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STRUCTURAL AND THERMAL DECOMPOSITION CHARACTERISTICS OF MIXED-LIGAND COMPLEXES OF Cu(II), Ni(II), Co(II) AND Zn(II)

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Mixed-ligand complexes of Cu(II), Ni(II), Co(II) and Zn(II) with 8-hydroxyquinoline and thiophene-2-carboxylic acid as two different ligands, have been isolated in pure state. The formation of these complexes has been inferred potentiometrically. The isolated complexes have been characterized by their elemental analyses, IR and electronic spectra, conductivity and magnetic measurements. Solid state dehydration of the hydrated complexes and subsequent decomposition of the anhydrous complexes have been studied by simultaneous DTA and TG techniques. The thermal stability order of the hydrated compounds is Cu > Co > Ni > Zn, but in the decomposition process the trend observed is Co > Zn > Ni > Cu. Some parameters like activation energy and order of reaction for each process have been computed.

Antifungal antibacterial properties of some mixed-ligand complexes of transition and inner-transition metal ions have been reported [1, 2] in the literature. The compounds containing nitrogen and sulphur atoms play an important role in many process of biological importance [3]. 8-hydroxyquinoline and its derivatives have long been used as potential antimicrobiol agents and drugs [4, 5]. The role of mixed-ligand complexes in biological process has well recognized [6]. In the present communication, synthesis, structural and thermal decomposition characteristics of the aforesaid mixed-ligand chelates have been discussed with a view to study their stability behaviour.

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Experimental

The solution of metal nitrates and the ligands used were prepared and standardized [7]. The experimental conditions, the instrument and method adopted for potentiometric studies were same as reported earlier [8].

The IR spectra of the complexes and the corresponding ligands were recorded on Perkin-Elmer-521 spectrophotometer in KBr matrix. Magnetic measurements were carried out at 20° using Guoy's method. The electronic spectra were recorded in DMF on Shimadzu Double Beam Spectrophotometer UV-150-02. Molar conductance of the complexes were measured in their DMF solution using Toshniwal conductivity bridge (Cl-01.10A).

Simultaneous DTA and TG analysis of the compounds were carried out at Regional Sophisticated Instrumentation Centre, Nagpur. TG curves were utilized for calculating the activation energies of the process involved. Elemental analysis were carried out by microanalytical techniques. The analytical results fall well in agreement with the calculated values within the limits of experimental error.

Results and discussion

Potentiometric studies show the priority of chelation of HQ with the metal ion which is further supported by the formation of a heterogeneous phase right from the beginning. The lowering in initial pH in comparison to the curves representing the titration of the ligands and binary systems, corresponds to the addition of secondary ligand (TCA) to the initially formed 1:2,M(II)-HQ complex resulting in the formation of 1:1:1,M(II)-TCA-HQ insoluble species. These complexes are stable only in the pH range 4.8-5.75. Beyond this range, the partial dissolution of solid phase occurs which may probably be due to the disproportionation of the initially formed 1:1:1, complex into 1:2,M(II)-HQ complex and to the simultaneous precipitation of the remaining metal as metal hydroxide.

The formation of above ternary complexes is further supported by the non-superimposable nature of the theoretical composite curve [9] with the experimental curve in the region of mixed-ligand complex formation, IR spectral studies and elemental analyses data of the isolated complexes.

All the complexes are soluble in DMF and DMSO. The molar conductance of all the complexes in DMF (10^{-3} M) solution fall in the 3-6 ohm^{-1} cm^{2} mol^{-1} range indicating that the complexes are non-electrolytes [10]. The small conductivity observed may be due to their partial solvolysis.

IR spectra

A comparative study of the IR spectra of the complexes with those of the involved ligands shows the appearance of some new bands as well as lowering in the stretching frequencies of active groups in the case of complexes. The appearance of new bands at 3400 and 1600 cm^{-1} indicate the antisymmetric and symmetric OH stretching and bending vibrations respectively due to the co-ordinated water molecules [11]. A sharp band at 1695 cm^{-1} corresponds to $O\text{–}C=O$ stretching of the free acid which is lowered (~1675 cm^{-1}) in the case of complexes showing its chelation to metal ions through carboxylic group. A sharp absorption band at 3270 cm^{-1} due to OH stretching vibration in the free ligand (HQ) almost disappears in the spectra of metal chelates probably due to the deprotonation of the OH group. Further, the presence of strong bands in the region of 1170-1120 cm^{-1} indicate the presence of coordinate oxine [12] in the complexes. Ring breathing modes at 845 cm^{-1} in the case of thiophene-2-carboxylic acid is lowered in the case of metal complexes. It clearly indicates the involvement of sulphur of thiophene ring in complexation. The coordination of the ligands to the metal ions through S, N and O is further supported by the appearance of some new bands at 360-380, 410-430 and 580-600 cm^{-1} due to the formation of M-S, M-N and M-O bonds respectively [13] in the resulting complexes.

