THERMAL AND SPECTRAL STUDIES OF SOME MIXED LIGAND COMPLEXES OF Co(II), Ni(II) AND Cu(II) INVOLVING ALIPHATIC AND HETEROCYCLIC β-DIKETONE

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ABSTRACT

Mixed ligand complexes of the type MLL'·nH_2O, where M = Co(II), Ni(II) or Cu(II), L = acetylacetone, benzoylacetone or dibenzoylmethane and L' = 1-phenyl-3-methyl-4-benzoyl-2-pyrazoline-5-one, have been synthesized by the reactions of two different ligands L and L' in aqueous alcoholic medium. The pyridine adducts of the mixed ligand complexes [MLL'(py)$_2$] have also been synthesized and all complexes are suitably characterized. Thermal studies of the mixed ligand complexes and their pyridine adducts have been carried out to determine their mode of decomposition, apparent activation energy and the order of each thermal reaction. Infrared and thermogravimetric analyses suggest that two water molecules are present in the coordination sphere of the Co(II) and Ni(II) mixed ligand complexes showing that they are paramagnetic and octahedral in geometry.

INTRODUCTION

The β-diketones are well known ligands capable of formation of stable complexes with various metal ions [1–4] which have the general structure

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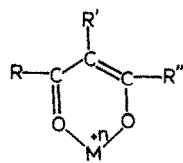
where R, R', R" = H, alkyl or aryl group, n = oxidation number and M = metal ion. Less well characterized are the complexes of pyrazolone which are of the type [5,6]

(II)
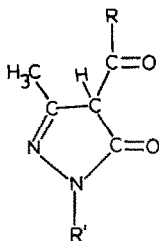
where R = H, alkyl or aryl group and R' = C_6H_5. 4-Acyl pyrazolones-5 are a class of potentially bidentate ligands which were originally investigated by Jensen [5] as reagents for radiochemical separations. These molecules are similar to β-diketones since in both classes keto-enol tautomerism is possible. Pyrazolone and its derivatives have been used widely as potential fungicides [7,8]. A literature survey revealed that only binary metal chelates have been formed from the ligands type I and II. In this work it was of interest to determine the nature of the mixed ligand complexes which form when a heterocyclic β-diketone and aliphatic β-diketone compete for coordination sites with bivalent metal ions. In the present communication we report the preparation and detailed investigations of some mixed ligand complexes of Co(II), Ni(II) and Cu(II) and their pyridine adducts.

EXPERIMENTAL

Chemicals

Acetylacetone, benzoylacetone and dibenzoylmethane (Fluka) were used. 1-Phenyl-3-methyl-2-pyrazoline-5-one and benzoyl chloride were obtained from Aldrich Chemical Co., U.S.A. All metal salts, pyridine (BDH) and sodium acetate were of AR grade. DMF, ethanol, methanol and chloroform were purified by distillation before use.

Synthesis of the ligand

The ligand, 1-phenyl-3-methyl-4-benzoyl-2-pyrazoline-5-one (Hpmbzp) was prepared from 1-phenyl-3-methyl-2-pyrazoline-5-one and benzoyl chloride as reported earlier [9].

Preparation of mixed ligand complexes

[M(pmbzp)(acac)] · nH_2O, [M(pmbzp)(bzac)] · nH_2O and [M(pmbzp)(dbm)] · nH_2O complexes were prepared by adding a methanolic solution of 1-phenyl-3-methyl-4-benzoyl-2-pyrazoline-5-one (0.01 M, 50 ml) and acetylacetone, benzoylacetone (0.02 M, 25 ml) or dibenzoylmethane (0.01 M, 50 ml) to an aqueous solution of metal salt (0.02 M, 25 ml) in a 1:1:1 ratio. After mixing, the pH was raised by sodium acetate solution (1 M) to ~ 5.5. The reaction mixture was stirred well and refluxed for 6 h. Upon cooling, solid complexes separated out. These were filtered by suction and washed with hot water and ethanol and stored over P_4O_{10}.

Preparation of pyridine adducts of mixed ligand complexes

For [(pmbzp)(acac)(py)$_2$]Co(II) or Ni(II), [(pmbzp)(bzac)(py)$_2$]Co(II) or Ni(II) and [(pmbzp)(dbm)(py)$_2$]Co(II) or Ni(II), a solution of pyridine (0.5

ml) in 10 ml ethanol was added to a suspension of (1 g) mixed ligand complexes of Co(II) or Ni(II) in 50 ml ethanol. The reaction mixture was stirred well and refluxed for 4–6 h. Coloured complexes separated out on cooling. They were filtered, washed with ethanol and dried over P_4O_{10}.

