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Preparation, characterisation and thermal reactivity of transition metal complexes of hydrazine with citric acid

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Abstract

Hydrazinium metal citrate hydrates of compositions $N_2H_5M(Hcit)H_2O$ (M = Mn, Co, Ni or Zn; H_4cit = citric acid) and $(N_2H_5)_2Ni(cit)4H_2O$ and metal citrate hydrazinates of formulae $M_3(Hcit)_26N_2H_4$ (M = Co, Ni, Zn or Cd] and $Cu_2(cit)N_2H_42H_2O$ have been prepared and characterised by elemental analysis, IR spectroscopy, X-ray powder diffraction and thermal studies. IR absorption bands give evidence for the coordination of $N_2H_5^+$ cation as a monodentate and neutral hydrazine as a bidentate bridging ligands in the complexes. Dehydration and dehydrazination followed by decomposition of the organic component produced the corresponding metal oxide as the final residue. The coordination of water has been substantiated by thermal analyses. The X-ray powder diffraction patterns show isomorphism among similar set of complexes.

Keywords: Hydrazinium; Hydrazine; Citric acid; Metal complexes; Thermal decomposition

1. Introduction

Thermal studies on metal carboxylates with hydrazine are of more interest than their non-carboxylate counterparts due to their easier combustibility to yield fine particles of the metal or metal oxides [1–3]. Further, the interaction of hydrazine with the metal ion in the presence of a carboxylate system is versatile and at different ratio of mixing of metal ion and ligand solutions containing hydrazine hydrate and carboxylic acid leads to different products [4,5]. The thermal decomposition and IR spectroscopic analysis of many metal carboxylates with hydrazine have been reported [6–14]. However, as far as we are aware, except glycolates [15], no work has been done on the thermal analysis of metal hydrazine complexes of hydroxycarboxylic acids in general, and citric acid in particular (hydroxy tricarboxylic acid, $C_6H_8O_7$-H_4cit). Many metal complexes with citrate anion have been studied both in solution [16–19] and in the solid state [20–25]. Although, many metal complexes including ammonium [24,25], potassium [22,24], sodium [24], pyridinium and neocupronium [23] metal citrates have been reported, the corresponding hydrazinium and also the hydrazinate metal citrates are not known. The extraordinary versatility of citric acid on coordination is well known and this together with hydrazine may make the thermal chemistry of metal citrates particularly interesting like other carboxylate systems. This prompted us to prepare the metal hydrazinium/hydrazine citrates and characterise them by analytical, spectral, X-ray diffraction and thermal studies. This report presents the results of such studies.

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2. Experimental

2.1. Preparation of the complexes

Citric acid is a tribasic acid and is expected to form simple salts with hydrazine. However, attempts to isolate simple salts and use them as ligands were unsuccessful. Hence, an aqueous mixture containing citric acid and hydrazine hydrate in different mole ratios was used as a ligand for the preparation of the complexes.

$N_2H_5M(Hcit)H_2O$, where M = Mn, Co, Ni or Zn(II). These complexes were prepared by the addition of an aqueous solution (50 cm^3) containing a mixture of citric acid monohydrate (1.05 g, 0.01 mol) and hydrazine hydrate (0.75 cm^3, 0.03 mol) to the respective metal nitrate hexahydrates (e.g., 1.455 g, 0.01 mol of $Co(NO_3)_2 6H_2O$; in the case of Mn, manganese(II) acetate tetrahydrate 1.225 g, 0.01 mol was used) in distilled water (50 cm^3). The resulting clear solution ($pH < 6$) was concentrated to about half volume and left at room temperature to crystallise. After three days, the crystalline products were separated from the solutions and washed successively with distilled water, alcohol and ether and dried in air. Nickel complex was separated by the addition of alcohol.

