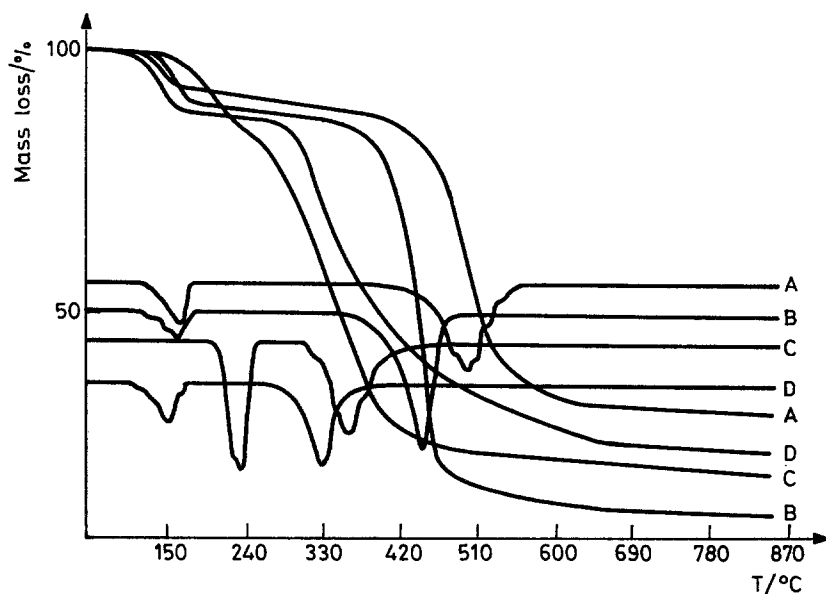


Fig.3 TG and DTA studies of complexes A: $\text{Co(II)(bipy)} \cdot \text{H}_2\text{O}$, B: $\text{Ni(II)(bipy)} \cdot \text{H}_2\text{O}$, C: $\text{Cu(II)(bipy)} \cdot \text{H}_2\text{O}$, D: $\text{Zn(II)(bipy)} \cdot \text{H}_2\text{O}$

The value of the rate of weight loss (dw/dt) was obtained from the plot of the loss in weight of the compound against time. The value of W_r have been calculated from the total loss in weight of the compound and the loss at predetermined and the plot of $\frac{\Delta [\log (dw / dt)]}{\Delta \log W_r}$ against $\frac{\Delta(1/T)}{\Delta \log W_r}$ is obtained (Figs 5–6). It is found that the order of reaction for the thermal decomposition of the compound is of first order and the values of energy of activation for thermal dehydration and decomposition process of the complexes are given in Tables 3 and 4.

The energy of activation for the thermal dehydration and decomposition process of the complexes have also been calculated by using Horowitz and Metzger's equation [31]. Horowitz and Metzger's equation may be written as:

$$\ln \ln (1 - \alpha)^{-1} = \frac{E}{R \cdot T_s^2} \cdot \theta$$

where, α = Fraction of compound decomposed at time t

E = Energy of activation

T_s = Temperature on absolute scale at which the rate of decomposition is maximum

$\theta = T - T_r$

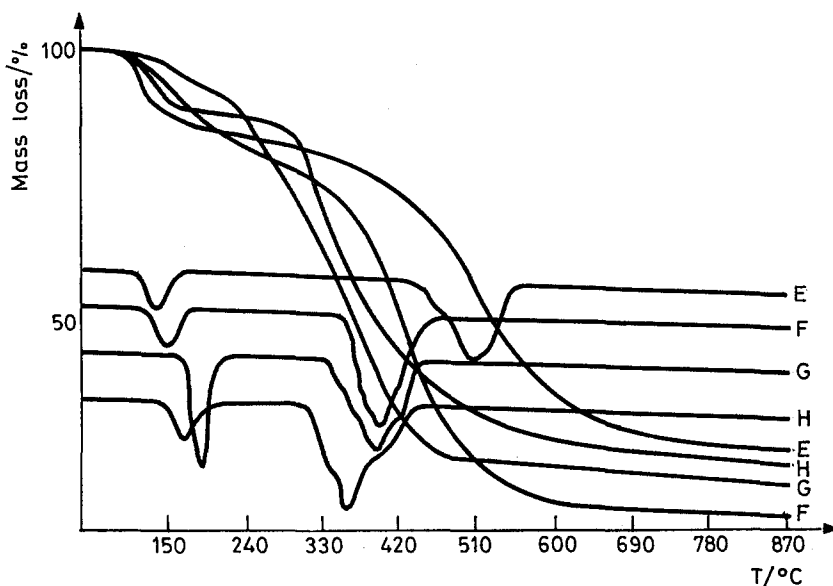


Fig. 4 TG and DTA studies of complexes E: Co(IM)(phen)·H₂O, F: Ni(IM)(phen)·H₂O, G: Cu(IM)(phen)·H₂O, H: Zn(IM)(phen)·H₂O