Analytical methods

Microanalyses for C, H and N were done by the microanalytical unit of the Department of Chemistry, Calcutta University, Calcutta. Metal analyses were carried out by standard procedure [10]. TLC analyses were done on silica gel G (Sichem) using a chloroform–ether (5:3) mixture as eluent. Magnetic susceptibilities were determined by the Gouy method. Conductance measurements were obtained on a Systronics model 302 conductivity bridge. Infrared spectra in the region 4000–400 cm^{-1} were recorded in the solid state (KBr pellets) on a Perkin-Elmer IR spectrophotometer. The electronic spectra of the complexes were taken in chloroform on a Beckman DB-GT UV-visible spectrophotometer at room temperature in the range 340–1200 nm. Thermal studies were done with a Mettler M-3 thermobalance (Switzerland) with a TA-3000 microprocessor at a heating rate of 10°C min^{-1} in air, using 5–10 mg samples. The thermobalance and temperature calibration (with Pt-100) were checked by the standard samples supplied by the Mettler Company. A Beckmann thermometer was used to determine molecular weight by a cryoscopic method.

RESULTS AND DISCUSSION

The analytical data and physical constants of the mixed ligand complexes are listed in Table 1. All the complexes are soluble in common organic solvents. The complexes are paramagnetic and their molecular weights suggest a monomeric nature. Low conductance in chloroform solution at room temperature indicates that the complexes are non-electrolytes. TLC of the mixed ligand complexes was performed, and single spots were observed for all the complexes. This indicates that they are single mixed ligand complexes and not mixture of the corresponding binary complexes.

Cobalt(II), nickel(II) and copper(II) aqueous solution on being treated with one mole each of Hpmbzp and acac, bzac, or dbm in alcoholic medium at specific pH, results in the formation of the mixed ligand complex III.
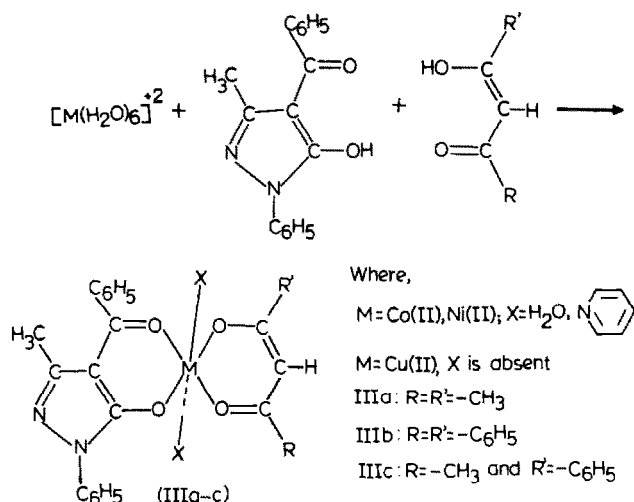
Magnetic measurement studies

The cobalt(II) mixed ligand complexes and their pyridine adducts exhibit magnetic moments in the range 4.38–5.23 BM indicating that they have very high orbital contributions. This high orbital contribution is attributed to the

TABLE 1

Physical and analytical data for some mixed ligand complexes and their pyridine adducts