$(N_2H_5)_2Ni(cit)4H_2O$. The reaction of an aqueous solution (50 cm^3) of nickel nitrate hexahydrate (1.46 g, 0.01 mol) with an aqueous solution (50 cm^3) containing citric acid monohydrate (1.05 g, 0.01 mol) and hydrazine hydrate (1 cm^3, 0.04 mol) yielded the titled product. While concentrating the resulting solution (pH 6 to 7), small amounts of product separated from the solution, but this was re-dissolved in the mother liquor as a clear solution. The product separated from the concentrated solution was washed with cold water, alcohol and dried in vacuo.

$M_3(Hcit)_2 6N_2H_4$, where M = Co, Ni, Zn or Cd. To an aqueous solution (50 cm^3) of the respective metal nitrate hexahydrates (e.g., 1.455 g of $Co(NO_3)_2 6H_2O$, 0.01 mol), an aqueous mixture (50 cm^3) containing citric acid monohydrate (1.05 g, 0.01 mol) and hydrazine hydrate (1.5 cm^3, 0.06 mol) was added slowly with constant stirring. The resulting clear solution ($pH > 8$) was concentrated on a water bath to half of its original volume except for cadmium. The concentrated solutions were left aside at room temperature for crystallisation. The products separated after two days were filtered, washed successively with water, alcohol and ether and dried in air. In the case of cadmium, the product was obtained immediately after the addition of the ligand solution.

$Cu_2(cit)N_2H_4 2H_2O$. This complex was prepared by the addition of an aqueous solution (50 cm^3) of citric acid monohydrate (1.05 g, 0.01 mol) and hydrazine hydrate (0.25 cm^3, 0.01 mol) to an aqueous solution (50 cm^3) of copper nitrate trihydrate (1.208 g, 0.01 mol). The product immediately formed was separated from the solution after 15 min and washed with water, alcohol and ether and air dried. Excess addition of hydrazine hydrate, that is more than 0.04 mol reduced the Cu(II) to metallic copper.

All the complexes were highly insoluble in water except dihydrazinium nickel citrate tetrahydrate which is partially soluble in cold water, but completely soluble in hot water. All are insoluble in alcohol and all other organic solvents and are stable in air and insensitive to light.

2.2. Physico-chemical techniques

All the chemicals used were pure commercial grade and the solvents were distilled before use. The hydrazine content of the complexes was determined volumetrically using a standard KIO_3 solution (0.025 M) under Andrews' conditions [26]. The metals after destroying the organic part and hydrazine by treatment with concentrated HNO_3 and evaporating the excess HNO_3, were determined volumetrically by EDTA titration. The reflectance spectra of the powdered complexes were recorded on a Shimadzu 240-A UV-Visible spectrophotometer in the 200–800 nm range. The magnetic susceptibility measurements were carried out using a Gouy balance and $Hg[Co(NCS)_4]$ as the calibrant at room temperature. IR spectra were recorded as KBr pellets with a Perkin-Elmer 597 model spectrophotometer in the 4000–200 cm^{-1} range. Simultaneous TG-DTA measurements were carried out on a STA 1500 thermal analyser. The experiments were carried out in air using platinium cups as sample holders with 5–10 mg of the samples at the heating rate of 10°C min^{-1}. X-ray powder diffraction patterns were obtained using a Philips X-ray diffractometer model PW 1050/70 and Cu K_α radiation with Ni filter.

Table 1
Analytical data

Compound	Colour	Percentage of hydrazine		Percentage of metal		Yield (%)
		Found	Calculated	Found	Calculated	
$N_2H_5Mn(Hcit)H_2O$	Pale pink	10.90	10.85	18.70	18.63	85
$N_2H_5Co(Hcit)H_2O$	Dark pink	10.85	10.70	19.40	19.71	90
$N_2H_5Ni(Hcit)H_2O$	Greenish blue	10.60	10.71	19.10	19.65	80
$N_2H_5Zn(Hcit)H_2O$	Colourless	10.70	10.48	21.20	21.41	85
$(N_2H_5)_2Ni(cit)4H_2O$	Blue	16.60	16.64	14.80	15.26	80
$Co_3(Hcit)_26N_2H_4$	Pink	25.30	25.71	23.70	23.67	90
$Ni_3(Hcit)_26N_2H_4$	Bluish violet	26.00	25.73	22.90	23.60	90
$Zn_3(Hcit)_26N_2H_4$	Colourless	24.90	25.06	25.20	25.60	80
$Cd_3(Hcit)_26N_2H_4$	Colourless	20.70	21.16	36.60	37.00	90
$Cu_2(cit)N_2H_42H_2O$	Dark blue	08.30	08.95	32.30	32.85	72