From the plot of $\ln \ln(1-\alpha)^{-1}$ against θ (Figs 7–8), the value of energy of activation is obtained. The value of energy of activation for the present systems is given in Tables 3 and 4.

Differential thermogravimetric analysis showed two exothermic peaks between 130°–175 °C and 310°–520 °C suggesting two step decomposition of the complexes. During the first step the complexes lose water molecule. The value of activation energy for the dehydration and decomposition process of the metal complexes (Tables 3 and 4) (Figs 9–10) have been calculated by using Piloyan's equation [32]:

$$\log h = C - \frac{E}{2.303RT}$$

where h is the deviation of the DTA curve in mm and C is a constant. The evaluated value of energy of activation is in good agreement with those calculated from thermal gravimetric studies of the complexes.

The various kinetic parameters for thermal dehydration and decomposition process of the complexes have been evaluated by using the equation [33]:

$$K = \frac{(A/m_0)^{n-1} (-dx/dt)}{(A-a)^n}$$

where K , A , m_0 , dx/dt and n are the specific rate constant, total area under the differential peak, initial mole fraction of the reactant, height of the differential peak for the reaction and the order of reaction with respect to the reactant, respectively.

The investigation of the dehydration and decomposition process has confirmed the first order reaction. On substituting the value of the order of reaction as equal to unity, one can obtain:

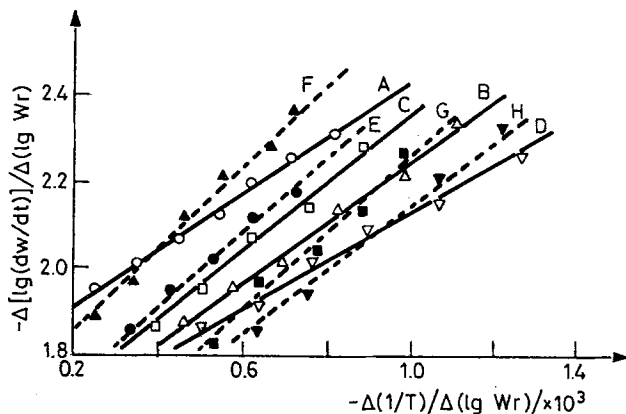


Fig.5 Freeman and Carroll's type of plots for the dehydration process

A: $\text{Co(IM)(bipy)} \cdot \text{H}_2\text{O}$, B: $\text{Ni(IM)(bipy)} \cdot \text{H}_2\text{O}$, C: $\text{Cu(IM)(bipy)} \cdot \text{H}_2\text{O}$,
D: $\text{Zn(IM)(bipy)} \cdot \text{H}_2\text{O}$, E: $\text{Co(IM)(phen)} \cdot \text{H}_2\text{O}$, F: $\text{Ni(IM)(phen)} \cdot \text{H}_2\text{O}$,