Compound	Molecular weight [a] (g mol⁻¹)	Colour	Yield (%)	Melting decomposition temp. (°C)	Analyses [a] (%)			
					C	H	N	M
[(pmbzp)(acac)(H$_2$O)$_2$]Co(II)	455.50 (470.94)	Pink	81	192(d)	56.00 (56.06)	4.98 (5.10)	5.92 (5.95)	12.45 (12.51)
[(pmbzp)(bzac)(H$_2$O)$_2$]Co(II)	510.00 (532.94)	Orange-pink	85	169(d)	60.80 (60.80)	4.85 (4.88)	5.20 (5.25)	11.00 (11.06)
[(pmbzp)(dbm)(H$_2$O)$_2$]Co(II)·H$_2$O	590.00 (612.94)	Orange-yellow	90	158(d)	62.21 (62.64)	3.74 (3.91)	4.69 (4.57)	9.87 (9.62)
[(pmbzp)(acac)]Cu(II)	422.08 (439.54)	Green	86	181(d)	60.02 (60.06)	4.56 (4.55)	6.35 (6.37)	14.42 (14.46)
[(pmbzp)(bzac)]Cu(II)	490.26 (501.54)	Greenish grey	89	253(d)	64.60 (64.60)	4.39 (4.39)	5.53 (5.58)	12.65 (12.66)
[(pmbzp)(dbm)]Cu(II)	548.12 (563.54)	Green	93	191(d)	68.13 (68.14)	4.25 (4.26)	4.96 (4.97)	11.25 (11.28)
[(pmbzp)(acac)(H$_2$O)$_2$]Ni(II)	452.24 (470.71)	Light green	83	205(d)	56.05 (56.09)	5.00 (5.10)	5.95 (5.95)	12.42 (12.47)
[(pmbzp)(bzac)(H$_2$O)$_2$]Ni(II)	518.95 (532.71)	Light green	88	174	60.80 (60.82)	4.88 (4.88)	5.30 (5.25)	11.00 (11.03)
[(pmbzp)(dbm)(H$_2$O)$_2$]Ni(II)	570.32 (594.71)	Light green	92	211(d)	64.52 (64.57)	4.70 (4.71)	5.70 (5.71)	9.84 (9.87)
[(pmbzp)(acac)(py)$_2$]Co(II)	578.45 (592.94)	Orange	93	191(d)	64.74 (64.76)	5.03 (5.06)	9.45 (9.45)	9.94 (9.94)
[(pmbzp)(bzac)(py)$_2$]Co(II)	640.25 (654.94)	Brown	82	115	67.76 (67.79)	4.88 (4.89)	8.51 (8.55)	9.06 (9.00)
[(pmbzp)(dbm)(py)$_2$]Co(II)	702.82 (716.71)	Orange	91	184(d)	70.35 (70.30)	4.76 (4.74)	7.82 (7.81)	8.24 (8.22)
[(pmbzp)(acac)(py)$_2$]Ni(II)	575.62 (592.71)	Sky blue	89	227(d)	64.72 (64.79)	5.04 (5.06)	9.47 (9.45)	9.89 (9.91)
[(pmbzp)(bzac)(py)$_2$]Ni(II)	635.32 (654.71)	Bluish green	90	175	67.79 (67.82)	4.89 (4.89)	8.52 (8.55)	8.94 (8.97)
[(pmbzp)(dbm)(py)$_2$]Ni(II)	698.92 (716.71)	Light green	94	192(d)	70.32 (70.31)	4.75 (4.74)	7.79 (7.81)	8.20 (8.19)

[a] Values in parentheses are calculated. Key: pmbzp = anion of 1-phenyl-3-methyl-4-benzoyl-2-pyrazoline-5-one; acac = anion of acetylacetone; bzac = anion of benzoylacetone; dbm = anion of dibenzoylmethane; py = pyridine; (d) = decomposition temperature.

Where,

$M = Co(II), Ni(II); X = H_2O, N\langle\rangle$

$M = Cu(II)$, X is absent

IIIa: $R = R' = -CH_3$

IIIb: $R = R' = -C_6H_5$

IIIc: $R = -CH_3$ and $R' = -C_6H_5$

three fold orbital degeneracy of the $^4T_{1g}$ ground term. These results indicate the distorted octahedral geometry of the cobalt(II) complexes.

The mixed ligand complexes of nickel(II) are light green in colour, whereas their pyridine adducts are sky blue to light green. These complexes are high-spin and have magnetic moments ranging from 2.97 to 3.4 BM depending on the magnitude of the orbital contribution [11], indicating that they are not square planar.

The mixed ligand copper(II) complexes exhibit magnetic moments ranging from 1.82 to 1.85 BM corresponding to one unpaired electron.

Visible spectral studies

Cobalt in the complexes [Co(acac)(pmbzp)] $\cdot$ nH$_2$O [Co(bzac)(pmbzp)] $\cdot$ nH$_2$O, [Co(dbm)(pmbzp)] $\cdot$ nH$_2$O and the pyridine adduct compounds has a coordination number of six and the expected geometry is a distorted octahedron. The ground state of octahedrally coordinated Co(II) is $^4T_{1g}$. The three transitions should take place, i.e. $^4T_{1g(F)} \rightarrow {}^4T_{2g}$, $^4A_{2g}$ and $^4T_{1g(P)}$. In the electronic spectra of cobalt(II) complexes two absorption bands are observed around 20,600 and 8,500 cm^{-1} regions, assignable [12] to an octahedral environment. Nickel(II) mixed ligand complexes and their pyridine adducts exhibit two bands at 16,000–15,115 cm^{-1} $\nu_2(^3T_{1g(F)} \leftarrow {}^3A_{2g})$ and 10,526–10,309 cm^{-1} $\nu_1(^3T_{2g} \leftarrow {}^3A_{2g})$. The third band is not resolved properly below 25,000 cm^{-1} $\nu_3(^3T_{1g(P)} \leftarrow {}^3A_{2g})$. It may be a charge transfer band. These regions are assignable to the characteristics of an octahedral environment. Copper(II) mixed ligand complexes show one broad band at ~ 14,925 cm^{-1}, which is attributed to a combination of three transitions in square planar stereochemistry.