Magnetic properties

The copper complex exhibits magnetic moment (Table 1) of the order 2.01 B.M. which agrees well the spin only value [14]. The magnetic moment value 3.21 B.M. observed for nickel complex is within the expected range (2.9-3.4 B.M.) for octahedral environment [15]. The observed magnetic moment 5.13 of cobalt complex is within the 4.7-5.2 B.M. range, reported for octahedral complexes. The zinc being d^{10} ion shows diamagnetism.

Table 1a Magnetic spectral data of Cu(II), Ni(II) and Co(II) complexes

S. No.	Complex	Band maxima	Assignment	Dq cm^{-1}	B cm^{-1}
1	Cu(TCA)(HQ).2H_2O	14190	$^2E_g \rightarrow {}^2T_{2g}$	1419	-
2	Ni(TCA)(HQ).2H_2O	9990	$^3A_{2g} \rightarrow {}^3T_{2g}$(F)	999	740
		16390	$\rightarrow {}^3T_{1g}$(F)		
		24690	$\rightarrow {}^3T_{1g}$(P)		
3	Co(TCA)(HQ).2H_2O	8540	$^4T_{1g} \rightarrow {}^4T_{2g}$(F)	779	711
		16330	$\rightarrow {}^4A_{2g}$(F)		
		19960	$\rightarrow {}^4T_{1g}$(P)		

Table 1b Electronic spectral data of Cu(II), Ni(II) and Co(II) complexes

S. No.	Complex	β	ν_2/ν_1	LFSE kcal.mol^{-1}	μeff. B.M.	Molar conductance, ohm^{-1}.cm^2.mol^{-1}
1	Cu(TCA)(HQ).2H_2O		-	24.33	2.01	3.68
2	Ni(TCA)(HQ).2H_2O	.71	1.64	34.25	3.21	4.02
3	Co(TCA)(HQ).2H_2O	.73	1.91	13.35	5.13	5.32

Electronic spectra

The electronic spectra of Cu(II), Ni(II) and Co(II) complexes are listed in Table 1 alongwith their ligand field parameters such as Dq, B, β and LFSE. The copper complex shows a single broad band with the maxima at 14190 cm^{-1}. This may originate due to $^2E_g \rightarrow {}^2T_{2g}$ transition, producing a distorted octahedral environment around the metal ion [16]. Three bands observed at 9990, 16390 and 24690 cm^{-1} for nickel complex may be assigned to $^3A_{2g} \rightarrow {}^3T_{2g}$(F), $^3A_{2g} \rightarrow {}^3T_{1g}$(F) and $^3A_{2g} \rightarrow {}^3T_{1g}$(P) transitions [16]. The ligand field parameters are calculated by using Ballhausen equation [17]. The Racah parameter B(740 cm^{-1}) is less than the free ion value (1041 cm^{-1}) suggesting a considerable overlap and delocalization of electrons on the metal ion. The ν_2/ν_1 ratio is within the range expected [14] for an octahedral geometry. The electronic spectra of cobalt complex exhibit three absorption bands at 8540, 16330 and 19960 cm^{-1} assigned to $^4T_{1g} \rightarrow {}^4T_{2g}$(F), $^4T_{1g} \rightarrow {}^4A_{2g}$(F) and $^4T_{1g} \rightarrow {}^4T_{1g}$(P) transitions [16]. The ν_2/ν_1 ratio is within the range expected for an octahedral environment. The value of Racah inter-electronic repulsion parameter B(711 cm^{-1}) is less than the free ion value suggesting a considerable covalent character of the bond. The spectral studies alongwith colour (pink) and magnetic moment of the complex point out the distored octahedral stereochemistry [15].

Thermal analysis

On gradual heating from room temperature, the hydrated metal complexes were completely dehydrated within the temperature range 120-228°. From the TG and DTA traces of the dehydration stage, it was found that all the metal complexes lost their respective water molecules in a single step. All these dehydration reaction are presented in Table 2.