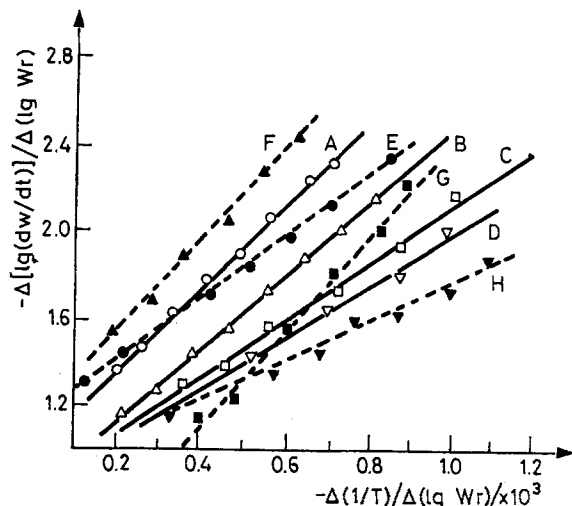


Fig.6 Freeman and Carroll's type of plots for the decomposition process

A: $\text{Co(IM)(bipy)} \cdot \text{H}_2\text{O}$, B: $\text{Ni(IM)(bipy)} \cdot \text{H}_2\text{O}$, C: $\text{Cu(IM)(bipy)} \cdot \text{H}_2\text{O}$,
D: $\text{Zn(IM)(bipy)} \cdot \text{H}_2\text{O}$, E: $\text{Co(IM)(phen)} \cdot \text{H}_2\text{O}$, F: $\text{Ni(IM)(phen)} \cdot \text{H}_2\text{O}$,
G: $\text{Cu(IM)(phen)} \cdot \text{H}_2\text{O}$, H: $\text{Zn(IM)(phen)} \cdot \text{H}_2\text{O}$,

Table 3 Dehydration process of hydrated metal complexes

Sample No.	Reaction	Weight loss / %		Energy of activation, $E / \text{kJ}\cdot\text{mol}^{-1}$			Frequency factor / Z / s^{-1}	Specific rate constant $K \cdot 10^2$	$-\Delta S^\ddagger$ $\text{JK}^{-1}\cdot\text{mol}^{-1}$	ΔG^\ddagger $\text{kJ}\cdot\text{mol}^{-1}$
		Found/	Calc.	Freeman-Carroll's method (TG)	Horowitz-Metzger's method (TG)	Pfloyan's method (DTA)				
1	$\text{Co}(\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_4)_2\cdot\text{H}_2\text{O} \rightarrow \text{Co}(\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_4)_2 + \text{H}_2\text{O}$	4.85 (4.94)		24.890	16.315	21.061	15.516	5.104	238.350	126.654
2	$\text{Ni}(\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_4)_2\cdot\text{H}_2\text{O} \rightarrow \text{Ni}(\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_4)_2 + \text{H}_2\text{O}$	5.05 (4.95)		17.232	9.442	18.763	17.926	8.114	237.354	117.976
3	$\text{Cu}(\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_4)_2\cdot\text{H}_2\text{O} \rightarrow \text{Cu}(\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_4)_2 + \text{H}_2\text{O}$	4.92 (4.88)		26.805	17.822	26.326	68.387	7.337	233.369	134.376
4	$\text{Zn}(\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_4)_2\cdot\text{H}_2\text{O} \rightarrow \text{Zn}(\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_4)_2 + \text{H}_2\text{O}$	4.70 (4.86)		16.274	7.243	17.018	12.613	7.373	238.215	118.828
5	$\text{Co}(\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}_4)_2\cdot\text{H}_2\text{O} \rightarrow \text{Co}(\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}_4)_2 + \text{H}_2\text{O}$	4.75 (4.64)		34.343	26.328	26.805	170.531	5.729	228.199	118.769
6	$\text{Ni}(\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}_4)_2\cdot\text{H}_2\text{O} \rightarrow \text{Ni}(\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}_4)_2 + \text{H}_2\text{O}$	4.60 (4.64)		31.016	22.313	21.001	25.074	6.403	236.241	120.931
7	$\text{Cu}(\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}_4)_2\cdot\text{H}_2\text{O} \rightarrow \text{Cu}(\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}_4)_2 + \text{H}_2\text{O}$	4.65 (4.58)		39.249	28.149	28.719	116.286	5.684	231.271	133.484
8	$\text{Zn}(\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}_4)_2\cdot\text{H}_2\text{O} \rightarrow \text{Zn}(\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}_4)_2 + \text{H}_2\text{O}$	4.50 (4.56)		22.975	12.297	18.380	11.106	6.506	239.318	121.286