3. Results and discussion

Preparation of the compounds depends on pH control and the mole ratio of the reactants. The chemical formulae proposed were in good agreement with the analytical data presented in Table 1.

3.1. Magnetic moments and electronic spectra

The magnetic moments and electronic spectral data (Table 2) indicate that the complexes had a high-spin octahedral co-ordination [27] except the copper complex which had square planar co-ordination [12]. The zinc and cadmium complexes were diamagnetic as expected.

3.2. Infrared spectra

Characteristic IR absorption freqencies of the free acid and the complexes are listed in Table 3. The mixed modes of O–H of the citric acid and the coordinated water showed a distinct broad band in the region 3500–3360 cm^{-1} for the hydrazinium monohydrated metal citrate complexes. However, all the hexahydrazine complexes, showed a band around 3400 cm^{-1} ascribable to O–H stretching of the citrate ions. Further, this band position is almost the same as in the case of free acid indicating that the hydroxyl group was not ionised. The medium intensity bands around 3500 and 3500–3400 cm^{-1} due to the dihydrazinium nickel and copper hydrazine com-

Table 2
Magnetic moments and electronic spectral data

Compound	Magnetic moment (BM)	Absorption maxima (cm^{-1})	Assignment
$N_2H_5Mn(Hcit)H_2O$	5.90	24390	$^6A_{1g}\rightarrow{}^4A_{1g}(G)$, $^4E_g(G)$
		29410	$^6A_{1g}\rightarrow{}^4E_g(D)$
$N_2H_5Co(Hcit)H_2O$	5.10	20000	$^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$
$N_2H_5Ni(Hcit)H_2O$	2.90	17200	$^3A_{2g}\rightarrow{}^3T_{1g}(F)$
		26300	$^3A_{2g}\rightarrow{}^3T_{1g}(P)$
$N_2H_5Zn(Hcit)H_2O$	Diamagnetic	–	–
$(N_2H_5)_2Ni(cit)4H_2O$	3.40	17000	$^3A_{2g}\rightarrow{}^3T_{1g}(F)$
		27000	$^3A_{2g}\rightarrow{}^3T_{1g}(P)$
$Co_3(Hcit)_26N_2H_4$	4.90	20600	$^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$
$Ni_3(Hcit)_26N_2H_4$	3.20	17200	$^3A_{2g}\rightarrow{}^3T_{1g}(F)$
		26300	$^3A_{2g}\rightarrow{}^3T_{1g}(P)$
$Zn_3(Hcit)_26N_2H_4$	Diamagnetic	–	–
$Cd_3(Hcit)_26N_2H_4$	Diamagnetic	–	–
$Cu_2(cit)N_2H_42H_2O$	1.80	15500	$^2B_{1g}\rightarrow{}^2E_g$

Table 3
Important infrared spectral frequencies (4000–200 cm^{-1})

