

# HYDRAZINIUM METAL(II) AND METAL(III) ETHYLENEDIAMINE TETRAACETATE HYDRATES

## Spectral, thermal and XRD studies

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Hydrazinium metal ethylenediaminetetraacetate complexes of molecular formula  $(N_2H_5)_2[Mg(edta)\cdot H_2O]$ ,  $(N_2H_5)_3[Mn(edta)\cdot H_2O](NO_3)\cdot H_2O$ ,  $N_2H_5[Fe(edta)\cdot H_2O]$ ,  $N_2H_5[Cu(Hedta)\cdot H_2O]$  and  $N_2H_5[Cd(Hedta)\cdot H_2O]\cdot H_2O$  have been synthesized and characterized by elemental and chemical analysis, conductivity and magnetic measurements and spectroscopic techniques.

The thermal behaviour of these complexes has been studied by thermogravimetry and differential thermal analysis. The data set provided by the simultaneous TG-DTA curves of the complexes shows the occurrence of three or four consecutive steps such as dehydration, ligand pyrolysis and formation of metal oxides. X-ray powder diffraction patterns of copper and cadmium complexes show that they are not isomorphous. These studies suggest seven coordination for Mg, Mn, Fe complexes and six coordination for Cu and Cd derivatives.

**Keywords:** EDTA, HEDTA, hydrazinium metal complexes, metal oxides, TG-DTA, X-ray powder pattern

### Introduction

Ethylenediaminetetraacetic acid ( $H_4edta$ ) is an aminopolycarboxylic acid, which is known to exist as zwitter ion. It contains four replaceable hydrogen atoms which are acidic and hence forms di, tri and tetra sodium and potassium salts when neutralized with strong bases such as sodium and potassium hydroxides, respectively. However, weak bases like ammonia and hydrazine form only di-salts which is quite understandable because, the pKa values of two protons are very high and cannot be replaced by weak bases when compared to the other two protons [1].

$H_4edta$  is a versatile chelating ligand which is capable of coordination with several metal ions to give stable 1:1 complexes. During complexation  $H_4edta$  binds to the metal ions in various forms [2–8] like  $H_2edta^{2-}$ ,  $Hedta^{3-}$  or  $edta^{4-}$  which depends on the oxidation state of the metal ions and pH of the medium. Besides these simple metal complexes, several sodium, potassium, rubidium, calcium and ammonium metal complexes have been extensively studied [9–15]. These complexes are stable both in solid state and in solution and their stability has been attributed to the formation of chelates in the coordination sphere.

Structural information on  $edta^{4-}$  complexes obtained by X-ray investigations reveals that different coordination numbers are observed for metal ions. During complexation  $edta^{4-}$ ,  $Hedta^{3-}$  and  $H_2edta^{2-}$  are different species bound to metal ions as hexadentate, pentadentate or tetradentate ligand, respectively. It appears that the coordination numbers of the metal

ions in these  $edta^{n-}$  complexes are generally higher than six by further coordination of water. However, it has been general practice to formulate these as 1:1 complexes as having an octahedral structure with hexadentate  $edta$ .

Hydrazine is a simplest diamine, weakly basic, weaker than ammonia and forms several salts with mineral as well as carboxylic acids [16–18]. Hydrazinium salts are used as ligands in the preparation of hydrazinium metal complexes. In many instances  $N_2H_5^+$  ions behaves similar to that of  $NH_4^+$  ions in the sense that in the complexes,  $N_2H_5^+$  ion was present outside the coordination sphere. However, complexes are known where  $N_2H_5^+$  ion, which still retains a basic site, involved in the coordination [19–21]. Hydrazine forms only one type of crystalline salt with  $H_4edta$ , the dihydrazinium dihydrogenethylene diaminetetraacetate,  $(N_2H_5)_2H_2edta$  in aqueous as well as alcoholic media [22].

During the course of our research, we have reported several hydrazinium and hydrazine metal carboxylates and their hydrates including simple amino carboxylates such as glycinate [23–25]. However, hydrazinium complexes with  $Hedta^{3-}$  and  $edta^{4-}$  are scarce [26] inspite of plenty of simple metal– $edta$  complexes are known and well characterized. Hence, in the present investigation, we wish to report some new hydrazinium complexes of Mg(II), Mn(II), Fe(III), Cu(II) and Cd(II) containing either  $Hedta^{3-}$  or  $edta^{4-}$  ions as charge neutralizing and chelating ligands. Further, for the first time we are reporting some seven coordinated metal ions with hydrazinium cation.