Infrared spectral studies

Examination of the infrared spectra of the mixed ligand complexes shows the disappearance of the –OH ligand band near the 2700–2600 cm^{-1} region, indicating the replacement of protons from both the ligands during complex formation. In all mixed ligand complexes there are two bands observed at 1610 and 1580 cm^{-1}, corresponding to the C=O stretching frequency of pmbzp and acac, bzac or dbm, respectively, in which there is delocalization of π-electrons. Similarly, two sharp bands observed at 1570 and 1560 cm^{-1} may be due to the C=C stretching mode of aliphatic β-diketones and pmbzp, respectively. The C=N (cyclic) stretching observed at 1590 cm^{-1} of the pmbzp ligand does not undergo any change in the complexes, ruling out coordination through this nitrogen. The infrared spectra of cobalt(II) and nickel(II) mixed ligand complexes before heating and after heating at 120°C show a broad band in the region 3400–3240 cm^{-1}, indicative of the presence of the coordinated water molecules [13], whereas in all copper(II) complexes this band is absent. This band disappears in pyridine adduct complexes of cobalt(II) and nickel(II), indicating that two water molecules have been replaced by pyridine molecules. The octahedral geometry of the complexes accounts for the association of two water or pyridine molecules with the metal ion.

Thermal studies

The use of thermogravimetric data to evaluate kinetic parameters of solid state reactions involving weight loss has been investigated by a number of workers [14–16]. We followed the method of Broido [17]. This is a simple sensitive graphical method of treating TGA data. The kinetic parameters of each decomposition step were calculated from TG curves, and are presented in Table 2. The probability that a molecule possesses energy in excess of an amount E per mole, at a temperature T is related to the Boltzmann factor $e^{-E/RT}$ where R is the molar gas constant. The reaction rate is dependent upon the product of A, which is the frequency factor and $e^{-E/RT}$. Thus the decomposition equation of a first order reaction of the type $A_{(s)} \rightarrow B_{(s)} + C_{(g)}$ will be $K = A\,e^{-E/RT}$. For a first order reaction, i.e. $n = 1$, this equation takes the form $\ln(\ln(1/y)) = -(E/R)(1/T) + \text{constant}$, where the fraction not yet decomposed, (i.e. residual weight fraction) $y = (W_t - W_\infty)/(W_0 - W_\infty)$, W_t is the weight of the substance at temperature t, W_0 is the weight of the substance at initial stage, and W_∞ is the weight of the residue at the end of decomposition.

TG curves are shown for all mixed ligand complexes in Fig. 1. The TG/DTG curves of complexes [(pmbzp)(dbm)]Co(II) or Ni(II) · nH$_2$O, [(pmbzp)(dbm)(Py)$_2$]Co(II) or Ni(II) (Fig. 2) show three decomposition steps. In [(pmbzp)(dbm)]Co(II) · nH$_2$O, a first step begins at 36°C, and the