Compound	$\nu_{(O–H)}$hydro and water	$\nu_{(C=O)}$	$\nu_{asym(COO)}$	$\nu_{sym(COO)}$	$\nu_{(N–N)}$
$C_6H_8O_7$	3497 3291	1748 1705	–	–	–
$N_2H_5Mn(Hcit)H_2O$	3500–3400	–	1630	1410 1390	985
$N_2H_5Co(Hcit)H_2O$	3500–3400	–	1636	1405	985
$N_2H_5Ni(Hcit)H_2O$	3500–3400	–	1640	1398	990
$N_2H_5Zn(Hcit)H_2O$	3500–3400	–	1650	1416	998
$(N_2H_5)_2Ni(cit)4H_2O$	3500	–	1620	1410	1000
$Co_3(Hcit)_26N_2H_4$	3400	–	1622	1394	976
$Ni_3(Hcit)_26N_2H_4$	3400	–	1625	1398	976
$Zn_3(Hcit)_26N_2H_4$	3400	–	1625	1394	982
$Cd_3(Hcit)_26N_2H_4$	3400	–	1630	1398	972
$Cu_2(cit)N_2H_42H_2O$	3500–3400	–	1660 1630	1440 1400 1380	960

plexes, respectively, can be attributed to O–H stretching of water [28].

In citric acid, the carbonyl stretchings of the carboxyl groups were observed between 1740 and 1700 cm^{-1}. This band split into two bands because citric acid had two types of carboxyl groups. However, in these complexes, the carbonyl stretchings were observed between 1660 and 1550 cm^{-1} as broad and unresolved bands indicating the ionisation of all the carboxyl groups leading to complex formation and also these bands were mixed with NH_2 bending frequencies. In both the hydrazinium and hydrazinate complexes, the carbonyl asymmetric and symmetric stretching frequencies were in the range 1660–1550 and 1410–1380 cm^{-1}, respectively. Thus, the $\Delta\nu$ ($\nu_{asy}-\nu_{sym}$) separation was between 170 and 250 cm^{-1}, which suggested the unidentate coordination of the carboxylate groups [28]. However, the bridging behaviour of the anion was not completely ruled out, since the citrate ion was complexes in nature towards coordination. If the carboxylate groups were involved in bridging, the $\Delta\nu$ was expected to be less than 170 cm^{-1}.

In the hydrazinium metal citrate complexes the N–N stretching frequency was in the range 1000–985 cm^{-1} which coincided with the N–N stretching of the coordinated $N_2H_5^+$ cation [29]. Whereas in the hydrazinate complexes, the N–N stretching was seen in the range 960–980 cm^{-1} confirming the bridging bidentate coordination of hydrazine [29].

3.3. X-ray powder diffraction studies

X-ray powder diffraction patterns of the monohydrazinium and hexahydrazinate compounds were recorded in order to determine if they were isomorphic or not. The hydrazinium metal citrate monohydrates of Mn, Co, Ni and Zn had nearly identical patterns and so must have the same structure. Slight differences in lattice spacing were found as the radius of the metal ion changes (data are listed in Table 4). Similarly, the

Table 4
Lattice spacings in A°

$N_2H_5M(Hcit)H_2O$				$M_3(Hcit)_26N_2H_4$			
Mn	Co	Ni	Zn	Co	Ni	Zn	Cd
7.08	7.66	7.73	7.69	8.47	8.48	8.47	8.53
6.46	–	–	–	–	7.12	6.71	8.42
6.03	5.56	5.56	5.58	5.93	6.59	5.92	6.74
5.37	5.05	5.08	5.06	–	4.92	4.94	6.00
4.85	4.78	4.81	4.76	3.94	4.95	–	4.96
4.21	4.40	4.40	4.41	–	4.10	4.24	4.25
3.75	3.64	3.64	3.65	–	3.92	4.01	4.01
3.54	3.52	3.52	3.52	3.03	3.32	3.94	3.93
3.24	3.29	3.29	3.30	–	2.77	3.37	3.37
2.84	2.98	2.96	2.96	–	2.58	3.18	3.18
2.55	2.27	2.27	2.27	–	2.52	3.06	3.06
				1.98	2.42	2.77	2.60
				–	2.30	2.68	2.42
				–	2.18	2.28	2.28
				–	1.96	1.97	2.18

hexahydrazinates of Co, Ni, Zn and Cd also exhibited isomorphism among themselves (Table 4). The former set of compounds showed sharp diffractograms indicating the crystalline nature as compared to the latter set of compounds.

