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THERMAL STUDIES OF COBALT(II) COMPLEXES OF HYDRAZINE IN THE SOLID PHASE

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ABSTRACT

Cobalt(II) complexes, $CoL_nX_2 \cdot m\ H_2O$, where $L = N_2H_4$; $n = 2.5$, 2 or 1.5 and $X = F^-$, Cl^-, Br^- or $\frac{1}{2}\ SO_4^{2-}$; $m = 2$, 1, 0.5 or 0, have been synthesized from solution and their thermal investigations carried out. In addition, CoL_nX_2 complexes, where $n = 1.5$, 1, 0.75 or 0.25; $X = Cl^-$ or $\frac{1}{2}\ SO_4^{2-}$, have been synthesized in the solid state by temperature-arrest technique from their parent complexes derived from solution. The decomposition of these complexes has been found to occur through the formation of thermally stable as well as unstable complex species. The complexes have been characterized by elemental analysis, magnetic, IR and electronic (mull) spectral data. The probable path for each decomposition step is proposed.

INTRODUCTION

A good number of hydrazine complexes are known in the literature [1–4], but thermal studies of only a few hydrazine complexes have been reported [5–8]. Recently, we reported [9–12] thermal studies on the nickel(II), manganese(II), zinc(II) and cadmium(II) complexes of hydrazine. As a result, thermal studies on the cobalt(II) complexes of hydrazine are relevant. The present work reports the synthesis of hydrazine complexes of cobalt(II) fluoride, chloride, bromide and sulfate and their thermal investigations.

EXPERIMENTAL

Preparation

$[CoL_{1.5}F_2(H_2O)]$ (1), ($L = NH_2NH_2$) was prepared by the addition of (3 mmol) hydrazine hydrate (80%) to a concentrated aqueous solution of cobalt(II) fluoride (1 mmol) with constant stirring. Fine, reddish pink

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crystals separated out which were filtered, washed first with an ethanol–water mixture (1 : 1) and finally with dry ethanol, and dried in a vacuum desiccator.

$[CoL_{1.5}F_2(H_2O)]$ (2) was prepared by adding (3 mmol) hydrazine hydrate dropwise with constant stirring to a concentrated ammoniacal solution of (1 mmol) cobalt(II) fluoride. Fine, reddish pink crystals separated out which were filtered, washed first with an ethanol–water mixture (1 : 1) and finally with dry ethanol, and dried in a vacuum desiccator.

$[CoL_{1.5}Cl_2(H_2O)]$ (3) was synthesized following the same procedure as for the preparation of complex (**1**).

$[CoL_{0.75}Cl_2]$ (3A) was obtained by pyrolysis of $[CoL_{1.5}Cl_2(H_2O)]$ (**3**) at 250°C in an atmosphere of nitrogen.

$[CoL_{0.25}Cl_2]$ (3B) was obtained by pyrolysis of $[CoL_{1.5}Cl_2(H_2O)]$ (**3**) at 320°C in an atmosphere of nitrogen.

$[CoL_2Cl(H_2O)]Cl$ (4) was synthesized following the same procedure as for the preparation of complex (**2**).

$[CoL_{1.5}Cl(H_2O)]Cl$ (4A) was obtained by pyrolysis of $[CoL_2Cl(H_2O)]Cl$ (**4**) at 205°C in an atmosphere of nitrogen.

$[CoL_{2.5}(H_2O)]Cl_2$ (5) was synthesized by the treatment of hydrazine hydrate (2 mmol) with $[CoL_{1.5}Cl(H_2O)]Cl$ (**4A**).

$[CoL_3]Br_2$ (6) was synthesized following the same procedure as for the preparation of complex (**1**).

$[CoL_2(H_2O)_2]Br_2$ (7) was synthesized following the same procedure as for the preparation of complex (**2**)..

$[CoL_2(H_2O)_2]SO_4$ (8) was obtained following the same procedure as for the preparation of complex (**1**).

$[CoLSO_4]$ (8A) was derived by pyrolysis of complex $[CoL_2(H_2O)_2]SO_4$ (**8**) at 255°C in an atmosphere of nitrogen.

$[CoL_2(H_2O)_2]SO_4$ (9) was synthesized by the treatment of hydrazine hydrate (2 mmol) with the complex species $[CoLSO_4]$ (**8A**) derived from complex (**8**) by pyrolytic technique.

$[CoL_3]SO_4 \cdot 0.5\ H_2O$ (10) was prepared following the same procedure as for the preparation of complex (**2**).

$[CoLSO_4]$ (10A) was synthesized by heating complex (**10**) at 245°C in an atmosphere of nitrogen.

$[CoL_{2.5}SO_4] \cdot H_2O$ (11) was prepared by the treatment of (2 mmol) hydrazine hydrate with the complex (**10A**) derived from complex (**10**) by pyrolysis in an atmosphere of nitrogen.

Thermal, spectral and magnetic measurements

These were the same as reported previously [9–12].

RESULTS

The thermal curves of $[CoL_{1.5}F_2(H_2O)]$ (**1**) are shown in Fig. 1. The TG curve shows that complex (**1**) transforms to metal fluoride at 330°C through the formation of nonisolable $[CoL_{1.5}F_2]$ and $[CoL_{0.5}F_2]$, but its DTA curve suggests that the elimination of hydrazine takes place in more steps (Fig. 1). On the other hand, both TG and DTA curves of complex (**2**) (Fig. 1) show that it loses its water molecule first like complex (**1**) and then hydrazine is lost in a single step.

