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The chemistry of hydrazine derivatives—thermal behavior and characterisation of hydrazinium salts and metal hydrazine complexes of 4,5-imidazoledicarboxylic acid

T. Premkumar, S. Govindarajan*

Department of Chemistry, Bharathiar University, Coimbatore 641046, India

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Abstract

New hydrazinium hydrogen-4,5-imidazoledicarboxylate (N_2H_5Himdc), its monohydrate, N_2H_5Himdc·H_2O, (H_2imdc = 4,5-imidazoledicarboxylic acid) and the metal complexes of the type M(imdc)0.5N_2H_4·H_2O, where M = Mn,Co or Cd and M(imdc)N_2H_4·H_2O, where M = Ni or Zn have been prepared. The compounds have been characterised by analytical, electronic and IR spectral and thermal studies. Electronic spectral data suggest that the Co and Ni complexes are of spin-free (high spin) type with octahedral geometry. The IR absorption bands of N–N stretching in the range 970–960 cm^{-1} unambiguously prove the bidentate bridging nature of the N_2H_4 ligands. IR spectra also confirm the unidentate coordination behaviour of carboxylate ($\nu_{asy} = 1570\,cm^{-1}$ and $\nu_{sym} = 1390\,cm^{-1}$) groups of the imidazoledicarboxylate dianion. Simultaneous TG and DTA of the free acid show a single-step complete endothermic (281 °C) decomposition whereas its anhydrous and hydrated hydrazinium salts show endotherm followed by exotherm decomposition. All the metal complexes undergo endothermic decomposition around 100 °C with the loss of hydrazine and water, via the metal 4,5-imidazoledicarboxylate which further decomposes exothermically in the range 110–560 °C to give the respective metal oxide as the end product.

Keywords: Hydrazinium; Hydrazine; 4,5-Imidazoledicarboxylic acid; Metal complexes; Thermal decomposition

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1. Introduction

Hydrazine is a versatile ligand and it offers the possibility of different modes of coordination towards transition metal ions [1–3]. It can function as a monodentate [4,5] or bridging bidentate [6–9] ligand. Thermal reactivity of metal coarboxylates with hydrazine is of increasing interest, since they serve as precursors to fine-particle oxide materials [10–12]. Our recent interest in hydrazine chemistry began with the preparation and characterisation of metal complexes of nitrogen containing heterocyclic, both mono and dicarboxylic acids. Heteroaromatic dicarboxylates have been extensively used for investigations in coordination chemistry, most reports are on pyrazines, some of which have been reviewed [13]. We have become particularly interested in the 4,5-imidazoledicarboxylic acid (H_2imdc), since it has a number of attractive features. They are sterically compact, planar and have multi-donor coordination sites. The thermal decomposition and IR spectral analysis of many metal carboxylates such as formate [14,15], acetate [6,16], propionate [17], oxalate [18,19], malonate [16,20], succinate [20], benzoate and phthalate [21] with hydrazine have been reported. However, to the best of our knowledge, no work has been done on the thermal property of metal hydrazine complexes as well as simple hydrazinium salt of heteroaromatic

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* Corresponding author. Fax: +91-422-4222387.

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acids in general and H_2imdc in particular. Hence, keeping this in view, this work was undertaken to study the thermal stability and coordinating ability of hydrazine in the presence of H_2imdc, on the complexation and the results are given here.

2. Experimental

2.1. Preparation of hydrazinium hydrogen-4,5-imidazoledicarboxylate and its monohydrate salt

The anhydrous hydrazinium and its monohydrate salts of H_2imdc have been prepared by mixing hydrazine hydrate and the acid, in 1:1 and 2:1 molar ratio (0.5 cm^3, 0.01 mol and 1.1561 g, 0.01 mol; 1 cm^3, 0.02 mol and 1.561 g, 0.01 mol), respectively, in 50 cm^3 of distilled water. The resulting turbid solutions were heated over waterbath for 1 h to get clear solutions, which were kept for crystallisation in a vacuum desiccator over calcium chloride. While the anhydrous salt separated out after 24 h as white powder, the monohydrated hydrazinium salt deposited as white spongy crystals only after a couple of days. It is worth mentioning that the 1:2 ratio of base and acid also yielded the monohydrated salt. Both the salts are soluble in hot water.