3.4. Thermal decomposition studies

The thermal data of the complexes are given in Table 5. Such data not only corroborate the stoichiometric formulae and number of included hydrazine and water molecules, but also reveal different intermediates formed including the end products.

$N_2H_5M(Hcit)H_2O$, where M = Mn, CO, Ni or Zn. Simultaneous TG-DTA curves of these complexes exhibited two-step decomposition, see (Fig. 1) as a representative example. In the first step of TG, one molecule of water and hydrazine were lost in the temperature range 100–320°C. In DTA, this decomposition was observed as an endotherm above 200°C. Such a high temperature dehydration confirms the presence of coordinated water molecule [30]. The intermediate formed in all the complexes was the corresponding metal citrates. The metal citrates were not thermally stable but underwent gradual decomposition in the temperature range 220–550°C to the respective metal oxides as the end product. The second step exothermic decomposition temperature varied from metal to metal as shown in Table 5.

$(N_2H_5)_2Ni(cit)4H_2O$. This compound showed two-step decomposition, an endothermic and an exothermic decomposition behaviour (Fig. 2). In the first two steps, two water molecules were lost successively in the low temperature regions 58–75°C and 75–116°C. The corresponding endothermic DTA peak temperatures were seen at 74°C and at 116°C. Such a low temperature endothermic dehydrations indicated that the water molecules were not coordinated to the metal. The final decomposition process started gradually at 116°C and ended at 350°C giving NiO as the final

Table 5
Thermal decomposition modes for isolated compounds ((+): endotherm; (−): exotherm; ^{d}: doublet)

Complex	DTA peak temperature (°C)	Thermogravimetry		Decomposition product
		Temperature range (°C)	Mass loss (%)	
			Found (calculated)	
$N_2H_5Mn(Hcit)H_2O$	210(+)	200–220	16.70 (16.95)	$Mn_3(Hcit)_2$
	358(−)	222–365	71.50 (70.52)	MnO_2
$N_2H_5Co(Hcit)H_2O$	280(+)	230–310	16.00 (16.73)	$Co_3(Hcit)_2$
	410(−)	310–530	74.50 (73.15)	Co_3O_4
$N_2H_5Ni(Hcit)H_2O$	260(+)	100–300	18.00 (16.74)	$Ni_3(Hcit)_2$
	360(−)	300–500	75.00 (74.99)	NiO
$N_2H_5Zn(Hcit)H_2O$	250(+)	240–320	16.00 (16.37)	$Zn_3(Hcit)_2$
	380(−)	320–550	70.00 (73.35)	ZnO
$(N_2H_5)_2Ni(cit)4H_2O$	74(+)	58–75	9.00 (9.36)	$(N_2H_5)_2Ni(cit)2H_2O$
	116(+)	75–116	16.65 (18.72)	$(N_2H_5)_2Ni(cit)$
	337(−)^d 347(−)^d	116–350	74.40 (80.58)	NiO
$Co_3(Hcit)_26N_2H_4$	330(−)	120–350	70.00 (67.76)	Co_3O_4
$Ni_3(Hcit)_26N_2H_4$	170(−)	100–200	8.50 (8.58)	$Ni_3(Hcit)_24N_2H_4$
	240(−)	200–260	95.00 (69.97)	NiO
$Zn_3(Hcit)_26N_2H_4$	190(+)	175–200	14.50 (14.62)	$Zn_3(Hcit)_22.5N_2H_4$
	446(−)	200–490	67.50 (68.13)	ZnO
$Cd_3(Hcit)_26N_2H_4$	130(+)	90–195	7.00 (7.05)	$Cd_3(Hcit)_24N_2H_4$
	228(+)	195–260	14.10 (14.11)	$Cd_3(Hcit)_22N_2H_4$
	490(−)	260–555	58.20 (57.54)	CdO
$Cu_2(cit)N_2H_42H_2O$	90(+)	84–95	5.00 (4.65)	$Cu_2(cit)N_2H_4H_2O$
	195(−)	95–196	19.00 (17.58)	$Cu_2(cit)$
	232(−)	196–300	57.00 (57.90)	CuO