Table 4 Decomposition process of anhydrous metal complexes

Sample No.	Reaction	Weight loss %		Energy of activation, E / $\text{kJ}\cdot\text{mol}^{-1}$			Frequency factor Z / S^{-1}	Specific rate constant $\text{K}\cdot 10^2$	$-\Delta S^\ddagger$ / $\text{JK}^{-1}\cdot\text{mol}^{-1}$	ΔD^\ddagger / $\text{kJ}\cdot\text{mol}^{-1}$
		Found/	Calc.	Freeman-Carrrol's method	Horowitz-Metzger's method (TG)	Piloyan's method (TG)				
1	$\text{Co}(\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_4) \rightarrow \text{Co}_2\text{O}_3 + \text{Products}$	30.10		29.102	43.559	34.942	3.961	1.607	247.809	224.021
		(29.35)								
2	$\text{Ni}(\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_4) \rightarrow \text{NiO} + \text{Products}$	20.41		33.697	47.911	40.207	52.369	4.887	237.687	204.924
		(20.52)								
3	$\text{Cu}(\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_4) \rightarrow \text{CuO} + \text{Products}$	21.75		34.463	50.717	43.079	28.297	1.978	241.691	215.405
		(21.56)								
4	$\text{Zn}(\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_4) \rightarrow \text{ZnO} + \text{Products}$	21.72		17.615	20.033	23.933	1.373	3.480	251.849	221.131
		(21.95)								
5	$\text{Co}(\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}_4) \rightarrow \text{Co}_2\text{O}_3 + \text{Products}$	32.15		36.378	42.660	38.292	14.473	1.708	242.209	203.721
		(32.47)								
6	$\text{Ni}(\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}_4) \rightarrow \text{NiO} + \text{Products}$	19.58		40.419	50.485	39.728	16.554	2.669	242.425	219.849
		(19.25)								
7	$\text{Cu}(\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}_4) \rightarrow \text{CuO} + \text{Products}$	20.49		44.419	53.175	45.472	111.363	2.571	234.468	198.579
		(20.25)								
8	$\text{Zn}(\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}_4) \rightarrow \text{ZnO} + \text{Products}$	20.31		27.762	38.696	30.634	4.516	3.111	247.081	213.474
		(20.62)								

$$K = (-dx/dt)/(A-a)$$

To determine the value of specific rate constant (K), the area of peak ($A-a$) at a given temperature is obtained from DTA curve and (dx/dt) is evaluated from the depth of the trough at the total time taken in its formation. The frequency factor (Z) and entropy of activation (ΔS^\ddagger) have been calculated by employing the Arrhenius and Eyring's equation [34], respectively. The free energy of activation is thus obtained from Gibb's equation [35]. The value of K , Z , ΔS^\ddagger and ΔG^\ddagger are recorded in Tables 3 & 4.

It may be concluded that the metal complexes have uniform decomposition pattern and oxide being the end product. The decomposition step involves random nucleation mechanism. The small negative value of ΔS^\ddagger indicate that the transition state involved in the process has a more ordered structure, perhaps there is some agglomeration of particles before the start of random nucleation, a fact which may be implicit in lower value of Z . The negative value of entropy change, however, renders the change in free energy as positive.

Antifungal activity

All the ligands and their metal chelates were screened [36, 37] for their antifungal activity against *Aspergillus niger*, *Aspergillus flavus* and *Penicillium citrinum* fungi at 28°C. A closed and comparative study of Table 5 reveals that the ligands are fungitoxic. It has been found that the activity gradually increases with the increase in concentration. Iminodiacetic acid possess comparatively less activity against the growth of fungi even at relatively higher concentration which may be due to its lower lipid solubility. The ternary complexes were found more active as compared to the free metal and the involved ligands. The results are very much in agreement with our earlier observations [38-40].

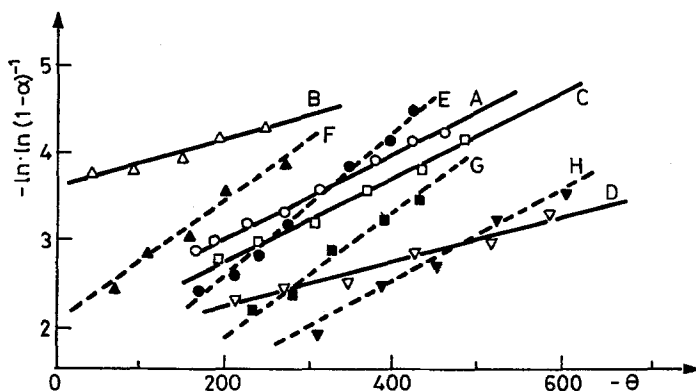


Fig.7 Horowitz and Metzger's type of plots for the dehydration process

A: $\text{Co(IM)(bipy)} \cdot \text{H}_2\text{O}$, B: $\text{Ni(IM)(bipy)} \cdot \text{H}_2\text{O}$, C: $\text{Cu(IM)(bipy)} \cdot \text{H}_2\text{O}$,
D: $\text{Zn(IM)(bipy)} \cdot \text{H}_2\text{O}$, E: $\text{Co(IM)(phen)} \cdot \text{H}_2\text{O}$, F: $\text{Ni(IM)(phen)} \cdot \text{H}_2\text{O}$,