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## Experimental

### Materials

Hydrazine hydrate and metal nitrate hydrates, ethylenediaminetetraacetic acid and other chemicals used were of analar grade. The solvents were distilled before use and double distilled water was used for the preparation of hydrazinium salts and complexes and also for the determination of hydrazine and metal ions.

### Preparation of $[\text{N}_2\text{H}_5]_2[\text{H}_2\text{edta}]$

$\text{H}_4\text{edta}$  (29.2 g, 0.1 mol) was suspended in 100 mL of 1:1 aqueous alcohol and 10 mL (0.2 mol) of hydrazine hydrate was added with constant stirring. After complete addition, the solution was warmed on a water bath so as to dissolve the acid. The resultant solution was filtered and allowed to crystallize at room temperature. The colourless crystalline salt formed after 24 h was filtered, washed with ethyl alcohol and dried in air.

### Preparation of $[\text{N}_2\text{H}_5]_2[\text{Mg}(\text{edta})\cdot\text{H}_2\text{O}]$ and $[\text{N}_2\text{H}_5]_3[\text{Mn}(\text{edta})\cdot\text{H}_2\text{O}][\text{NO}_3]\cdot\text{H}_2\text{O}$

To an aqueous solution (100 mL) of a metal nitrate hydrate (0.05 mol), an aqueous solution (50 mL) containing  $(\text{N}_2\text{H}_5)_2\text{H}_2\text{edta}$  (35.63 g, 0.1 mol) was added in portions with constant stirring. The resultant clear solution was allowed to stand at room temperature for about 6 h. The free acid,  $\text{H}_4\text{edta}$  precipitated was removed by filtration and the clear solution was concentrated to about 30 mL on a water bath and allowed to stand at room temperature for crystallization. The crystalline complexes formed after 10–12 days were filtered using a vacuum pump and washed with ice-cold water and dried in air. Analytical data are given in Table 1.

### Preparation of $[\text{N}_2\text{H}_5][\text{Fe}(\text{edta})\cdot\text{H}_2\text{O}]$ , $[\text{N}_2\text{H}_5][\text{Cu}(\text{Hedta})\cdot\text{H}_2\text{O}]$ and $[\text{N}_2\text{H}_5][\text{Cd}(\text{Hedta})\cdot\text{H}_2\text{O}]\cdot\text{H}_2\text{O}$

The iron complex was prepared by repeating the method mentioned above using  $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$  (20.2 g, 0.05 mol). In this case the final solution was evaporated on a water bath to 20 mL and the resultant dark brown solution on long standing for about 20 days yielded light brown crystals. The copper and cadmium complexes were prepared similarly. However, after removing the free acid the clear dilute solutions were allowed to crystallize at room temperature. The complexes crystallized out over a period of a month which were removed, washed with ice cold water and dried in air.

### Methods

The metal contents in the complexes were determined by complexometric titrations after carefully decomposing a known amount of complexes with concentrated nitric acid for several times to eliminate the organic portion of the molecule so as to get exclusively the respective metal nitrate hydrates [27]. The hydrazine contents were determined by volumetric analysis using a 0.025 M  $\text{KIO}_3$  solution under Andrew's conditions [27]. The C, H and N analysis were performed on a Perkin Elmer 1240 CHN analyzer.

The molar conductivity at room temperature was determined in conductivity water using a Century Digital Conductivity meter (model cc 601) and a dip type cell with a smooth platinum electrode. Room temperature magnetic susceptibility measurements were made using a Gouy balance and powdered samples of the complexes.  $\text{Hg}[\text{Co}(\text{NSC})_4]$  was used as the calibrant and the diamagnetic corrections were applied by summing up the Pascal's constants for the diamagnetic contributions of various atoms of the molecule. The electronic absorption spectra were recorded in distilled water on a Shimadzu 160A/240A UV-Visible spectrophotometer. The infrared spectra of the solid samples in the range  $4000\text{--}500\text{ cm}^{-1}$  were recorded on a Perkin-Elmer 597/1650 spectrophotometer using KBr pellets.