TABLE 2

Kinetic parameters of mixed ligand complexes and their pyridine adducts

Compound	Step	Temperature (°C)			Step analysis	
		Start	Peak	End	Wt. Loss (%)	Activation energy (kcal mol^{-1})
[(pmbzp)(acac)]Cu(II)	I	145	221	244	6.1046	12.7
	II	244	311	415	37.7910	18.5
	III	415	451	589	47.1950	16.7
[(pmbzp)(bzac)]Cu(II)	I	143	258	279	16.3110	10.5
	II	279	311	393	24.6780	11.7
	III	393	487	566	46.2010	9.3
[(pmbzp)(dbm)]Cu(II)	I	120	223	230	3.6393	5.6
	II	230	310	402	46.9200	22.8
	III	402	472	590	40.6890	11.9
[(pmbzp)(acac)(H$_2$O)$_2$]Ni(II)	I	48	156	182	7.1677	9.4
	II	300	349	423	44.6450	21.4
	III	423	516	556	38.9840	11.7
[(pmbzp)(bzac)(H$_2$O)$_2$]Ni(II)	I	38	41	162	8.0182	5.3
	II	270	342	399	42.9410	18.8
	III	399	433	545	37.3360	18.3
[(pmbzp)(dbm)(H$_2$O)$_2$]Ni(II)	I	54	125	180	7.7816	10.9
	II	264	345	400	46.3677	15.5
	III	400	473	551	33.2513	11.3
[(pmbzp)(acac)(H$_2$O)$_2$]Co(II)	I	38	79	130	10.6090	7.5
	II	265	376	405	38.5200	18.4
	III	405	480	554	41.5040	11.4
[(pmbzp)(bzac)(H$_2$O)$_2$]Co(II)	I	36	56	174	13.9080	2.0
	II	197	280	306	7.8161	5.5
	III	306	375	530	64.0230	8.4
[(pmbzp)(dbm)(H$_2$O)$_2$]Co(II)	I	36	61	71	5.7326	4.7
	II	75	102	191	6.7348	4.0
	III	192	383	544	75.3060	10.6
[(pmbzp)(acac)(py)$_2$]Ni(II)	I	112	198	210	8.3890	15.6
	II	210	347	405	47.186	28.5
	III	405	523	439	36.791	16.8
[(pmbzp)(bzac)(py)$_2$]Ni(II)	I	111	204	253	15.6990	5.9
	II	253	343	418	44.7040	14.1
	III	418	475	522	26.902	13.2
[(pmbzp)(dbm)(py)$_2$]Ni(II)	I	48	178	188	7.7822	13.3
	II	188	341	375	47.5439	13.7
	III	375	427	528	36.3491	11.3
[(pmbzp)(acac)(py)$_2$]Co(II)	I	115	170	183	5.7544	13.6
	II	183	221	294	12.1400	7.3
	III	294	370	580	72.8630	10.4
[(pmbzp)(bzac)(py)$_2$]Co(II)	I	125	182	205	7.0177	6.0
	II	205	262	311	19.7033	10.4
	III	311	434	509	59.9810	13.1
[(pmbzp)(dbm)(py)$_2$]Co(II)	I	97	162	261	21.738	13.2
	II	261	293	301	6.2334	4.5
	III	301	372	495	63.747	15.2
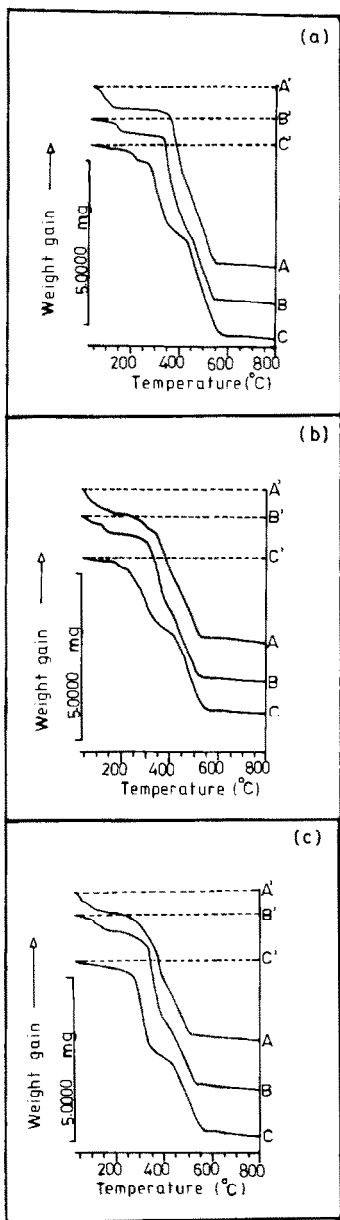
Fig. 1. TG curves for mixed ligand complexes. (a) [(pmbzp)(acac)(H$_2$O)$_m$]M(II), (b)[(pmbzp)(bzac)(H$_2$O)$_m$]M(II), (c)[(pmbzp)(dbm)(H$_2$O)$_m$]M(II), where M(II) = Co(II) or Ni(II) and $m = 2$, and M(II) = Cu(II) and $m = 0$. A', B' and C' are the base lines.