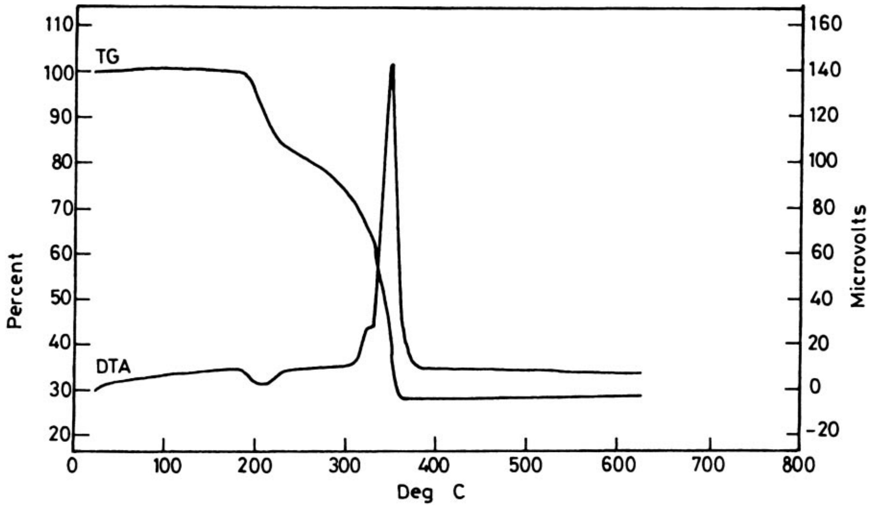

Fig. 1. Simultaneous TG-DTA of $N_2H_5Mn(Hcit)H_2O$.

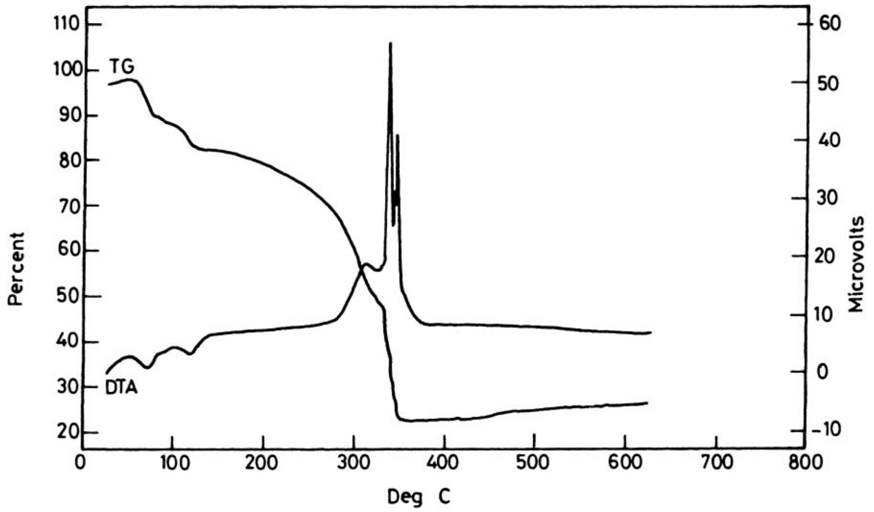

Fig. 2. Simultaneous TG-DTA of $N_2H_5Ni(cit)4H_2O$.

residue. In DTA, this step occurred as a sharp exothermic doublet at 337°C and 347°C with a shoulder around 320°C.

$M_3(Hcit)_2 6N_2H_4$, where M = Co, Ni, Zn or Cd. Quite a different decomposition behaviour was observed with each complex, but the final residue was always the metal oxide.