Simultaneous TG-DTA experiments in air were carried out using a STA 1500 thermal analyzer. The heating rate employed was  $10^\circ\text{C min}^{-1}$  and platinum cups were used as to hold about 5–10 mg of the samples for the experiments. The X-ray powder diffraction of the complexes were obtained with a Philips PW 1050/70 diffractometer using  $\text{CuK}_\alpha$  radiation ( $\lambda=1.5406\text{ \AA}$ ).

## Results and discussion

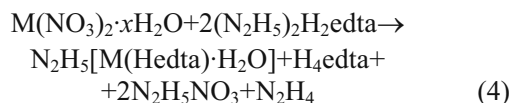
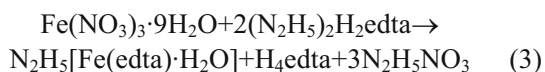
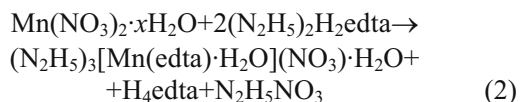
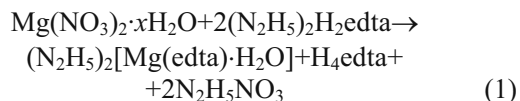
The ligand hydrazinium salt of  $\text{H}_4\text{edta}$  was prepared by neutralizing  $\text{H}_4\text{edta}$  with hydrazine hydrate in 1:2 ratio. In aqueous alcohol the product was crystallized within 24 h. However, in aqueous solution the compound required at least 3 days for complete crystallization, the yield also was high. This salt is utilized as the ligand for the preparation of metal complexes.

Hydrazinium metal ethylenediaminetetraacetate monohydrates were prepared by the aqueous reaction between respective metal nitrate hydrate and the ligand in 1:2 ratio, Eqs (1)–(4). All the complexes are stable in air, soluble in water and insoluble in alcohol and other organic solvents such as ether, chloroform etc. Though the metal to ligand ratio in all the cases was 1:1, the composition however differed in the complexes. Although in iron, copper and cadmium complexes only one hydrazinium ion is present,

Table 1 Analytical data

Complex [empirical formula]	Colour (molecular mass)	Metal/%			C/% found (calc.)	H/%	N/%	Magnetic moments $\mu_{\text{eff}}$ / BM	Molar conductance/ $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$
		N <sub>2</sub> H <sub>4</sub> /%							
(N <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> [Mg(edta)·H <sub>2</sub> O] [MgC <sub>10</sub> H <sub>24</sub> O <sub>9</sub> N <sub>6</sub> ]	colourless (470.85)	5.90 (6.13)	16.30 (16.16)	30.10 (30.28)	6.15 (6.10)	21.02 (21.19)	diamagnetic	220	
(N <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> [Mn(edta)H <sub>2</sub> O](NO <sub>3</sub> )·H <sub>2</sub> O [MnC <sub>10</sub> H <sub>31</sub> O <sub>13</sub> N <sub>6</sub> ]	colourless (396.64)	10.80 (10.17)	18.10 (17.79)	22.35 (22.23)	5.68 (5.78)	23.12 (23.33)	5.8	490	
N <sub>2</sub> H <sub>5</sub> [Fe(edta)·H <sub>2</sub> O] [FeC <sub>10</sub> H <sub>19</sub> O <sub>9</sub> N]	yellowish brown (540.35)	14.80 (14.13)	8.30 (8.11)	30.20 (30.40)	4.76 (4.85)	14.04 (14.18)	5.7	125	
N <sub>2</sub> H <sub>5</sub> [Cu(Hedta)·H <sub>2</sub> O] [CuC <sub>10</sub> H <sub>19</sub> O <sub>9</sub> N <sub>4</sub> ]	dark blue (395.13)	15.30 (15.74)	8.10 (7.94)	29.55 (29.74)	4.87 (4.74)	13.95 (13.87)	1.85	120	
N <sub>2</sub> H <sub>5</sub> [Cd(Hedta)·H <sub>2</sub> O]·H <sub>2</sub> O [CdC <sub>10</sub> H <sub>22</sub> C <sub>10</sub> N <sub>4</sub> ]	colourless (403.84)	23.30 (23.87)	6.70 (6.81)	25.65 (25.51)	4.63 (4.71)	12.05 (11.90)	diamagnetic	120	

attempts to prepare them by the reaction of metal nitrate hydrate with ligand in 1:1 ratio was not successful. Hence, the excess of hydrazine in solution was essential for the formation of hydrazinium complexes.



where  $M = \text{Cu}$  or  $\text{Cd}$ .