2.2. Preparation of the metal complexes

An aqueous mixture (50 cm^3) containing H_2imdc (1.561 g, 0.01 mol) and hydrazine hydrate (2 cm^3, 0.04 mol) was added slowly to an aqueous solution (50 cm^3) of the respective metal nitrate hydrates (e.g. 2.91 g of $Co(NO_3)_2{\cdot}6H_2O$, 0.01 mol; in the case of Mn, manganese(II) acetate tetrahydrate 2.45 g, 0.01 mol was used) with constant stirring. The solid products immediately formed were filtered off after 1 h and washed with water, alcohol and diethyl ether and air-dried.

2.3. 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' condition [22]. 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 [22]. The reflectance spectra of the powdered complexes were recorded on a Shimadzu 240-A UV–VIS spectrophotometer in the range 300–800 nm. IR spectra were recorded as KBr pellets with a Perkin-Elmer 597-model spectrophotometer in the 4000–400 cm^{-1} range. Elemental analyses were performed on Perkin-Elmer 240 B CHN analyser. Simultaneous TG-DTA measurements were carried out on a STA 1500 thermal analyser. The experiments were carried out in air using platinum cups as sample holders with 5–10 mg of the samples at the heating rate of 10 °C min^{-1}.

3. Results and discussion

Dibasic acids with hydrazine are known to form $N_2H_4{\cdot}H_2A$ (N_2H_5HA) or (N_2H_6A), $2N_2H_4{\cdot}H_2A$

Table 1
Analytical data[a]

Compound	Yield (%)	Colour	Found (calculated) (%)				
			Hydrazine	Metal	Carbon	Hydrogen	Nitrogen
$HimdcN_2H_5$	90	Dull white	17.40 (17.01)	–	30.13 (31.89)	3.98 (4.28)	28.96 (29.77)
$HimdcN_2H_5{\cdot}H_2O$	75	White	15.10 (15.52)	–	28.96 (29.11)	4.23 (4.89)	19.86 (20.38)
$Mn(imdc)0.5N_2H_4{\cdot}H_2O$	90	Light yellow	6.40 (6.53)	22.30 (22.60)	23.97 (24.68)	1.98 (2.07)	16.23 (17.28)
$Co(imdc)0.5N_2H_4{\cdot}H_2O$	95	Dark pink	6.30 (6.47)	23.50 (23.85)	23.95 (24.20)	1.96 (2.04)	16.83 (17.00)
$Ni(imdc)N_2H_4{\cdot}H_2O$	97	Bluish violet	12.40 (12.72)	21.90 (22.34)	22.53 (22.83)	2.56 (2.66)	19.93 (21.30)
$Zn(imdc)N_2H_4{\cdot}H_2O$	90	White	12.60 (12.72)	26.20 (25.99)	23.42 (23.86)	1.87 (1.99)	21.93 (22.26)
$Cd(imdc)0.5N_2H_4{\cdot}H_2O$	85	White	5.40 (5.31)	37.00 (37.28)	19.27 (19.96)	1.53 (1.67)	13.21 (13.97)

[a] H_2imdc = 4,5-imidazoledicarboxylic acid.

Table 2
IR spectral data (cm^{-1})

Compound	$\nu_{(OH)}$ of acid/water[a]	$\nu_{(NH)}$	$\nu_{(C=O)}$ of acid	$\nu_{asy(OCO)}$	$\nu_{sym(OCO)}$	$\nu_{(N-N)}$
H_2imdc	3423	3173	1660	1585	1382	–
	–	2955	–	–	–	–
N_2H_5Himdc	3328	3146	1600	1521	1380	977
	–	2974	–	–	–	
N_2H_5Himdc·H_2O	3463 (b)	3148	1610	1525	1386	974
	3330	2974	–	–	–	–
Mn(imdc)0.5N_2H_4·H_2O	3382 (b)	3214	–	1571	1386	962
Co(imdc)0.5N_2H_4·H_2O	3393 (b)	3327	–	1572	1391	967
Ni(imdc)N_2H_4·H_2O	3393 (b)	3313	–	1575	1388	970
Zn(imdc)N_2H_4·H_2O	3423 (b)	3288	–	1573	1389	962
Cd(imdc)0.5N_2H_4·H_2O	3423 (b)	3284	–	1570	1380	960

[a] b: broad.