Figure 2 shows the thermal curves of $[CoL_{1.5}Cl_2(H_2O)]$ (**3**). Complex (**3**) first becomes anhydrous and then immediately transforms to metal chloride via stable intermediates $[CoL_{0.75}Cl_2]$ and $[CoL_{0.25}Cl_2]$. On heating $[CoL_2Cl(H_2O)]Cl$ (**4**) transforms to the isolable $[CoL_{1.5}ClH_2O]Cl$ (**4A**) in a single step, then on further heating transforms to the metal chloride via a nonisolable species $CoCl_2 \cdot H_2O$ (Fig. 3). The DTA curve of complex (**4**) (Fig. 3) shows that the species (**4A**) transforms to $CoCl_2 \cdot H_2O$ in two steps. On heating, $[CoL_{2.5}H_2O]Cl_2$ (**5**) first loses its coordinated water and then immediately loses hydrazines in two steps through the formation of the nonisolable $[CoLCl_2]$ species.

On heating, $[CoL_3]Br_2$ (**6**) transforms to the metal salt in a single step (Fig. 4). On the other hand, the TG curve of $[CoL_2(H_2O)_2]Br_2$ (**7**) shows that elimination of two coordinated water molecules and one hydrazine molecule takes place first and then the elimination of residual hydrazine

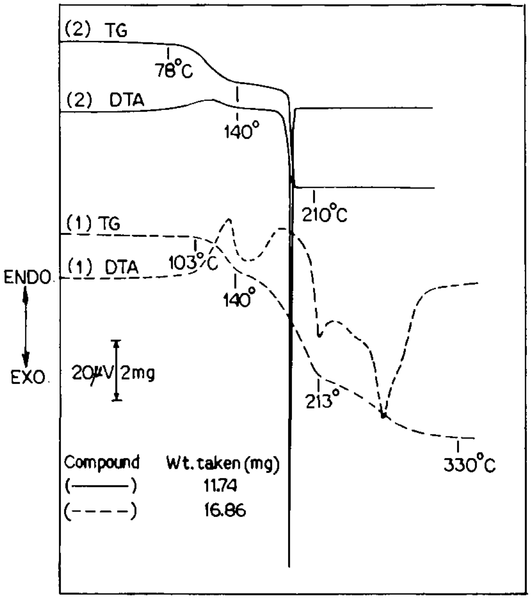

Fig. 1. Thermal curves of $[CoL_{1.5}F_2(H_2O)]$ (**1**) and $[CoL_{1.5}F_2(H_2O)]$ (**2**).

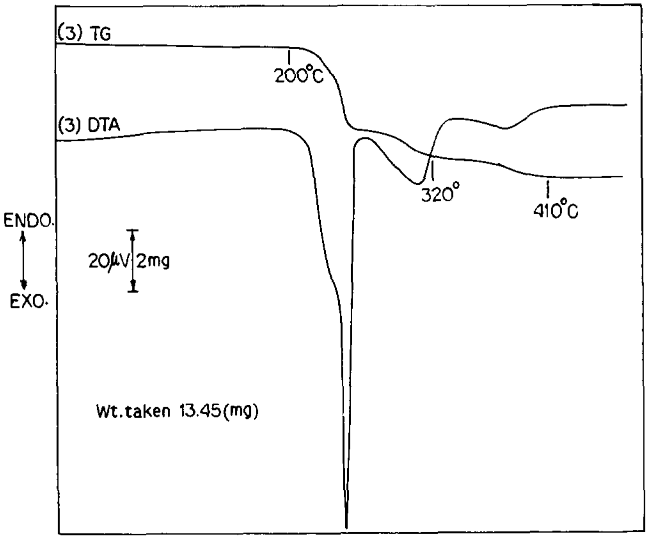

Fig. 2. Thermal curves of $[CoL_{1.5}Cl_2(H_2O)]$ (**3**).

occurs in a single step. The corresponding DTA curve shows that formation of the monohydrazine bromo complex occurs in two steps and the decomposition of the monohydrazine species to metal bromide takes place in three steps.

On heating, $[CoL_2(H_2O)_2]SO_4$ (**8**) transforms first to $[CoL_2SO_4]$, as evident from its thermal curves (Fig. 5), and then on further heating to metal

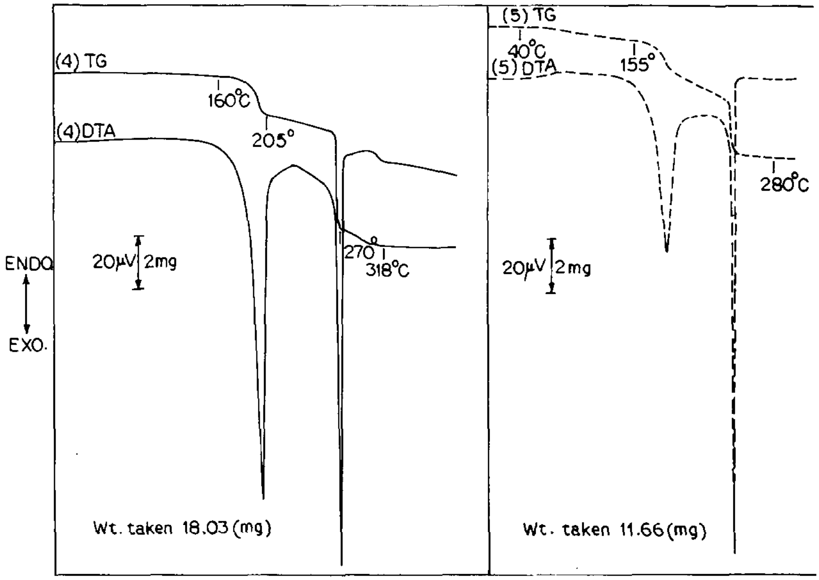

Fig. 3. Thermal curves of $[CoL_2Cl(H_2O)]Cl$ (**4**) and $[CoL_{2.5}(H_2O)]Cl_2$ (**5**).