Hydrazinium complexes of  $\text{Fe}^{3+}$  ion are scarce due to its ease of reduction to  $\text{Fe}^{2+}$  ion in the presence of reducing agents like hydrazine and hence one would expect  $\text{Fe}(\text{II})$  complexes. Furthermore, the pH of the solution plays an important role in the formation of complex. If the medium is basic, precipitation of hydroxide is favoured rather than complexation. However, in the present case the medium was slightly acidic which was suitable for the formation of hydrazinium complex.

Formation of copper complex is again a surprise because, except few cases like hydrazinium oxalate [28] and citrate [29], other ligands reduce  $\text{Cu}^{2+}$  ion to copper metal. In the present case even the excess hydrazine present in the solution than required for complexation did not affect the complex formation. The reason for the above observations might be attributed to the strong chelating ability of edta and stability of metal–edta system. As is evident from Eqs (1)–(4), hydrazinium nitrate is formed as a by-product in these reactions which being highly soluble in water, remains in the mother liquor. Hence, it is not surprising to note that one of these molecules would have added as adduct during the crystallization of manganese complex.

Studies on metal complexes of  $\text{H}_4\text{edta}$  and its derivatives afforded some interesting and even surprising results concerning the structure of these complexes. These investigations have shown that the radius of the central metal ion must be small to obtain chelates of octahedral or distorted octahedral symmetry in which all the six donor atoms of  $\text{edta}^{4-}$  are coordinated to the metal atom. Other ligands, such as  $\text{H}_2\text{O}$  molecule, are absent from the inner sphere. In the solid-state even the edta complex of  $\text{Mg}(\text{II})$ ,  $\text{Mn}(\text{II})$  and  $\text{Fe}(\text{III})$  have the structures  $\text{Mg}(\text{edta})(\text{H}_2\text{O})^{2-}$ ,  $\text{Mn}(\text{edta})(\text{H}_2\text{O})^{2-}$  and  $\text{Fe}(\text{edta})(\text{H}_2\text{O})^-$ , respectively

[9, 12, 14]. Hence in addition to the six donor atoms of edta, the water molecule is bound in the inner sphere of these complexes. Thus the central metal atom has a coordination number of seven. In the present case, the structure of manganese complex has been determined by X-ray single crystal method. The manganese ion was found to be seven coordinated. The  $\text{edta}^{4-}$  coordinated to the metal ion as a hexadentate ligand through four carboxylate oxygen atoms and two tertiary nitrogen atoms, the seventh coordination site being occupied by a water molecule.

On the other hand the composition of analogous chelates in acid medium is  $\text{M}(\text{Hedta})(\text{H}_2\text{O})^-$  ( $M = \text{Co}(\text{II})$ ,  $\text{Ni}(\text{II})$ ,  $\text{Cu}(\text{II})$  and  $\text{Zn}(\text{II})$ ) or  $\text{M}(\text{Hedta})(\text{H}_2\text{O})$  ( $M = \text{Fe}(\text{III})$ ,  $\text{Cr}(\text{III})$  or  $\text{Ga}(\text{III})$ ) [12] where Hedta (HY) is a pentadentate ligand and the sixth coordination site is occupied by  $\text{H}_2\text{O}$ . One of the  $-\text{CH}_2\text{COOH}$  groups of  $\text{H}_4\text{edta}$  is free.

#### Molar conductance

The molar conductance values (Table 1) of magnesium and manganese complexes were found to be 220 and 490  $\text{ohm}^{-1} \text{cm}^2 \text{m}^{-1}$  respectively indicating the presence of three ions for magnesium complex five ions for manganese complex in dilute solution. The Fe, Cu and Cd complexes show molar conductance in the range 120–125  $\text{ohm}^{-1} \text{cm}^2 \text{m}^{-1}$ . Indicating that they are 1:1 electrolytes. Hence in all the cases the hydrazinium ions are expected to be present outside the coordination sphere.