The Cobalt complex showed a single exothermic decomposition at 330°C giving Co_3O_4 as the final residue (Fig. 3). Whereas the nickel complex underwent complete exothermic decomposition in two steps to give nickel oxide as the final product. In the first step, the dehydrazination of two hydrazine molecules took place in the temperature range 100–200°C and the rest in the next step accompanying the anionic part leaving nickel oxide within the temperature of 260°C. The violent exothermicity made the spurting of almost all the nickel oxide from the platinium cup.

With the zinc and cadmium complexes, the loss of part of hydrazines was endothermic in contrast to

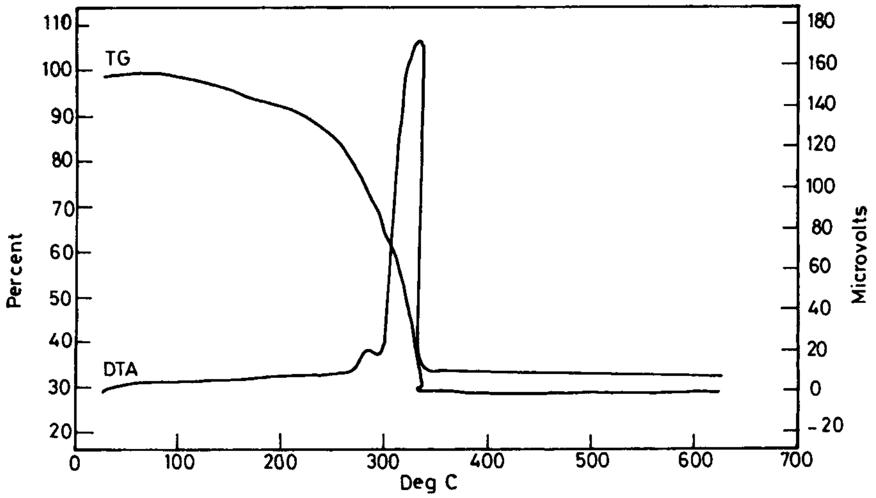

Fig. 3. Simultaneous TG-DTA of $Co_3(Hcit)_2 6N_2H_4$.

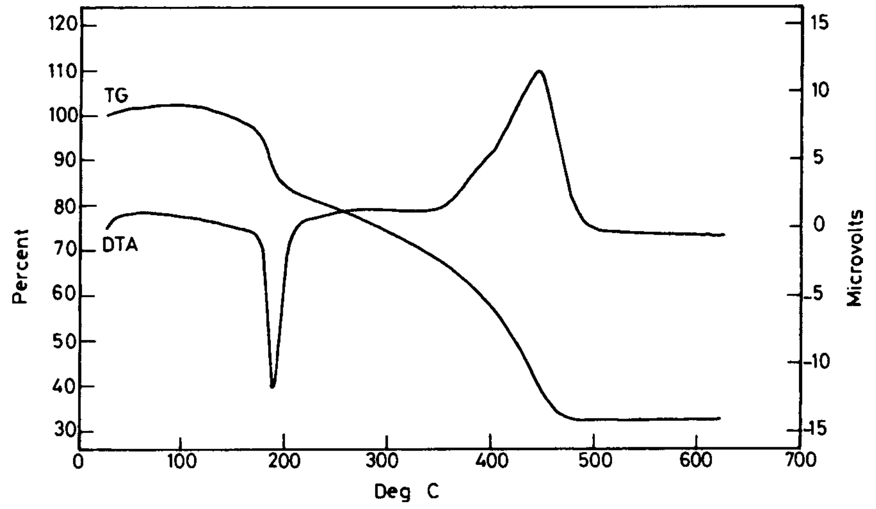

Fig. 4. Simultaneous TG-DTA of $Zn_3(Hcit)_2 6N_2H_4$.