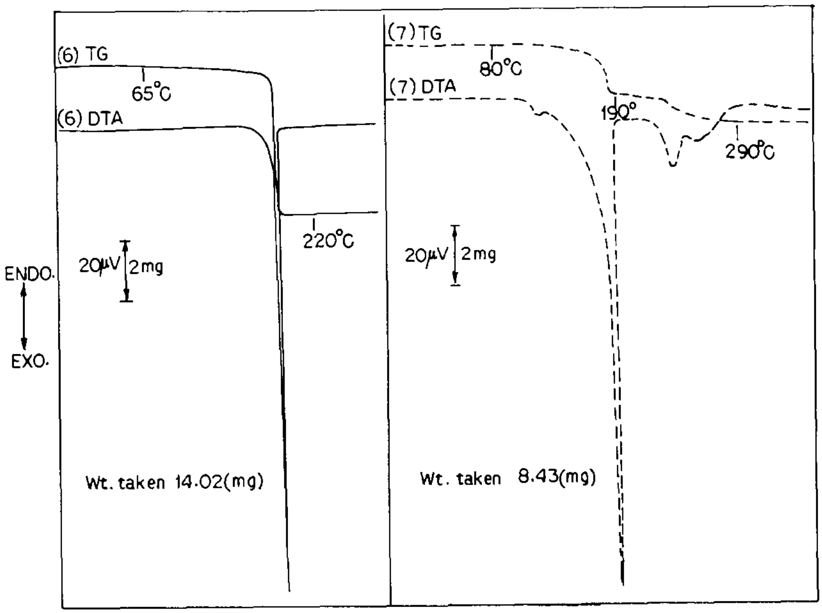

Fig. 4. Thermal curves of $[CoL_3]Br_2$ (**6**) and $[CoL_2(H_2O)_2]Br_2$ (**7**).

sulfate through the formation of isolable $[CoLSO_4]$ (**8A**). But its DTA curve shows a total of four peaks for the hydrazine elimination which suggests that the elimination of hydrazine takes place in more stages (Fig. 5). On heating,

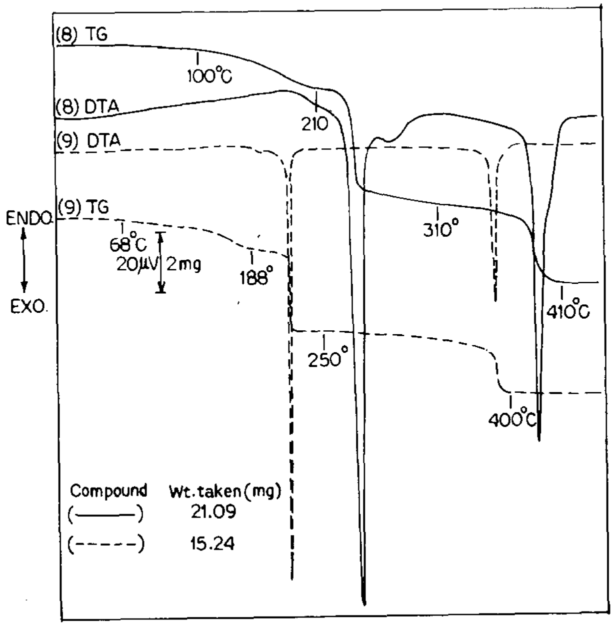

Fig. 5. Thermal curves of $[CoL_2(H_2O)_2]SO_4$ (**8**) and $[CoL_2(H_2O)_2]SO_4$ (**9**).

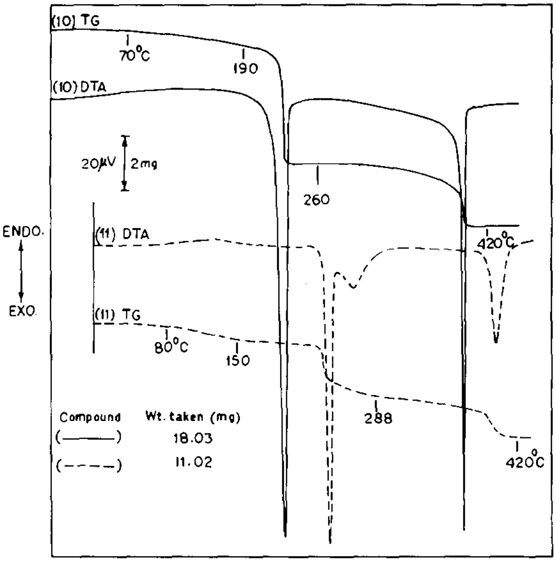

Fig. 6. Thermal curves of $[CoL_3]SO_4 \cdot 0.5\ H_2O$ (**10**) and $[CoL_{2.5}(SO_4)] \cdot H_2O$ (**11**).

$[CoL_2(H_2O)_2]SO_4$ (**9**) transforms to isolable $[CoLSO_4]$ through deaquated species (Fig. 5). On further heating it transforms to metal sulfate in a single step. The thermal curves (Fig. 6) of $[CoL_3]SO_4 \cdot 0.5\ H_2O$ (**10**) show that it becomes anhydrous first at 190°C and then transforms to the monohydrazine species in a single step at 230°C. The derived $[CoLSO_4]$ (**10A**) on further heating transforms to $CoSO_4$ in a single step. On the other hand, $[CoL_{2.5}SO_4] \cdot H_2O$ (**11**) generates isolable anhydrous species at 150°C (Fig. 6). The derived anhydrous species transforms to metal sulfate at 410°C through the formation of nonisolable $[CoL_{1.5}SO_4]$ and $[CoLSO_4]$ as intermediates.