#### Magnetic moments and electronic spectra

The magnetic moment values (Table 1) of manganese, iron complexes are in accordance with the high spin nature of the metal ions [30]. The  $\mu_{\text{eff}}$  value for copper(II) complex (1.7 BM) indicates the presence of one unpaired electron. The magnesium and cadmium complexes are diamagnetic as expected.

The electronic spectra of  $\text{Mn}(\text{II})$  and  $\text{Fe}(\text{III})$  complexes show only very weak and sharp band as expected for the spin forbidden transitions of  $d^5$  system.

#### Infrared spectra

The infrared spectra of the complexes show few bands in the region 3000–3440  $\text{cm}^{-1}$  due to the N–H and O–H stretchings of hydrazinium ions, water molecule and Hedta.

The copper and cadmium complexes show a sharp band at 1710  $\text{cm}^{-1}$  which is a strong evidence for the presence of free carboxylic acid group in these complexes. Absence of this band in other complexes indicates the absence of free acid [31]. A strong band in the region 960–965  $\text{cm}^{-1}$  in all the complexes is at-

tributed to the presence of non-coordinated  $N_2H_5^+$  ions [32]. Two distinct bands in the regions 3300–3350 and 850–870  $cm^{-1}$  have been attributed to the presence of coordinated water.

#### Thermal degradation studies

Thermal degradation is an important tool for coordination compounds to derive many conclusions about their nature and thermal stability. Especially the nature and number of water molecules present in the hydrated complexes may be deduced on the basis of the temperature range at which it is eliminated.

The TG-DTA traces of magnesium complex shows multi-step decomposition. No mass loss is observed below 170°C which is a clear indication of absence of water molecules outside the coordination sphere. From 173 to 207°C a sharp fall in the TG curve with 17% mass loss was observed. This may be due to the elimination of two hydrazine moieties which are expected to be present outside the coordination sphere as charge neutralizing species. Further loss of about 9% was observed in the next stage which is ascribed for the dehydration. However, for the first two stages DTA show an endotherm at 196°C the residue, Mg–edta complex formed as an intermediate undergo continuous and gradual decomposition upto 605°C. The calculated mass loss for the formation of MgO is well in accordance with the TG profile. The DTA also shows a broad exotherm corresponding to the last stage of degradation.

The manganese complex, as expected, initially decomposes endothermically before 100°C indicating the dehydration of non-coordinated water molecule. Further degradation from 140–178°C takes place endothermically for the elimination of  $HNO_3$  molecules. Then the intermediate shows a gradual and multi-step degradation upto 350°C for which a broad endotherm is observed. This is followed by a sharp decomposition resulting in the formation of manganese oxide as the end residue. The DTA curve shows a strong exotherm corresponds to the final stage of degradation.

As expected and observed in many of the previous cases, the iron complex decomposes at lower temperature than the other complexes. The TG curve shows a three-step and continuous decomposition between the temperatures ranges 170–300, 300–350 and 350–415°C to give  $Fe_2O_3$  as the final decomposition residue. DTA curve shows a broad endotherm at 195°C which clearly indicates the coordinated water present in the complex. After dehydration two strong exotherms are observed at 272 and 399°C for the decomposition of anhydrous complex to  $Fe_2O_3$ .

The copper complex decomposes in three stages. In the first stage dehydration takes place at 150–200°C.

The DTA shows an endotherm as doublet at 170 and 190°C. In the next stage the anhydrous complex degrades in two stages to give the copper oxide residue. DTA shows a sharp exotherm at 220°C and then a broad exotherm at 420°C for the pyrolysis of ligand.

The thermal degradation pattern of cadmium complex shows a broad endotherm corresponding to the dehydration which starts at 120 and completes at 170°C. This may probably due to the elimination of both coordinated and non-coordinated water molecules. The anhydrous complex undergoes dehydrazination followed by the elimination of edta gradually to yield the CdO as the final residue.

The DTA shows broad and weak exotherms upto 450°C and then shows a sharp and strong exotherm at 488°C for the final stage. Due to the continuous decomposition it is very difficult to assign the composition of the intermediates on the basis of TG profile.