$(N_2H_5)_2A$ and N_2H_4·$2H_2A$ (N_2H_5HA·H_2A) types of salts (H_2A-dibasic acid). The hydrazinium salts of these types with different dibasic acids have been reported [21,23,24]. The best known of these are only N_2H_4·H_2A and $2N_2H_4$·H_2A with dicarboxylic acids. But, only the former type of salt is obtained with H_2imdc. The 2:1 mole ratio aqueous solutions of hydrazine hydrate and H_2imdc always resulted in the formation of hydrazinium hydrogen-4,5-imidazoledicarboxylate monohydrate instead of dihydrazinium salt. The reason for this could be a strong internal hydrogen bond between the COOH and COO$^-$ groups of the bicarboxylate anion [16,25]. The metal complexes were highly insoluble in water and other common organic solvents. All of them are monohydrated and stable in air (Table 1).

3.1. Electronic spectra

The electronic spectra of the cobalt complex shows a strong band around 22,730 cm^{-1} which is assigned to the $^4T_{1g}(P) \rightarrow {}^4T_{1g}$ transition of typical six-coordinated

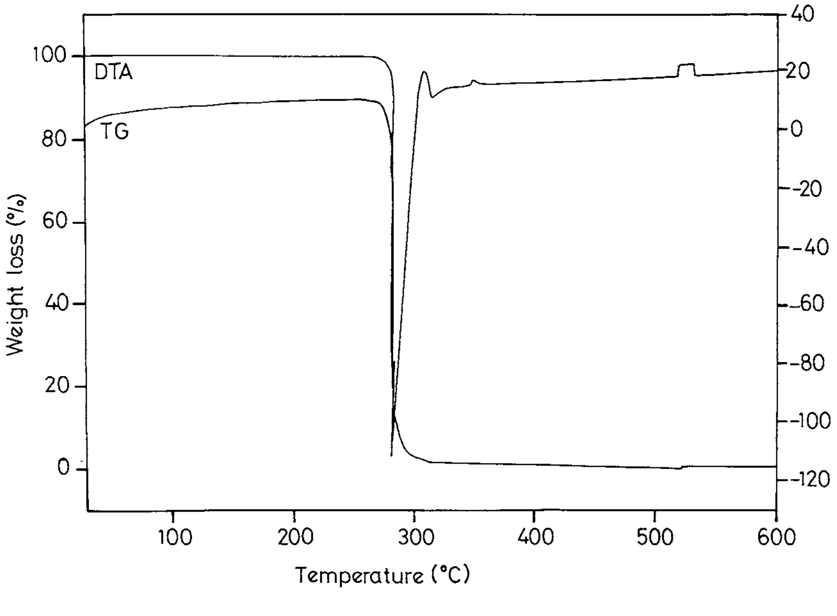

Fig. 1. Simultaneous TG-DTA of H_2imdc.

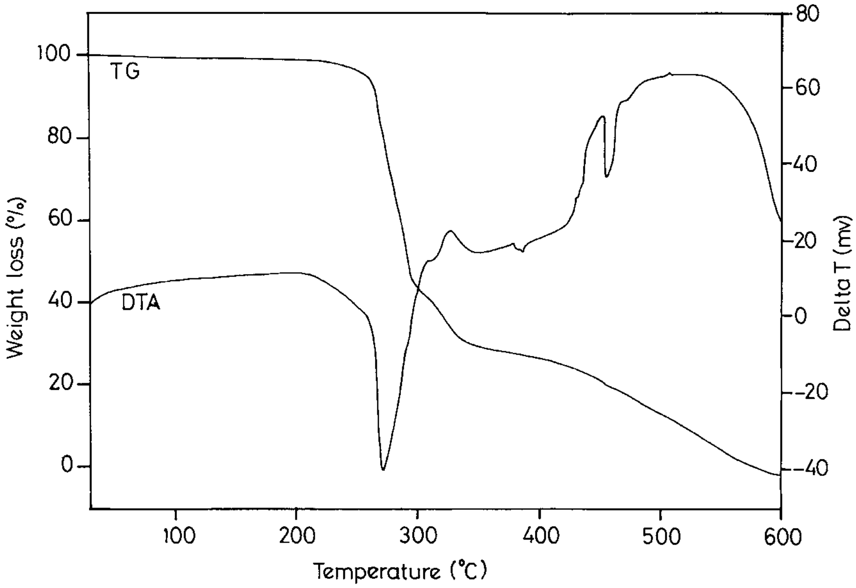

Fig. 2. Simultaneous TG-DTA of N_2H_5Himdc.