The decomposition reactions of the complexes, along with the temperature ranges and stepwise DTA peak temperatures are reported in Table 1. The color, elemental analyses and magnetic moments of the complexes are shown in Table 2. Electronic (mull) and IR spectral data are shown in Tables 3 and 4.

DISCUSSION

Complexes derived from CoF_2 and hydrazine

The complexes (**1**) and (**2**) are identical in composition as well as in color. IR spectra (Table 4) suggest that the water molecule [13] as well as fluoride ions [14] are coordinated to the metal ion and also indicate the bridging bidentate character [2,15] of hydrazine in both of them. Electronic spectra (mull) (Table 3) as well as magnetic data (Table 2) suggest O_h geometry [16] in both cases. However, these two hydrazine complexes show differences in thermal behavior (Table 1), indicating some type of structural differences, although electronic spectral (mull) as well as magnetic data cannot distinguish the differences. The band at 550 cm^{-1} in the IR spectrum of complex (**1**) is expected to be due to ν(M–F) and the corresponding band seems to be split at 530 and 580 cm^{-1} in complex (**2**). Consequently, the fluoride ions are presumed to be in the *trans* position in complex (**1**) and *cis* position in complex (**2**). The $\delta(NH_2)$ and $\rho_w(NH_2)$ bands [17] of complex (**2**) are comparatively broad compared with those of complex (**1**) which indicates that the hydrogens of the NH_2 groups of complex (**2**) are probably strongly hydrogen bonded, whilst in complex (**1**), the hydrogens of the NH_2 groups are possibly not hydrogen bonded. The results (Fig. 1, Table 1) show

TABLE 1

Thermal parameters of the cobalt(II) complexes of hydrazine (L)

Decomposition reactions	Temp. range (°C)	DTA peak temp. (°C)
$[CoL_{1.5}F_2H_2O]$ (**1**) $\rightarrow CoL_{1.5}F_2$	103–140	130
$CoL_{1.5}F_2 \rightarrow CoL_{0.5}F_2$	140–213	180, 190, 210
$CoL_{0.5}F_2 \rightarrow CoF_2$	213–330	263, 278
$[CoL_{1.5}F_2H_2O]$ (**2**) $\rightarrow CoL_{1.5}F_2$	78–140	118
$CoL_{1.5}F \rightarrow CoF_2$	140–190	190
$[CoL_{1.5}Cl_2H_2O]$ (**3**) $\rightarrow CoL_{1.5}Cl_2$	200–232	225
$CoL_{1.5}Cl_2 \rightarrow CoL_{0.75}Cl_2$	232–250	240
$CoL_{0.75}Cl_2 \rightarrow CoL_{0.25}Cl_2$	275–320	305
$CoL_{0.25}Cl_2 \rightarrow CoCl_2$	360–400	380
$[CoL_2ClH_2O]Cl$ (**4**) $\rightarrow CoL_{1.5}ClH_2OCl$	160–205	205
$CoL_{1.5}ClH_2OCl \rightarrow CoCl_2 \cdot H_2O$	230–270	260, 270
$CoCl_2 \cdot H_2O \rightarrow CoCl_2$	270–318	306
$[CoL_{2.5}H_2O]Cl_2$ (**5**) $\rightarrow CoL_{2.5}Cl_2$	40–155	85
$CoL_{2.5}Cl_2 \rightarrow CoLCl_2$	155–248	193
$CoLCl_2 \rightarrow CoCl_2$	248–250	250
$[CoL_3]Br_2$ (**6**) $\rightarrow CoBr_2$	65–190	190
$[CoL_2(H_2O)_2]Br_2$ (**7**) $\rightarrow CoLBr_2$	80–190	120, 180
$CoLBr_2 \rightarrow CoBr_2$	190–290	235, 265, 280
$[CoL_2(H_2O)_2]SO_4$ (**8**) $\rightarrow CoL_2SO_4$	100–230	185
$CoL_2SO_4 \rightarrow CoLSO_4$	230–280	250, 270
$CoLSO_4 \rightarrow CoSO_4$	340–410	390, 400
$[CoL_2(H_2O)_2]SO_4$ (**9**) $\rightarrow CoLSO_4$	68–220	170, 215
$CoLSO_4 \rightarrow CoSO_4$	290–400	395
$[CoL_3]SO_4 \cdot 0.5\ H_2O$ (**10**) $\rightarrow CoLSO_4$	70–230	225
$CoLSO_4 \rightarrow CoSO_4$	290–400	400
$[CoL_{2.5}SO_4] \cdot H_2O$ (**11**) $\rightarrow CoL_{2.5}SO_4$	80–150	115
$CoL_{2.5}SO_4 \rightarrow CoL_{1.5}SO_4$	220–240	238
$CoL_{1.5}SO_4 \rightarrow CoLSO_4$	240–288	270
$CoLSO_4 \rightarrow CoSO_4$	298–410	393

TABLE 2

Analytical data and magnetic moments of cobalt(II) complexes of hydrazine (L)