Table 2a Dehydration process of hydrated metal complexes

S. No.	Reaction	Initiation temp., % °C	Peak temp., °C	Completion temp., °C	Weight loss, found/calc.
1	$Cu(C_{14}H_9NO_3S).2H_2O \rightarrow$ $Cu(C_{14}H_9NO_3S) + H_2O$	150	206	228	9.86 (9.72)
2	$Ni(C_{14}H_9NO_3S).2H_2O \rightarrow$ $Ni(C_{14}H_9NO_3S) + 2H_2O$	120	132	156	10.32 (9.84)
3	$Co(C_{14}H_9NO_3S).2H_2O \rightarrow$ $Co(C_{14}H_9NO_3S) + 2H_2O$	125	135	161	9.77 (9.84)
4	$Zn(C_{14}H_9NO_3S).2H_2O \rightarrow$ $Zn(C_{14}H_9NO_3S) + 2H_2O$	115	129	154	9.81 (9.67)

Initiation, peak and completion temperature of the dehydration processes alongwith the corresponding weight loss are given in Table 2 and the results of decomposition processes are given in Table 3. All the anhydrous complexes exhibit considerable thermal stability and undergo decomposition within the temperature range 287-498°. The resultant final products were the metal oxide in all the cases.

The plots of the loss in weight of the metal complexes, W against time, T is shown in Fig. 1. The results of the thermal decomposition of the metal complexes have been explained in terms of various equations. The energy of activation for the thermal dehydration (Table 2) and decomposition (Table 3) has been calculated by using Horowitz and Metzger's equation [18]. The plot of $\ln(1-\alpha)^{-1}$ against θ is shown in Fig. 2.

Table 2b Kinetic data of hydrated metal complexes

S. No.	Reaction	E_a, kcal.mol^{-1} Horowitz and Metzger method	E_a, kcal.mol^{-1} Freeman and Carrol method	n
1	$Cu(C_{14}H_9NO_3S).2H_2O \rightarrow$ $Cu(C_{14}H_9NO_3S) + 2H_2O$	2.861	2.528	1
2	$Ni(C_{14}H_9NO_3S).2H_2O \rightarrow$ $Ni(C_{14}H_9NO_3S) + 2H_2O$	2.157	2.207	1
3	$Co(C_{14}H_9NO_3S).2H_2O \rightarrow$ $Co(C_{14}H_9NO_3S) + 2H_2O$	3.238	3.019	1
4	$Zn(C_{14}H_9NO_3S).2H_2O \rightarrow$ $Zn(C_{14}H_9NO_3S) + 2H_2O$	1.901	1.821	1

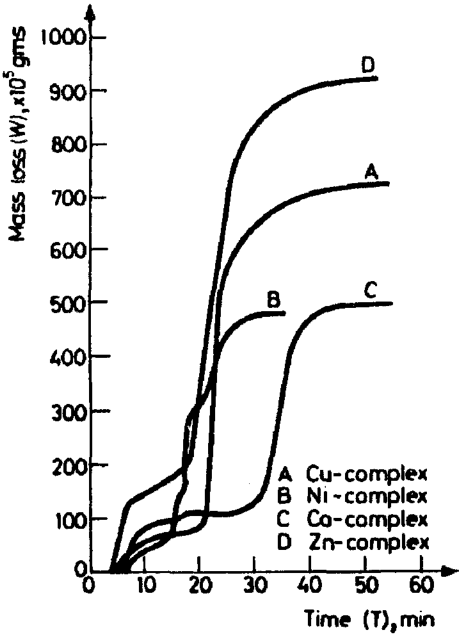

Fig. 1 Thermal decomposition of complexes weight loss vs. time

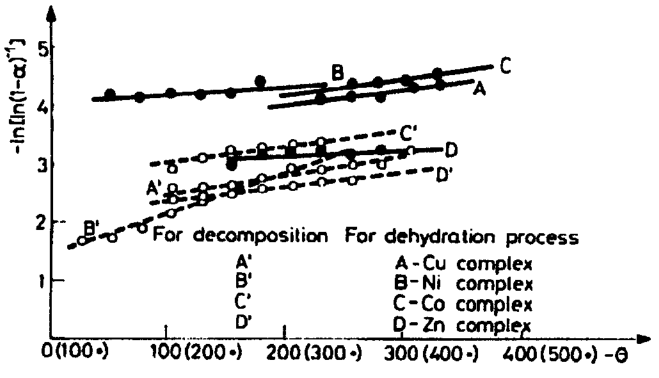

Fig. 2 Horowitz and Metzger's type of plot for dehydration and decomposition process of metal complexes