cobalt(II) complex [26]. The nickel complex exhibits two bands at 14,124 and 22,123 cm^{-1}, which are ascribable to $^3A_{2g} \rightarrow {}^3T_{1g}$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions, respectively, characteristic of octahedral geometry [26].

3.2. Infrared spectra

In Table 2 the main bands in the infrared spectra of the free acid, its salts and metal complexes are listed and are assigned on the basis of earlier studies [8,27]. The IR

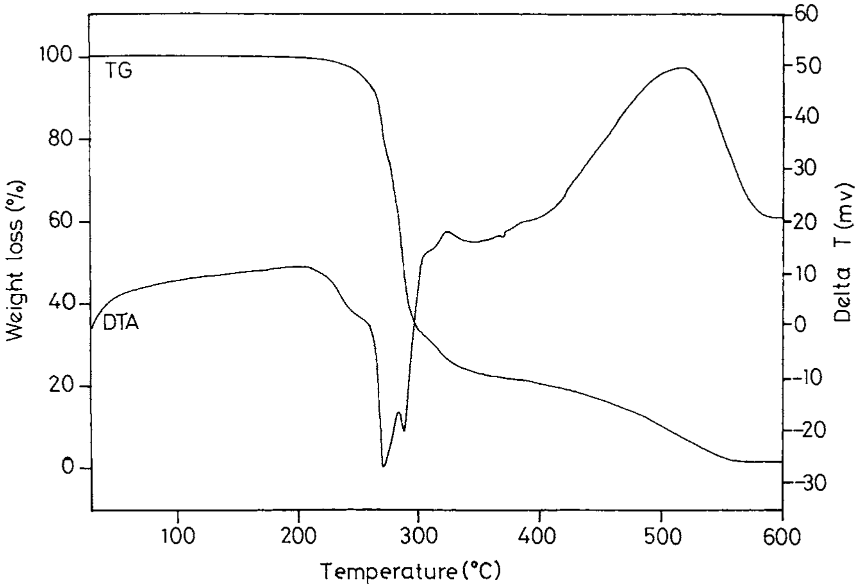

Fig. 3. Simultaneous TG-DTA of N_2H_5Himdc·H_2O.

spectra of the H_2imdc and its salt show the absorption frequencies in the region 3423–3328 cm^{-1}, due to O–H stretching of the free COOH group. The carboxyl stretching frequencies of free carbonyl groups in these cases register their absorption bands in the region 1660–1610 cm^{-1}. In addition to 3330 cm^{-1}, there is a broad band at 3463 cm^{-1} in the monohydrate salt, indicating the presence of water molecule. The IR frequencies in the region 1386–1380 and 1525–1521 cm^{-1} for these simple salts are assigned for symmetric and asymmetric stretching frequencies of the carboxylate ions, respectively. The N–N stretching frequencies in the range 977–974 cm^{-1} are indicative of the presence of $N_2H_5^+$ ion in the salt [23].

The infrared spectra of the metal complexes show a broad band in the region 3423–3382 cm^{-1} due to O–H stretching frequency of water molecule. In these complexes, the asymmetric and symmetric stretching frequencies of the carboxylate ions are seen in the ranges 1575–1570 and 1391–1380 cm^{-1}, respectively, with an average separation $\Delta\nu$ ($\nu_{asy}-\nu_{sym}$) of 185 cm^{-1}, indicating the monodentate coordination behaviour of both carboxylate groups [28] in the dianion. The N–N stretching frequency of these complexes appears in the

Table 3
Thermal decomposition data[a]