As discussed earlier due to the high hydrazine content and catalytic behaviour of metal ions, manganese, iron and copper complexes gives oxides at lower temperatures than magnesium and cadmium complexes. The simultaneous TG-DTA traces of the complex are shown from Figs 1–5. The thermal degradation data is given in Table 2.

Due to the continuous decomposition we were not able to isolate the intermediates. However, the fi-

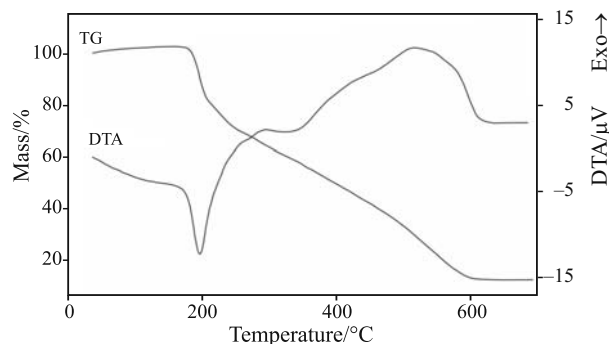


Fig. 1 Simultaneous TG-DTA of  $(N_2H_5)_2[Mg(edta)·H_2O]$  in air

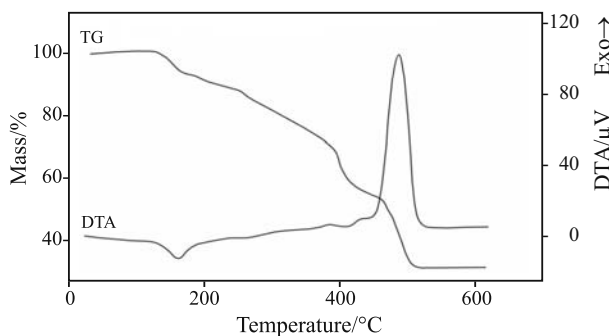
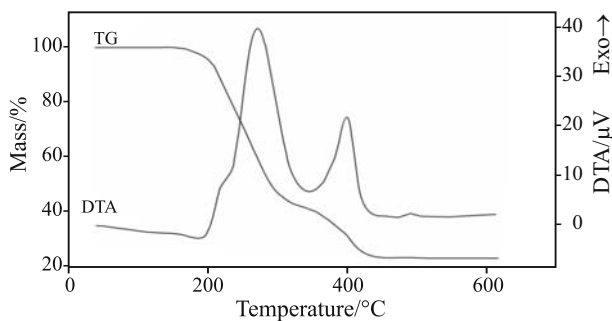
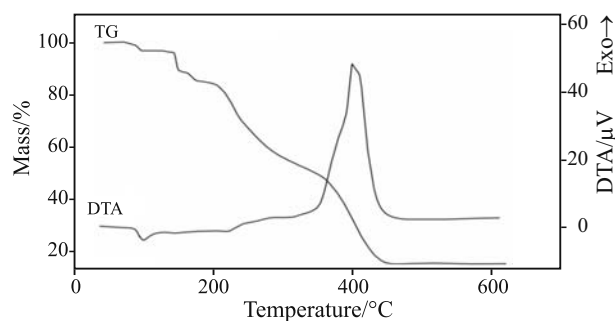
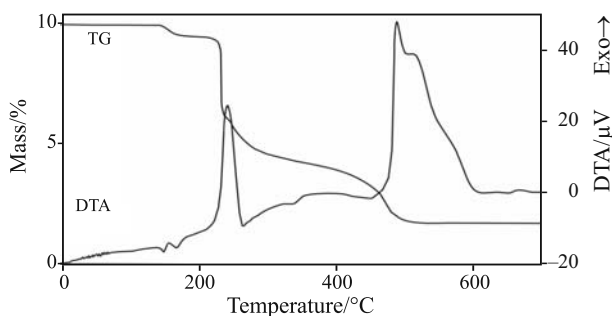