Complex		Color	Analytical data [a]			$\mu_{eff.}$ (B.M.)
			Co (%)	N (%)	X (%)	
$[CoL_{1.5}F_2H_2O]$	**(1)**	Pink	36.18 (36.17)	25.75 (25.77)	23.29 (23.32)	5.13
$[CoL_{1.5}F_2H_2O]$	**(2)**	Pink	36.15 (36.17)	25.74 (25.77)	23.30 (23.32)	5.21
$[CoL_{1.5}Cl_2H_2O]$	**(3)**	Pink	29.81 (30.08)	21.42 (21.43)	36.20 (36.23)	5.03
$[CoL_{0.75}Cl_2]$	**(3A)**	Bluish pink	38.27 (38.28)	13.60 (13.64)	45.91 (46.12)	5.49
$[CoL_{0.25}Cl_2]$	**(3B)**	Bluish pink	42.69 (42.72)	5.80 (5.79)	51.45 (51.47)	5.45
$[CoL_2ClH_2O]Cl$	**(4)**	Reddish pink	27.77 (27.80)	26.39 (26.42)	33.49 (33.50)	5.16
$[CoL_{1.5}ClH_2O]Cl$	**(4A)**	Violet	30.10 (30.08)	21.40 (21.43)	36.21 (36.23)	5.37
$[CoL_{2.5}H_2O]Cl_2$	**(5)**	Pink	25.82 (25.85)	30.67 (30.70)	31.11 (31.14)	5.12
$[CoL_3]Br_2$	**(6)**	Pink	18.68 (18.71)	26.64 (26.68)	50.75 (50.77)	5.37
$[CoL_2(H_2O)_2]Br_2$	**(7)**	Pink	18.45 (18.48)	17.52 (17.56)	50.00 (50.15)	5.16
$[CoL_2(H_2O)_2]SO_4$	**(8)**	Cream	22.98 (23.11)	21.94 (21.96)	12.53 (12.55) [b]	5.27
$[CoLSO_4]$	**(8A)**	Pink	31.50 (31.52)	14.94 (14.97)	16.91 (17.11) [b]	5.36
$[CoL_2(H_2O)_2]SO_4$	**(9)**	Cream	22.99 (23.11)	21.92 (21.96)	12.52 (12.55) [b]	5.20
$[CoL_3]SO_4 \cdot 0.5\ H_2O$	**(10)**	Light pink	22.63 (22.67)	32.28 (32.31)	12.30 (12.31) [b]	5.11
$[CoLSO_4]$	**(10A)**	Pink	31.49 (31.52)	14.94 (14.97)	16.93 (17.11) [b]	4.86
$[CoL_{2.5}SO_4] \cdot H_2O$	**(11)**	Pink	23.27 (23.30)	27.63 (27.67)	12.61 (12.65) [b]	5.14

[a] Calculated values are in parentheses.

[b] Sulphur.

TABLE 3

Electronic (mull) spectra of cobalt(II) complexes of hydrazine (L)

Complex		Absorption [a] maxima (nm)
$[CoL_{1.5}F_2H_2O]$	**(1)**	492, 460
$[CoL_{1.5}F_2H_2O]$	**(2)**	524(sh), 492, 452
$[CoL_{1.5}Cl_2H_2O]$	**(3)**	556(sh), 508, 452
$[CoL_{0.75}Cl_2]$	**(3A)**	700(sh), 532, 508, 460
$[CoL_{0.25}Cl_2]$	**(3B)**	692(sh), 620(sh), 540, 508
$[CoL_2ClH_2O]Cl$	**(4)**	644(sh), 548, 508, 448
$[CoL_{1.5}ClH_2O]Cl$	**(4A)**	668(sh), 620, 580, 556, 512, 452
$[CoL_{2.5}H_2O]Cl_2$	**(5)**	772(sh), 644(sh), 508, 460
$[CoL_3]Br_2$	**(6)**	560(sh), 520, 440
$[CoL_2(H_2O)_2]Br_2$	**(7)**	670(sh), 630(sh), 562, 518, 440
$[CoL_2(H_2O)_2]SO_4$	**(8)**	524(sh), 500, 468, 300
$[CoLSO_4]$	**(8A)**	524(sh), 508, 468, 300
$[CoL_2(H_2O)_2]SO_4$	**(9)**	532(sh), 500, 468
$[CoL_3]SO_4 \cdot 0.5\ H_2O$	**(10)**	476
$[CoLSO_4]$	**(10A)**	524(sh), 508, 468, 300
$[CoL_{2.5}SO_4] \cdot H_2O$	**(11)**	540(sh), 476, 300

[a] Arbitrary absorbance; sh = shoulder.

that isolation of any stable intermediate complex species from complexes (**1**) and (**2**) is not at all feasible. As a result, it is very difficult to follow the mechanism of decomposition of these complexes. However, complex (**1**) appears to be complicated in thermal behavior, as evident from its five overlapping exotherms compared with that of complex (**2**). But it is true that both the complexes become anhydrous first, as evident from their DTA profiles though it was not possible to isolate the deaquated species in the solid state. The reason for the instability of $CoL_{1.5}F_2$ is that Co^{2+} does not prefer pentacoordination. Interestingly, Table 1 shows that complex (**1**) is thermally more stable than complex (**2**). Another interesting point is that transformation of complex (**2**) to CoF_2 takes place at a lower temperature (Table 1) in comparison to that of complex (**1**).