peak temperature is 61° C, indicating that water molecules may be present outside the coordination sphere in this compound. In other compounds, the weight loss observed in the range 75–191° C may suggest the presence of
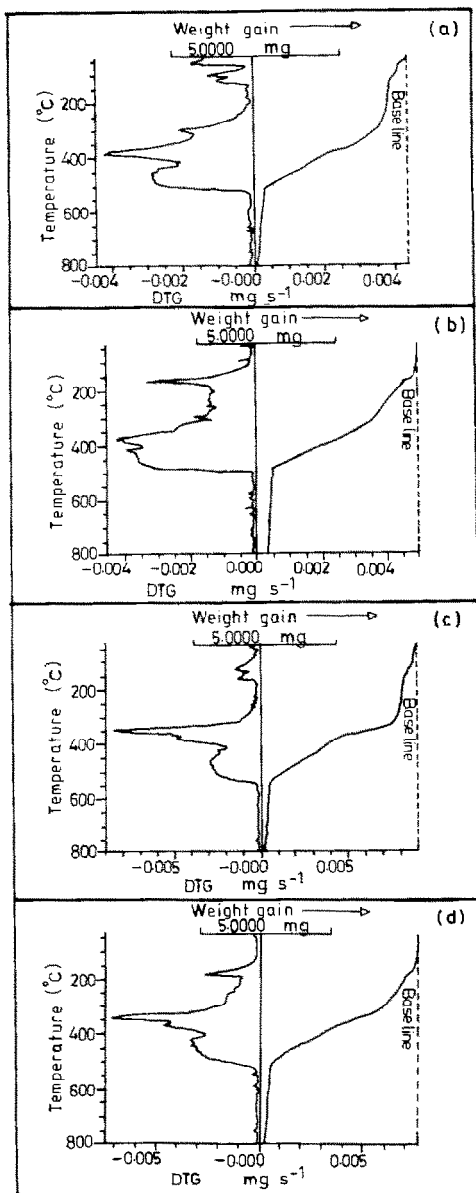
Fig. 2. TG/DTG curves for mixed ligand complexes. (a) [(pmbzp)(dbm)(H$_2$O)$_2$]Co(II)·H$_2$O, (b) [(pmbzp)(dbm)(py)$_2$]Co(II), (c)[(pmbzp)(dbm)(H$_2$O)$_2$]Ni(II), (d) [(pmbzp)(dbm)(py)$_2$]-Ni(II).

water molecules inside the coordination sphere. In pyridine adduct compounds the first decomposition step begins only at $\geqslant 110\,°$C, indicating the absence of any water molecules. From the step analysis of DTG curves, it was observed that there are three steps in the decomposition of each
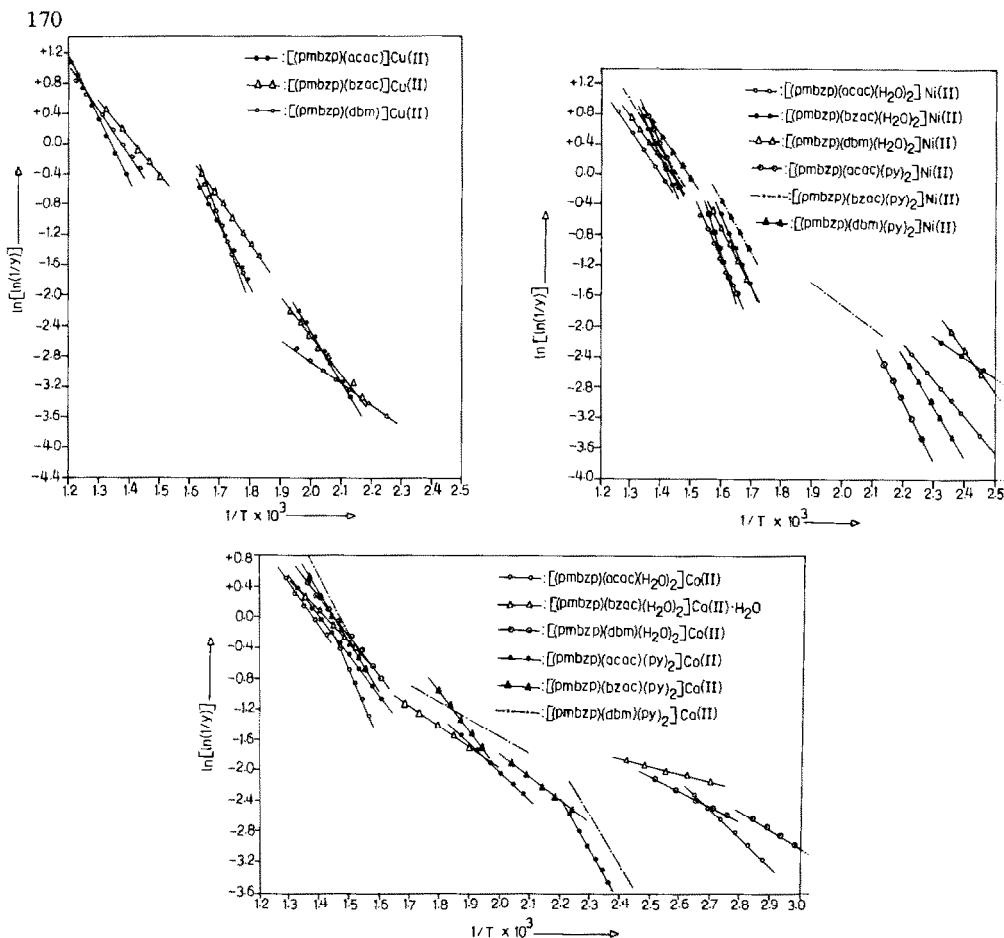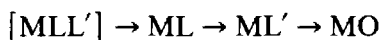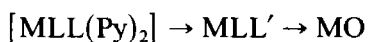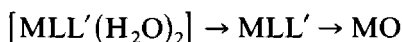
Fig. 3. Plots of $\ln(\ln(1/y))$ vs. $1/T$ for mixed ligand complexes.