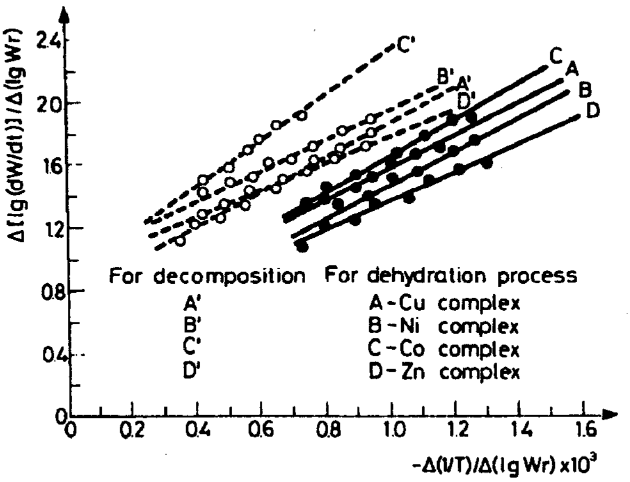

Fig. 3 Freeman and Carrol's type of plot for the dehydration and decomposition process of metal complexes

The value of energy of activation obtained from the slope of the curve for the dehydration of metal complexes are 2.861, 2.157, 3.238 and 1.901 k.cal.mol^{-1} for Cu(II), Ni(II), Co(II) and Zn(II) complexes respectively. The values of energy of activation for thermal decomposition of metal complexes according to this equation are 3.586, 5.126, 2.713 and 2.488 k.cal.mol^{-1} respectively for Cu(II), Ni(II), Co(II) and Zn(II) complexes (Tables 2, 3).

Table 3a Decomposition process of anhydrous metal complexes

S. No.	Reaction	Initiation temp., % °C	Peak temp., °C	Completion temp., °C	Weight loss, found/calc.
1	$Cu(C_{14}H_9NO_3S) \rightarrow$ CuO + Products	287	333	363	24.41 (23.75)
2	$Ni(C_{14}H_9NO_3S) \rightarrow$ NiO + Products	310	409	442	21.84 (22.64)
3	$Co(C_{14}H_9NO_3S) \rightarrow$ Co_2O_3 + Products	389	461	498	51.28 (50.23)
4	$Zn(C_{14}H_9NO_3S) \rightarrow$ ZnO + Products	378	412	448	25.26 (24.17)

Table 3b Kinetic parameters of anhydrous metal complexes

S. No.	Reaction	E_a, kcal.mol^{-1}		n
		Horowitz and Metzger method	Freeman and Carrol method	
1	$Cu(C_{14}H_9NO_3S) \rightarrow$ CuO + Products	3.586	3.252	1
2	$Ni(C_{14}H_9NO_3S) \rightarrow$ NiO + Products	4.126	4.987	1
3	$Co(C_{14}H_9NO_3S) \rightarrow$ Co_2O_3 + Products	2.713	2.839	1
4	$Zn(C_{14}H_9NO_3S) \rightarrow$ ZnO + Products	2.488	1.766	1

The values of rate of weight loss (dw/dt) are obtained from the plot of the loss in weight of the complex W against time T by drawing tangents at appropriate times. The values of Wr have been calculated from the total loss in weight of the complex and the loss at predetermined time. The plot of $\frac{\Delta(\log dw/dt)}{\Delta(\log Wr)}$ against $\frac{\Delta(1/T)}{\Delta(\log Wr)}$ is obtained (Fig. 3). The treatment of the thermogravimetric results according to Freemman-Carrol's equation [19] is done for the dehydration and decomposition processes separately. It is found that the order of reaction for the thermal dehydration and decomposition reaction is of first order and the values of energy of activation for thermal dehydration are 2.528, 2.207, 3.019 and 1.821 k.cal.mol^{-1} and for thermal decomposition are 3.252, 4.987, 2.839 and 1.766 k.cal.mol^{-1} respectively for Cu(II), Ni(II), Co(II) and Zn(II) complexes. The obtained results are in well agreement with the values obtained from Horowitz and Metzger's

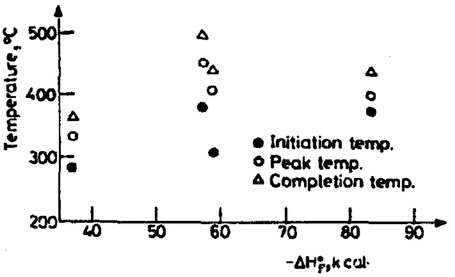

Fig. 4 Initiation peak and completion temperature of thermal decomposition of anhydrous metal complexes vs. heat of formation

equation (Tables 2, 3).