Compound	DTA peak temperature (°C)	Thermogravimetry (TG)			Decomposition phenomena/ decomposition product
		Temperature range (°C)	Mass loss (%)		
			Found	Calculated	
H_2imdc	281(+)	270–300	99.00	100.00	Complete decomposition
N_2H_5Himdc	272(+)	250–300	62.00	64.85	Dehydrazination and decarboxylation
	328(−)				
	422(−)sh				
	525(−)	300–600	99.00	100.00	Complete decomposition
N_2H_5Himdc·H_2O	246(+)				Dehydration, dehydrazination and decarboxylation
	271(+)d				
	289(+)d	240–300	66.00	67.00	
	322(−)				
	522(−)	300–600	99.00	100.00	Complete decomposition
Mn(imdc)0.5N_2H_4·H_2O	100(+)	55–120	13.50	13.99	Mn(imdc)
	382(−)	120–500	66.00	64.23	MnO_2
Co(imdc)0.5N_2H_4·H_2O	100(+)	50–125	15.00	13.76	Co(imdc)
	399(−)	125–465	69.00	67.05	Co_3O_4
Ni(imdc)N_2H_4·H_2O	105(+)				
	165(−)	50–170	20.00	19.03	Ni(imdc)
	257(−)				
	305(−)				
	378(−)	170–500	73.00	71.57	NiO
Zn(imdc)N_2H_4·H_2O	90(+)	50–110	16.00	18.55	Zn(imdc)
	380(−)				
	450(−)				
	486(−)				
	500(−)	110–560	69.00	67.60	ZnO
Cd(imdc)0.5N_2H_4·H_2O	91(+)	55–105	11.00	11.27	Cd(imdc)
	400(−)				
	412(−)sh				
	438(−)	105–560	55.00	57.41	CdO

[a] (+): endotherm; (−): exotherm; sh: shoulder; d: doublet.

range 970–960 cm^{-1} which is observed for the bidentate bridging hydrazine molecule [8].

3.3. Thermal studies

3.3.1. 4,5-imidazoledicarboxylic acid (H_2imdc)

The DTA of the H_2imdc shows a distinct endotherm (Fig. 1) at 281 °C due to complete decomposition of the acid into gaseous products. The TG shows distinct single-step decomposition between 270 and 300 °C with almost 100 % weight loss. This decomposition temperature of the free acid is in good agreement with the literature decomposition temperature [29].

3.3.2. Hydrazinium hydrogen-4,5-imidazoledicarboxylate (N_2H_5Himdc)

The simultaneous TG and DTA traces of this salt are given in Fig. 2. The TG of the salt shows two-step decomposition accordance with DTA showing a sharp endotherm followed by a broad exothermic multiplets. The endotherm at 272 °C is assigned to decorboxylation along with dehydrazination to give imidazole as an intermediate, which further undergoes continuous exothermic decomposition in the range 300–600 °C to gaseous products. This complete decomposition is in good agreement with TG weight loss, which is almost 100%.

3.3.3. Hydrazinium hydrogen-4,5-imidazoledicarboxylate monohydrate ($N_2H_5Himdc{\cdot}H_2O$)

Almost similar modes of decomposition as the anhydrous salt but for a endothermic doublets (271 and 289 °C) with a shoulder around 246 °C due to dehydration, which is clearly different from the anhydrous salt. The TG also shows (Fig. 3) a two-step decomposition, with dehydration, dehydrazination and decarboxylation, all taking place in a single-step, in the temperature range 240–300 °C to form imidazole which further decomposes exothermically as observed in the anhydrous salt.

3.3.4. Metal complexes

The thermal data of the complexes are summarised in the Table 3. The simultaneous TG-DTA of the complexes shows that they follow the same two-step decomposition with the isomeric metal imidazoledicarboxylate as intermediate. The formation of the intermediate is accompanied by a mass loss corresponding to the loss of a water molecule and hydrazine. This loss is observed as an endotherm around 100 °C, in all the compounds except nickel, which shows an endotherm at 105 °C followed by an exotherm at 165 °C. In the second step, the intermediate undergoes a continuous decomposition to give the