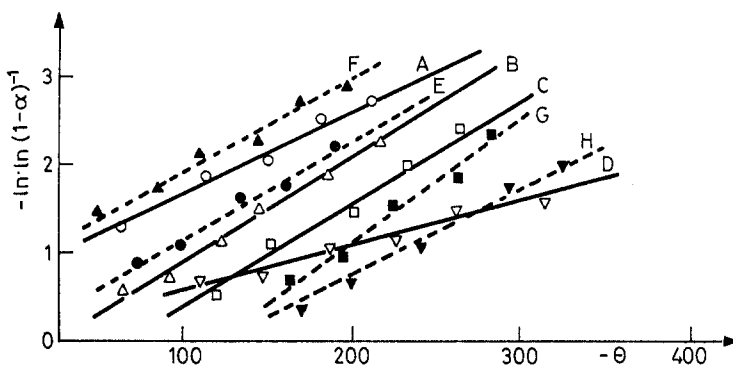


Fig. 8 Horowitz and Metzger's type of plots for the decomposition process
 A: Co(IM)(bipy)·H₂O, B: Ni(IM)(bipy)·H₂O, C: Cu(IM)(bipy)·H₂O,
 D: Zn(IM)(bipy)·H₂O, E: Co(IM)(phen)·H₂O, F: Ni(IM)(phen)·H₂O,
 G: Cu(IM)(phen)·H₂O, H: Zn(IM)(phen)·H₂O

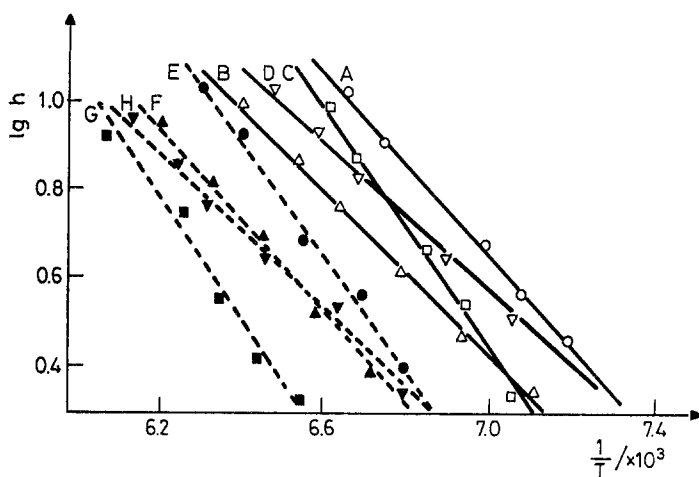
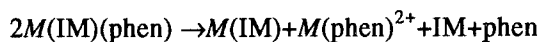
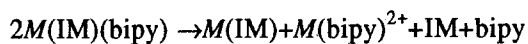


Fig. 9 Piloyan's type of plots for the dehydration process A: Co(IM)(bipy)·H₂O,
 B: Ni(IM)(bipy)·H₂O, C: Cu(IM)(bipy)·H₂O, D: Zn(IM)(bipy)·H₂O,
 E: Co(IM)(phen)·H₂O, F: Ni(IM)(phen)·H₂O, G: Cu(IM)(phen)·H₂O,
 H: Zn(IM)(phen)·H₂O

The comparable activity of the mixed-ligand complexes to that of ligands (H₂IM, bipy & phen) and 1:2, Metal-iminodiacetic acid complex even though the former possess less lipophilic character may be due to the dissociation of the mixed complexes at the site of action as below:



The 1:1, cationic complex thus formed may be acting as active moiety and responsible for the total activity. The binary complexes individually show very low activity due to their low lipid solubility which will not permit cationic complexes to go to the site of action.