Complexes derived from $CoCl_2$ and hydrazine

It is interesting to note that complexes (**3**) and (**4**), differing in elemental composition as well as in color, exist in O_h geometry as evident from their electronic (mull) spectra and magnetic data (Tables 2 and 3). Hydrazine here also exists as a bridging bidentate ligand. The water molecule present in both the complexes appears to be coordinated [18] as evident from the presence of sharp $\nu(OH)$ and $\delta(HOH)$ bands (Table 4) in their spectra. This is also supported by thermal profiles since water elimination takes place at a much elevated temperature. In general, the DTA curve shows an endotherm for the

TABLE 4

Infrared spectral data (cm^{-1}) of cobalt(II) complexes of hydrazine (L)

Complex		Band assignments [a]							
		$\nu(OH)$	$\nu(NH_2)$	$\delta(HOH)$ and/or $\delta(NH_2)$	$\delta(NH_2)$	$\rho_w(NH_2)$ and $\rho_w(HOH)$	$\rho_w(NH_2)$	$\nu(N-N)$	$\nu(M-X)$
$[CoL_{1.5}F_2H_2O]$	**(1)**	3460 br	3360 w 3310 w 3150 w, br	1650 w 1630 (sh) 1620 m	1590 s 1560 m	1392 m	1330 w 1302 w	965 m	550 m
$[CoL_{1.5}F_2H_2O]$	**(2)**	3460 (sh)	3310 m 3240 m 3160 (sh)	1660 m 1630 (sh)	1590 s, br	1380 (sh)	1365 m, br	980 w 960 m	580 m 530 m
$[CoL_{1.5}Cl_2H_2O]$	**(3)**	3540 m	3270 s 3220 m 3125 (sh)	1600 vs	1560 s	1395 m	1335 m 1300 m	970 m	360 (sh) 350 m 330 w
$[CoL_{0.75}Cl_2]$	**(3A)**	—	3290 s 3260 s 3220 m 3140 w	—	1590 s 1570 m	—	1305 vw 1330 m	965 m	300 m
$[CoL_{0.25}Cl_2]$	**(3B)**	—	3260 m	—	1600 s	—	1318 w	975 vw	335 m 270 (sh) 260 m
$[CoL_2ClH_2O]Cl$	**(4)**	3540 m	3270 s 3220 m 3125 (sh)	1600 vs	1560 s 1555 (sh)	—	1335 m 1300 m	970 m	345 m
$[CoL_{1.5}ClH_2O]Cl$	**(4A)**	3380 m, br	3275 (sh) 3265 s 3210 m 3130 (sh)	1610 (sh)	1598 s 1560 s 1550 s	1400 vw	1335 w 1302 m	968 m 960 (sh)	340 w, br

$[CoL_{2.5}H_2O]Cl_2$	**(5)**	3540 (sh) 3500 w	3280 s 3230 m 3150 w	1620 (sh)	1600 s 1570 s	1375 m, br	1338 m 1308 w	970 m 960 (sh)	—
$[CoL_3]Br_2$	**(6)**	—	3260 s 3205 m 3120 (sh)	—	1590 s 1555 m	—	1332 w 1305 w	960 m	—
$[CoL_2(H_2O)_2]Br_2$	**(7)**	3525 m	3250 s 3200 m 3125 (sh)	1630 (sh)	1595 s 1560 s	1398 m	1338 w 1308 m	965 m	—
$[CoL_2(H_2O)_2]SO_4$	**(8)**[b]	3400 br	3250 s 3200 w	1615 m	1590 s 1555 s 1550 (sh)	1380 w, br	1330 m 1300 m	955 m	—
$[CoLSO_4]$	**(8A)**[b]	—	3330 s 3320 (sh) 3280 m 3200 w	—	1572 s	—	—	972 vw	—
$[CoL_2(H_2O)_2]SO_4$	**(9)**[b]	3400 br	3310 s 3260 s 3200 w 3180 w	1620 m	1590 s 1575 (sh) 1560 m	1395 vw	1338 w 1305 w	965 m	—
$[CoL_3]SO_4 \cdot 0.5\ H_2O$	**(10)**[b]	3400 br	—	1618 m	1590 s 1555 s 1550 (sh)	—	1330 m 1300 m	960 m	—
$[CoLSO_4]$	**(10A)**[b]	—	3315 s 3270 m 3180 w	—	1580 (sh) 1575 s		—	975 vw	—
$[CoL_{2.5}SO_4] \cdot H_2O$	**(11)**[b]	3540 br	3250 s 3200 w	1630 (sh)	1595 s 1560 s	1400 vw	1340 m 1310 m	980 w 965 m	—

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[a] s, strong; m, medium; br, broad; w, weak; vw, very weak; sh, shoulder.

[b] The band positions and their assignments for the SO_4 group are mentioned in the text.

water elimination process but it is not observed here. The reason for this may be due to some kind of rearrangement taking place during elimination of water and hydrazine. These two complexes show a band at ~ 350 cm^{-1} which is probably due to ν(Co–Cl), indicating terminal chloride coordination [19]. The foregoing discussion suggests that all the chloride ions are coordinated to Co^{2+} in complex (**3**) and only one chloride ion is coordinated to Co^{2+} in complex (**4**) for attaining hexacoordination. The evaluation of conductance data for complexes (**3**) and (**4**) is not possible due to their insolubility in most of the solvents. It was not possible to isolate the deaquated species from complex (**3**) as the deaquated species probably attains an unfavorable pentacoordinated species. The species $[CoL_{0.75}Cl_2]$ (**3A**) synthesized pyrolytically in the solid state from complex (**3**) shows a higher magnetic value (μ_{eff} 5.49 BM). The bridging and bidentate characters of hydrazine are also maintained here. The ν(Co–Cl) band in the IR spectrum of (**3**) at ~ 340 cm^{-1} is shifted to 300 cm^{-1} in the case of (**3A**). The electronic spectrum (mull) of complex (**3A**) suggests $O_h \rightarrow T_d$ transformation [16,20] as the absorption bands of (**3**) are shifted towards a lower energy region in the case of complex (**3A**).