nickel and cobalt complexes which were exothermic. Simultaneous TG-DTA of zinc complex can be seen in Fig. 4 for comparison. The Zn complex showed two steps of decomposition. In the first step, three and a half molecules of hydrazine were lost endothermically at 190°C with the formation of $Zn_3(Hcit)_2 2.5N_2H_4$ which underwent further exothermic decomposition at 446 °C leaving ZnO. Unlike the other hexahydrazinates, the cadmium compound showed three steps of decomposition in TG (Table 5). In the first two steps, two molecules each of hydrazine were successively lost endothermically at 130°C and 228°C, giving tetra and dihydrazinate intermediates. This dihydrazinate intermediate further decomposed exothermically at 490°C to give CdO.

$Cu_2(cit)N_2H_4 2H_2O$. The TG-DTA curves of this complex showed three steps in the decomposition (Fig. 5). In the first, one water molecules was lost between 84°C and 95°C. The corresponding endothermic DTA peak temperature observed at 90°C. Such a

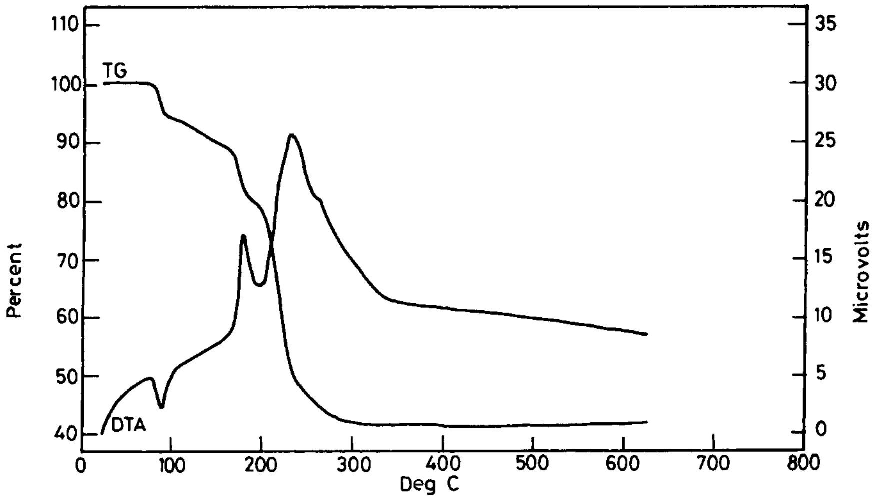

Fig. 5. Simultaneous TG-DTA of $Cu_2(cit)N_2H_22H_2O$.

low temperature dehydration confirms the presence of water molecule as lattice water. In the second step, one molecule of water and hydrazine were released exothermically from the monohydrated intermediate in the temperature range 95–196°C. The corresponding DTA peak temperature was observed at 195°C which confirmed the coordination of water to the metal [30]. But the thermal nature of transformation together with dehydrazination was exothermic. It is worth mentioning at this point that in the first set of hydrazinium metal citrate monohydrates, the dehydration of the coordinated water together with dehydrazination was an endothermic transformation in contrast to the above. Further, the formation of CuO was below 300°C showing thermal instability of the complex compared to other complexes discussed except nickel citrate hexahydrazinate in which violent exothermicity occurred at 240°C due to the fuelling nature of large number of hydrazine molecules. In the case of copper, the low temperature decomposition may be due to the catalytic activity of the copper compound [31].

4. Conclusions

The same molar mixture of citric acid and metal salts with different ratio of hydrazine hydrate gave both hydrazinium and hydrazinate complexes of different compositions. This indicates the versatile interaction of hydrazine and citric acid in solutions of different pH. Although the anion is the same in all the complexes, the thermal decomposition modes and temperatures of the individual complexes differ depending upon the composition, the metal ion and the nature of hydrazine. These compounds may be used as precursors to fine particle metal oxides due to their low temperature decompositions. The complexes are obtained only as powders and hence, structural studies could not be carried out.

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