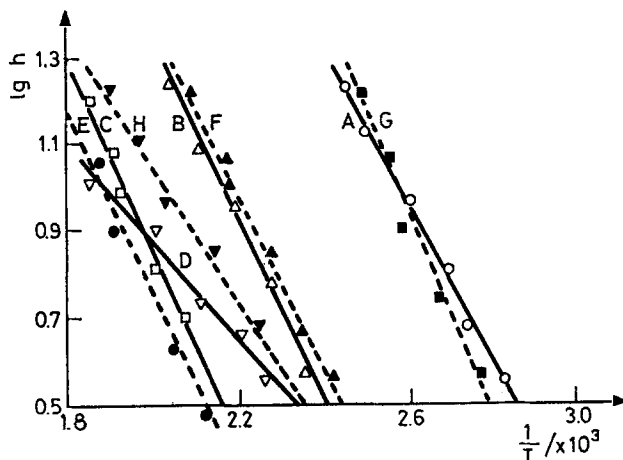


Fig.10 Piloyan's type of plots for the decomposition process A: Co(IM)(bipy)·H₂O, B: Ni(IM)(bipy)·H₂O, C: Cu(IM)(bipy)·H₂O, D: Zn(IM)(bipy)·H₂O, E: Co(IM)(phen)·H₂O, F: Ni(IM)(phen)·H₂O, G: Cu(IM)(phen)·H₂O, H: Zn(IM)(phen)·H₂O

The mechanism shows the formation of two binary complexes. It is well established that the stability of the metal complexes play an important role in the toxicological function. It is seen that the mixed-ligand complex disproportionate into 1:1, Metal-iminodiacetic acid and 1:1, Metal 2,2'-bipyridyl/*o*-phenanthroline. To see the stability of these cationic complexes, the stability constant of binary complexes have been evaluated. An attempt has been made to correlate the stability constant of binary and ternary complexes to the antifungal activity. The evaluated value of stability constant show the existence of 1:1 chelate in solution. These cationic complexes are found to be quite stable so it may take part in the mechanism. If the $\log K_{ML}^N$ ($\log K_{Co(IM)}^{Co} = 5.57$; $\log K_{Ni(IM)}^{Ni} = 6.19$; $\log K_{Cu(IM)}^{Cu} = 6.68$; $\log K_{Zn(IM)}^{Zn} = 5.26$) and $\log K_{MLL}^M$ (Table 1) values are compared to their antifungal activity, it appears that the activity is not dependent on either of these values.

Table 5 Antifungal activity of ligand/ metal complexes in terms of MIC ($\mu\text{g/ml}$)

Ligand/ Complex	Aspergillus niger	Aspergillus flavus	Penicillium citrinum
H ₂ I _M	–	100	100
bipy	65.05	75.10	70.50
phen	60.50	68.15	65.85
Co(IM)(bipy)·H ₂ O	20.15	25.70	29.35
Ni(IM)(bipy)·H ₂ O	30.35	28.25	33.75
Cu(IM)(bipy)·H ₂ O	36.65	32.55	35.35
Zn(IM)(bipy)·H ₂ O	42.15	45.70	38.40
Co(IM)(phen)·H ₂ O	20.25	19.70	25.35
Ni(IM)(phen)·H ₂ O	25.35	27.50	30.65
Cu(IM)(phen)·H ₂ O	30.10	30.30	33.05
Zn(IM)(phen)·H ₂ O	40.05	43.50	35.85

This points toward the role of cationic complexes. These investigations indicate that the chelation alone is not sufficient for enhancing the activity of a compound but it must be accompanied by lipid solubility also. The growth inhibition capacity of the model complexes follow the order Co(II)>Ni(II)>Cu(II)>Zn(II) and the stability order [41] in terms of metal ions is Cu(II)>Ni(II)>Co(II)>Zn(II).

* * *

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Zusammenfassung — Es wurde eine Reihe Mischligandenkomplexe von Co(II), Ni(II), Cu(II) und Zn(II) der allgemeinen Formel $M(IM)(L)\cdot H_2O$ (mit H_2IM = Iminodiessigsäure und L = 2,2'-Bipyridyl und *o*-Phenanthrolin) wurden untersucht und in reinem Zustand isoliert. Die Charakterisierung der Metallchelate erfolgte mittels Elementaranalyse, IR- und Elektronenspektroskopie sowie durch Leitfähigkeits- und magnetische Messungen.