The color, and magnetic values of complexes (**3A**) and (**3B**) are similar to each other, but their spectral data (electronic and IR) are different, though the characteristic IR bands (Table 4) for bridged hydrazine are almost identical with those of (**3A**). The bands at 335, 270 and 250 cm^{-1} in the IR spectrum of (**3B**) are probably due to terminal and bridged ν(Co–Cl). Analytical data of complex (**3B**) suggest the formula $CoL_{0.25}Cl_2$. These observations suggest complex (**3B**) to exist as $[Co_4LCl_8]$. The electronic spectral data of (**3B**) (Table 3) suggest that Co^{2+} exists in T_d geometry where six chloride ions are proposed to be bridged and the residual chloride ions are linked terminally. On the contrary, the magnetic moments of (**3A**) and (**3B**) are comparatively higher than what should be expected for T_d Co^{2+} stereochemistry. This discrepancy is not fully understood.

It is interesting to note that on heating complex (**4**) elimination of hydrazine starts initially instead of water elimination though water has a weak coordinating ability. Attachment of the water molecule with $CoCl_2$ at 270°C is verified by IR spectra as well as by its endothermic peak at 306°C in the DTA curve (Table 1). The species $CoL_{1.5}H_2OCl_2$ (**4A**), violet in color and synthesized from (**4**), shows a high magnetic value, and its electronic spectral bands shift towards the lower energy region in comparison to those of its parent compound. The pentacoordinated geometry of Co^{2+} in complex (**4A**) is characterized [21] by its electronic (mull) spectra (Table 3). On further heating of complex (**4A**), evolution of 1.5 molecules of hydrazine per Co^{2+} complex occurs sharply, suggesting the similar bonding pattern of hydrazines in the pentacoordinated species. It is very much peculiar behavior of complex (**4A**) that the water molecule present in the system evolves after elimination of hydrazines, as evident from its DTA profile. Although it was not possible to isolate $CoCl_2 \cdot H_2O$ in the pure form, we have taken IR spectrum isolating the hydrated species by temperature-arrest technique at ~ 270°C (Table 1) at which hydrazine elimination ends. This isolated species contains mainly $CoCl_2 \cdot H_2O$ which exhibits three distinct bands at 3400 [ν(OH)], 1620 [δ(HOH)] and 1395 cm^{-1}. The occurrence of the band at 1395 cm^{-1} suggests the presence of a $\rho_w(H_2O)$ band which is not generally found by the hydrated species. But it is not improbable to consider that the coordinated water may possess a similar symmetry (C_{2v}) to that of the NH_2 group, suggesting the appearance of a similar wagging frequency in an almost similar region i.e., ~ 1400 cm^{-1}. Consequently, it is clear from the IR spectrum that the water molecule is attached to Co^{2+} even after the elimination of residual hydrazines from (**4A**). The absence of the characteristic band at ~ 1400 cm^{-1} in complex (**4**) is probably due to the restriction of wagging of coordinated H_2O due to the strong hydrogen bonding of both hydrogens of the H_2O molecule. On the contrary, since the band at ~ 1400 cm^{-1} exists in complex (**4A**), it is expected that hydrogen bonding exists in the system but the wagging of coordinated H_2O probably does not become nullified due to some structural changes. It seems that ρ_w(HOH) appearing in the IR spectrum of the isolated product at ~ 270°C is not restricted at all as the hydrogen bonding is destroyed by evolution of the hydrazine molecule.

It is interesting to note that the treatment of hydrazine hydrate with complex (**4A**) gives $[CoL_{2.5}(H_2O)]Cl_2$ (**5**). It seems probable that as hydrazine is a potentially good ligand rather than Cl^-, it displaces Cl^- and coordinates to Co^{2+} in complex (**4A**), forming again an O_h species, as evident from its electronic spectrum in mull (Table 3). As the water molecule is strongly hydrogen bonded, the displacement of H_2O by N_2H_4 does not occur, but the appearance of ρ_w(HOH) at ~ 1400 cm^{-1} in complex (**5**) suggests the lower restriction of the H_2O molecule by hydrogen bonding causing the evolution of water molecule at the very initial stage by thermal treatment resulting in either $[CoL_{2.5}]Cl_2$ or hexacoordinated $[CoL_{2.5}Cl]Cl$ having possibly bridged hydrazine. The evolution of 1.5 molecules of hydrazine from the deaquated species may result in nonisolable four-coordinated $CoLCl_2$.

Complexes derived from $CoBr_2$ and hydrazine hydrate

The hydrazines present in complexes (**6**) and (**7**) are bridged [2,15]. The coordination of the water molecule in complex (**7**) is well characterized by the presence of some new bands, unlike complex (**6**), which are nothing but ν(OH), ρ_w(HOH) and ρ_r(HOH) in the IR spectrum (Table 4). Complexes (**6**) and (**7**) belong to O_h geometry, as evident from electronic spectra (mull) and magnetic data. However, some new bands in the lower energy region of the spectrum of complex (**7**) at 630 and 670 nm are probably due to the [CoO] chromophore [21] in complex (**7**). Three hydrazines from complex (**6**) evolve on heating for a time which implies that the hydrazines are bonded to Co^{2+} environmentally in such a manner that Co–N bonds possibly exist more symmetrically in the system. The DTA profile of complex (**7**) does not indicate clearly the presence of two water molecules. The observation of an exotherm at the beginning of decomposition followed by another very broad exotherm (Fig. 4) suggests that elimination of water and hydrazine takes place in parallel which results in suppression of the endothermic effect for the water elimination process by the extreme exothermic reaction due to hydrazine elimination. It was our expectation that complex (**7**) would generate CoL_2Br_2 after deaquation. The simultaneous elimination of two H_2O molecules and one hydrazine probably suggests that bromide ions prefer to exist bridged in $CoLBr_2$ (nonisolable intermediate formed during pyrolysis) rather than nonbridged [CoL_2Br_2 expected to be formed from complex (**7**)].