Fig. 2 Simultaneous TG-DTA of  $(N_2H_5)_3[Mn(Hedta)·H_2O](NO_3)·H_2O$  in air

**Table 2** Thermal data

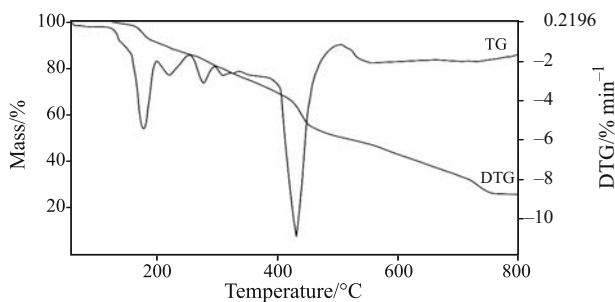
Complex	Stage	$T_{\text{range}}/^{\circ}\text{C}$	DTA peak temperature/ $^{\circ}\text{C}$	Mass loss/% found (calc.)	Group(s) eliminated	Residue ('a' values)
$(\text{N}_2\text{H}_5)_2[\text{Mg}(\text{edta})\cdot\text{H}_2\text{O}]$	I	173–207		17 (16.16)	$2\text{N}_2\text{H}_4$	–
	II	207–236	196 (+)	22 (20.70)	$\text{H}_2\text{O}$	–
	III	236–605	517 (–)	88 (89.84)	–	$\text{MgO}$ (4.2112)
$(\text{N}_2\text{H}_5)_3[\text{Mn}(\text{edta})\cdot\text{H}_2\text{O}](\text{NO}_3)\cdot\text{H}_2\text{O}$	I	84–100	98	3 (3.33)	$\text{H}_2\text{O}$	–
	II	140–178	145 (+,w)	13 (15.00)	$\text{HNO}_3$	–
	III	180–350	220 (+,w)	45 (46.86)	$3\text{N}_2\text{H}_4$	–
	IV	350–425	400 (–,s)	87 (86.87)	$0.2\text{H}_2\text{edta}$	$\text{MnO}$ (4.445)
$\text{N}_2\text{H}_5[\text{Fe}(\text{edta})\cdot\text{H}_2\text{O}]$	I	150–300	195 (+)			
	II	300–350	218 (–), 272 (–)	51 (49.65)	$\text{H}_2\text{O}, \text{N}_2\text{H}_4$	–
	III	350–415	399 (–)	78 (79.79)	$0.5\text{H}_2\text{edta}$	$\text{Fe}_2\text{O}_3$ (9.404)
$\text{N}_2\text{H}_5[\text{Cu}(\text{Hedta})\cdot\text{H}_2\text{O}]$	I	150–200	170 (+), 190 (+)	5 (4.46)	$\text{H}_2\text{O}$	–
	II	210–230	220 (–)	51 (48.32)	$\text{N}_2\text{H}_4, 0.5\text{H}_2\text{edta}$	$\text{CuO}$ a : (4.684)
	III	250–450	420 (–)	80 (80.30)	–	b : (3.425) c : (5.129)
$\text{N}_2\text{H}_5[\text{Cd}(\text{Hedta})\cdot\text{H}_2\text{O}]\cdot\text{H}_2\text{O}$	I	120–170	161 (+,w)			
	II	170–250	210 (+,w)	8 (7.65)	$2\text{H}_2\text{O}$	–
	III	250–391	275 (+,w)	13 (14.46)	$\text{N}_2\text{H}_4$	–
	IV	391–463	386 (–,w) 434 (–,w)	31 (29.87)	$0.25\text{H}_2\text{edta}$	$\text{CdO}$
	V	463–520	488 (–,s)	71 (72.73)	–	(4.6953)

**Fig. 3** Simultaneous TG-DTA of  $\text{N}_2\text{H}_5[\text{Fe}(\text{edta})\cdot\text{H}_2\text{O}]$  in air**Fig. 5** Simultaneous TG-DTA of  $\text{N}_2\text{H}_5[\text{Cd}(\text{Hedta})\cdot\text{H}_2\text{O}]\cdot\text{H}_2\text{O}$  in air**Fig. 4** Simultaneous TG-DTA of  $\text{N}_2\text{H}_5[\text{Cu}(\text{Hedta})\cdot\text{H}_2\text{O}]$  in air

nal residues, the respective metal oxides have been isolated by controlled heating of about 1 gm of the each complex and the residues were confirmed by X-ray powder diffraction. The unit cell dimensions for the oxides are given in Table 2.