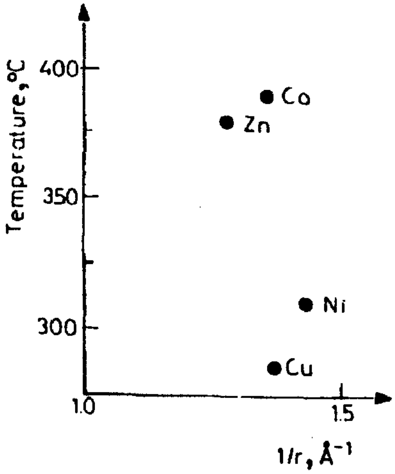

Fig. 5 Initiation temperature of thermal decomposition of anhydrous metal complexes vs. reciprocal of ionic radii

The plots of initiation, peak and completion temperature of thermal decomposition of anhydrous metal complexes against the negative heat of formation (H_f^o) [20] of the respective metal oxides (Fig. 4) exhibit interesting trends alongwith the rise of the values of -ΔH_f^o. Such variation as reflected in Fig. 4 is close to the behaviour expected from the thermal stability order observed in this study. Only zinc complex deviates from this trend.

Table 4

Compound	Initiation kcal.mol^{-1} °C	Peak temp., °C	Completion temp., °C	$H_f^o$of oxides* kcal.mol
Cu(TCA)(HQ)	287	333	363	-37.10
Ni(TCA)(HQ)	310	409	442	-58.40
Co(TCA)(HQ)	389	461	498	-57.20
Zn(TCA)(HQ)	378	412	448	-83.17
*Ref. 25				

Table 5

Compound	Initial weight loss temp., A^{o-1} °C	1/r*
Cu(TCA)(HQ)	287	1.369
Ni(TCA)(HQ)	310	1.428
Co(TCA)(HQ)	389	1.351
Zn(TCA)(HQ)	378	1.333
*Ref. 26		

The plot of initiation temperature of thermal decomposition of the metal complexes against the corresponding reciprocal ionic radii (Fig. 5, Table 5) exhibit some definite trends [21]. This behaviour is close to the general behaviour of gradual decrease of the stability of metal complexes with a decrease in the ionic radii. Copper and zinc complexes deviates from this general trend.

In the single step dehydration processes represented in Table 2, the activation energies are in the order: Co > Cu > Ni > Zn. The thermal stability of hydrated complexes follows the order: Cu > Co > Ni > Zn. In the decomposition proceses of the anhydrous metal complexes represented in Table 3, the energies of activation follow the order: Ni > Cu > Co > Zn. The thermal stability of anhydrous complexes obtained from the initiation and peak temperatures follow the order: Co > Zn > Ni > Cu.

The general series found by Irving and Williams [22] for the stability of complexes in solution is almost the reverse of the above series for the thermal stability in the solid state. The same sequence as suggested by us, was reported for the thermal stability of the same metal ions by earlier workers [23, 24]. This behaviour may be accounted for by assuming that the strength of intermolecular bonds play a significant role in determining thermal stability of compounds in solid state.

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Zusammenfassung -- Komplexe der Metalle Cu(II), Ni(II), Co(II) und Zn(II) mit unterschiedlichen Liganden (8-Hydroxychinolin und Thiophen-2-carbonsäure) wurden rein hergestellt. Auf die Bildung dieser Komplexe wurde potentiometrisch geschlossen. Die isolierten Komplexe wurden mittels Elementaranalyse, IR- und Elektronenspektren, Leitfähigkeit und magnetischen Untersuchungen beschrieben. Mittels eines Verfahrens von simultaner DTA und TG wurde im festen Zustand die Dehydratation der hydratierten Komplexe und anschließend daran die Zersetzung der dehydratierten Komplexe untersucht. Die thermische Stabilität der hydratierten Komplexe nimmt in der Reihenfolge Cu-Co-Ni-Zn ab, bei der Zersetzung konnte aber die Reihenfolge Co-Zn-Ni-Cu beobachtet werden. Für jeden Vorgang wurden Parameter wie Aktivierungsenergie und Reaktionsordung berechnet.