compound. The decrease in weight with increase in temperature corresponds to the formation of a $1:1:1$ complex after the loss of two different ligand molecules. These intermediates formed after the first weight loss have been confirmed on the basis of their elemental analyses and infrared spectra. At $\sim 550\,°C$ the stable metallic oxide was formed. The plot of $\ln(\ln(1/y))$ vs. $1/T$ results in a straight line of slope $= E/R$ (Fig. 3). The order of the reaction was assumed to be one in all cases. The plots made according to the Broido method are found to be linear over the entire range of decomposition, and this supplements the assumption regarding the overall order of the thermal decomposition reaction. The apparent activation energy was calculated for the solid state decomposition reactions

$$\left[\text{MLL}'(\text{H}_2\text{O})_2\right] \rightarrow \text{MLL}' \rightarrow \text{MO}$$

$$\left[\text{MLL}(\text{Py})_2\right] \rightarrow \text{MLL}' \rightarrow \text{MO}$$

$$\left[\text{MLL}'\right] \rightarrow \text{ML} \rightarrow \text{ML}' \rightarrow \text{MO}$$

where M = Co(II) or Ni(II) for the first and second reactions, and M = Cu(II) for the third.

The thermal decomposition range and the calculated apparent activation energy are presented in Table 2. It is observed from activation energy data that the activation energy of H_2O outside the coordination sphere is less than that for H_2O which bonds to metal atom, i.e. inside the coordination sphere. Similarly, in the pyridine adduct compound the activation energy of the first step is higher than that of water coordinated compounds. This indicates that the M–N bond is more stable than the $M-OH_2$ bond. The thermal stability order of the metal chelates Ni(II) > Cu(II) > Co(II) was derived from the activation energy values obtained from Broido curves.

TABLE 3

Magnetic susceptibilities, electronic spectral bands, their assignments and the stereochemistry assigned to some mixed ligand complexes and their pyridine adducts