#### *TG-DTA of $\text{N}_2\text{H}_5[\text{Cd}(\text{Hedta})\cdot\text{H}_2\text{O}]\cdot\text{H}_2\text{O}$ in nitrogen*

One of the important factors which affect the thermal degradation behaviour of complexes is heating atmosphere. In the present case thermal degradation in nitrogen atmosphere for cadmium complex has been carried out because of its purity and crystalline nature. This study has been carried out for comparison.



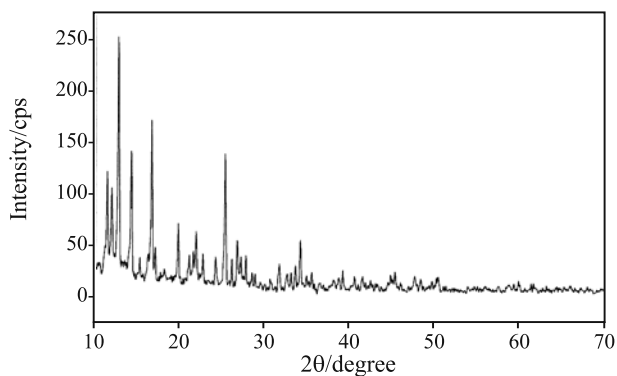
**Fig. 6** Simultaneous TG-DTG of  $N_2H_5[Cd(Hedta) \cdot H_2O] \cdot H_2O$  in nitrogen

The TG profile shows continuous degradation with a change in trend at different temperature ranges. The multi-step degradation shows that the dehydration, dehydrazination and ligand pyrolysis takes place continuously to give CdO as the final residue. However, in nitrogen atmosphere the final residue is formed only at much higher temperature around  $760^\circ C$  when compared to that in air. The thermal degradation pattern of  $N_2H_5[Cd(Hedta) \cdot H_2O] \cdot H_2O$  in nitrogen atmosphere is shown in Fig. 6.

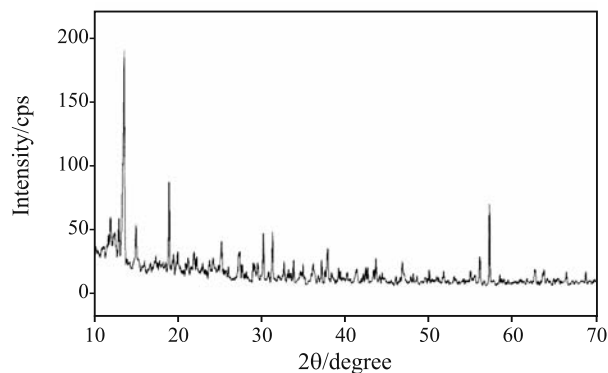
#### X-ray powder diffraction

Since the reported complexes have either different composition or metals in different oxidation state, the X-ray powder data may not give fruitful information to compare the structure of complexes.

However, in the case of copper and cadmium complexes with the compositions  $N_2H_5[Cu(Hedta) \cdot H_2O]$  and  $N_2H_5[Cd(Hedta) \cdot H_2O] \cdot H_2O$ , respectively, except one water molecule present outside the coordination sphere, the remaining part of the complexes are same and hence, with respect to the coordination sphere, both the metal ions are expected to have similar structure. Hence, the X-ray powder diffraction patterns for these two complexes have been recorded. This result indicates that these complexes are not isomorphous. This is in favour of different coordination mode of Hedta in these two complexes. The X-ray powder diffraction patterns of copper and cadmium complex are shown in Figs. 7 and 8, respectively.



**Fig. 7** X-ray powder pattern of  $N_2H_5[Cu(Hedta) \cdot H_2O]$



**Fig. 8** X-ray powder pattern of  $N_2H_5[Cd(Hedta) \cdot H_2O] \cdot H_2O$

#### Coordination geometry

Based on analytical, conductivity, spectral, thermal and XRD data seven coordinations around the metal has been proposed for magnesium, manganese and iron complexes. The copper and cadmium complexes, since they have one free carboxylic acid group in Hedta, the octahedral structure has been assigned for these two complexes. Further the mode of coordination of Hedta in copper and cadmium complexes differs markedly. This is evident from their non-superimposable X-ray powder patterns. However, the exact structure could be given only the X-ray single crystal studies are carried out. Fortunately, in the case of copper and cadmium complexes also, we were able to isolate pure single crystals suitable for X-ray crystallographic studies and the structural studies are in progress.

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