Complexes derived from $CoSO_4$ and hydrazine hydrate

Electronic (mull) spectra as well as magnetic data of complexes (**8**) and (**11**) suggest that both belong to O_h symmetry, but the appearance of only one absorption band at 476 nm for complex (**10**) suggests its more symmetric nature and possession of [CoN_6] chromophores [22]. The appearance of more than one band in the same region (Table 4) in complex (**8**) is probably due to the presence of a [CoN_4O_2] chromophore [21]. The IR spectral data (Table 4) of these two complexes show that hydrazine molecules are bridged and the water molecule is coordinated to Co^{2+} in complex (**8**) only. The electronic spectrum (mull) of complex (**10**) does not agree with that of complex (**6**). The multiple bands observed near 500 nm for complex (6) are probably due to the transition $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ in admixture with spin forbidden transition [21] to doublet states which are mainly from the free ion 2_G and 2_H terms. Such a transition is not possible in complex (**10**), causing only a single band at ~ 500 nm. The structure of intermediate complex species (**10A**) would be more symmetric than that of the species (**8A**) as the magnetic moment of complex (**8A**) is comparatively higher than that of complex (**10A**) which would indicate that the orbital contribution to magnetic moments would be much higher in complex (**8A**) due to less symmetry. However, the electronic spectra (mull) of these two complexes do not differ at all, indicating the presence of some chromophore, whilst the distortional phenomenon as expected should have displayed any characteristics in the electronic spectra (mull) but this could not be traced out here. The IR spectra of complexes (**8A**) and (**10A**) are similar in all respects except a split [585, 600 cm^{-1} of complex (**8A**)] of the band at 590 cm^{-1} of complex (**10A**). This band is expected to be responsible for ν(Co–N) [23] which would imply that hydrazine molecules should be bonded to Co^{2+} in the *trans* position for complex (**10A**), whilst one Co–N bond would be at basal and the other

Co–N would be at apical for complex (**8A**) as SO_4^{2-} ion should be tetradentate in both cases, as evident from IR spectra. The only broad band due to SO_4^{2-} at ~ 1110 cm^{-1} would probably be due to its T_d nature [24] if all the oxygen atoms of SO_4^{2-} are bonded to Co^{2+} which must happen for formation of O_h geometry in the intermediate species. Moreover, the ν(N–N) bands for the complex species (**8A**) and (**10A**) are found to be very weak, probably due to the formation of hydrogen bonding of NH hydrogen with the oxygen of the SO_4 group.

It is interesting to note that the band $\nu(NH_2)$ at 3250 cm^{-1} of complex (**8**) splits at 3280 and 3330 cm^{-1} and shifts to a higher energy region in complex (**8A**). The bands $\rho_w(NH_2)$ at 1300 and 1330 cm^{-1} of complex (**8**) become IR inactive in complex (**8A**), whilst the band $\rho_r(NH_2)$ which may be merged with the band at ~ 600 cm^{-1} in complex (**8**) is found to appear distinctly at 625 cm^{-1} with a shoulder at 640 cm^{-1} in complex (**8A**). These observations would lead to the idea that the symmetry (with respect to N) of N_2H_4 is probably different in the two cases. However, it is reported in the literature [25] that N_2H_4 exists in the *gauche* form in all physical states, but such a type of symmetry change is expected in the hydrazine complexes if the *gauche* form of N_2H_4 changes to either the *cis* or *trans* form.

Complexes (**9**) and (**11**) derived from complexes (**8A**) and (**10A**) belong to O_h geometry. The IR spectrum of complex (**9**) shows that the basic structure of complex (**8A**) exists in the system as evident from $\nu(NH_2)$, $\rho_w(NH_2)$, $\rho_r(NH_2)$ and ν(Co–N) bands (Table 4). The coordinated sulfate group in (**8A**) is displaced by hydrazine, resulting in $[CoL_2(H_2O)_2]SO_4$ (**9**). The noncoordination of SO_4 group in (**9**) is identified by the appearance of IR bands as observed in the case of coordinated H_2O molecules in complexes (**7**) and (**8**). The thermal decomposition also supports the water coordination as the elimination of water molecule along with one hydrazine molecule occurs at a time. The mode of elimination of the residual hydrazine is similar to that of (**8A**), as evident from the TG and DTA curves of complexes (**8**) and (**9**).

It is also interesting to note that the basic structure of complex (**11**) is in agreement with that of complex (**10**), unlike complex (**10A**), as evident from the similar $\nu(NH_2)$, $\rho_w(NH_2)$ and $\rho_r(NH_2)$ bands as observed in complexes (**10**) and (**11**). But in this case, the SO_4 group is found to be monodentate [24], as evident from the split bands due to the SO_4 group at 1112 and 1170 cm^{-1}. Moreover, the appearance of two bands, like complexes (**8**) and (**9**), in the electronic spectrum (mull) of complex (**11**) is possibly due to the similar chromophoric nature with respect to complexes (**8**) and (**9**).

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