Compound	μ_{eff} (BM)	λ_{max} (cm^{-1})	Band assignments	Stereochemistry assigned
[(pmbzp)(acac)]Cu(II)	1.82	14,925		Square planar
[(pmbzp)(bzac)]Cu(II)	1.85	15,925		Square planar
[(pmbzp)(dbm)]Cu(II)	1.84	14,925		Square planar
[(pmbzp)(acac)(H$_2$O)$_2$]Co(II)	4.59	8,500	$^4T_{1g(F)} \rightarrow {}^4T_{2g}$	Octahedral
		20,600	$^4T_{1g(F)} \rightarrow {}^4T_{1g(P)}$	
[(pmbzp)(bzac)(H$_2$O)$_2$]Co(II)	4.38	8,584	$^4T_{1g(F)} \rightarrow {}^4T_{2g}$	Octahedral
		20,000	$^4T_{1g(F)} \rightarrow {}^4T_{1g(P)}$	
[(pmbzp)(dbm)(H$_2$O)$_2$]Co(II)·H$_2$O	4.41	8,695	$^4T_{1g(F)} \rightarrow {}^4T_{2g}$	Octahedral
		19,607	$^4T_{1g(F)} \rightarrow {}^4T_{1g(P)}$	
[(pmbzp)(acac)(H$_2$O)$_2$]Ni(II)	2.97	10,309	$^3A_{2g} \rightarrow {}^3T_{2g}$	Octahedral
		15,115	$^3A_{2g} \rightarrow {}^3T_{1g(F)}$	
[(pmbzp)(bzac)(H$_2$O)$_2$]Ni(II)	3.22	10,416	$^3A_{2g} \rightarrow {}^3T_{2g}$	Octahedral
		15,385	$^3A_{2g} \rightarrow {}^3T_{1g(F)}$	
[(pmbzp)(dbm)(H$_2$O)$_2$]Ni(II)	3.36	10,471	$^3A_{2g} \rightarrow {}^3A_{2g}$	Octahedral
		15,504	$^3A_{2g} \rightarrow {}^3T_{1g(F)}$	
[(pmbzp)(acac)(py)$_2$]Co(II)	4.69	8,700	$^4T_{1g(F)} \rightarrow {}^4T_{2g}$	Octahedral
		19,608	$^4T_{1g(F)} \rightarrow {}^4T_{1g(P)}$	
[(pmbzp)(bzac)(py)$_2$]Co(II)	4.98	8,500	$^4T_{1g(F)} \rightarrow {}^4T_{2g}$	Octahedral
		20,250	$^4T_{1g(F)} \rightarrow {}^4T_{1g(P)}$	
[(pmbzp)(dbm)(py)$_2$]Co(II)	5.23	8,600	$^4T_{1g(F)} \rightarrow {}^4T_{2g}$	Octahedral
		20,400	$^4T_{1g(F)} \rightarrow {}^4T_{1g(P)}$	
[(pmbzp)(acac)(py)$_2$]Ni(II)	3.02	10,450	$^3A_{2g} \rightarrow {}^3T_{2g}$	Octahedral
		15,873	$^3A_{2g} \rightarrow {}^3T_{1g(F)}$	
[(pmbzp)(bzac)(py)$_2$]Ni(II)	3.29	10,500	$^3A_{2g} \rightarrow {}^3T_{2g}$	Octahedral
		15,400	$^3A_{2g} \rightarrow {}^3T_{1g(F)}$	
[(pmbzp)(dbm)(py)$_2$]Ni(II)	3.46	10,600	$^3A_{2g} \rightarrow {}^3T_{2g}$	Octahedral
		15,100	$^3A_{2g} \rightarrow {}^3T_{1g(F)}$	

REFERENCES

1 J.P. Fackler, Jr., Prog. Inorg. Chem., 7 (1966) 734.
2 J.C. Hammel, J.A. Smith and E.J. Wilkins, J. Chem. Soc. A, (1969) 46.
3 B. Bock, K. Flatau, R. Junge, M. Kuhr and H. Musso, Angew. Chem. Int. Ed. Eng., 10 (1971) 225.
4 A.E. Martell and R.M. Smith, Critical Stability Constants, Vol. 3, Plenum Press, New York, 1977.
5 B.S. Jensen, Acta Chem. Scand., 13 (1959) 1347, 1668, 1890.
6 E.R. Menzel, D.R. Lorenz, J.R. Wasson, K.R. Radigan and B.J. McCorwick, J. Inorg. Nucl. Chem., 38 (1976) 993.
7 A. Allais and P. Girault, Chem. Abstr., 72 (1970) 21685 ^{e}.
8 B. Nanda, S. Padnanavan, B. Tripathy and A.S. Mitra, J. Indian Chem. Soc., 52 (1975) 533.
9 B.V. Patel and B.T. Thaker, Synth. React. Inorg. Met. Org. Chem., 16 (1986), 1319.
10 A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, Geen, London, 1961.
11 F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Interscience, New York, 1962, p. 738.
12 A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amserdam, 1968.
13 J.S. Dwivedi and U. Agarwal, J. Inorg. Nucl. Chem., 35 (1973) 561.
14 E.S. Freeman and B. Caroll, J. Phys. Chem., 62 (1958) 394.
15 A. Berlin and R.J. Robinson, Anal. Chim. Acta, 27 (1962) 50.
16 A.W. Coats and J.P. Redfern, Nature, 201 (1964) 68.
17 A. Broido, J. Polym. Sci. Part A-2, 7 (1969) 1761.