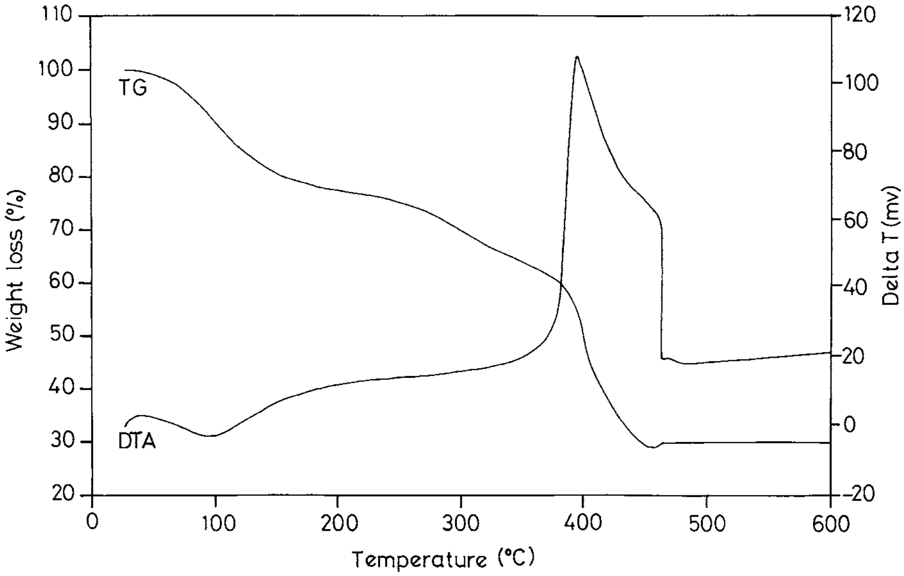

Fig. 4. Simultaneous TG-DTA of Co(imdc)$0.5N_2H_4{\cdot}H_2O$.

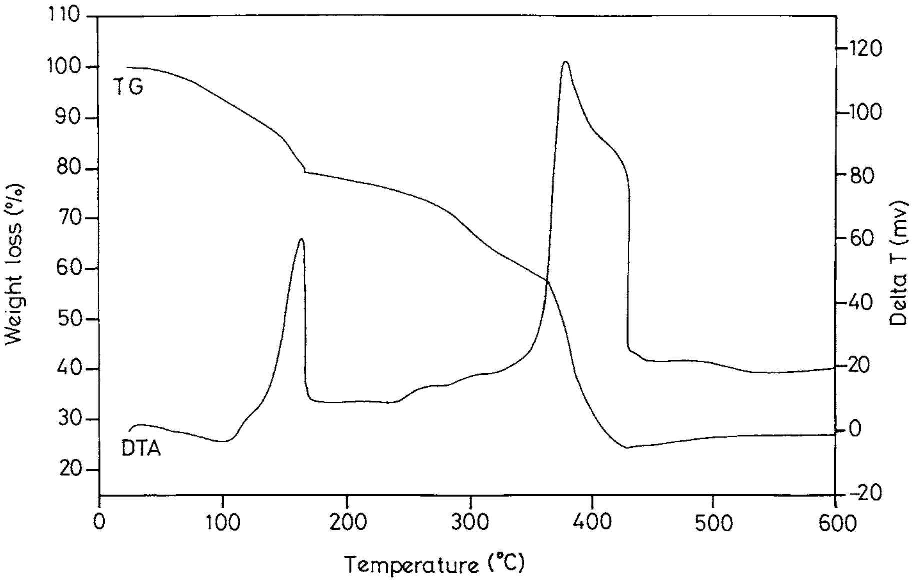

Fig. 5. Simultaneous TG-DTA of Ni(imdc)$N_2H_4{\cdot}H_2O$.

respective metal oxide as the end product. This is seen as a broad exotherm with subtle differences. The simultaneous TG-DTA of the cobalt and nickel compounds are shown in Figs. 4 and 5, respectively, as representative examples.

4. Conclusions

The H_2imdc forms only monohydrazinium salts and not the dihydrazinium derivatives due to internal hydrogen bonding.

The reaction of metal salts with H_2imdc and hydrazine hydrate give neutral hydrazine complexes. It is interesting to note that nickel and zinc form monohydrazinate type complexes whereas, other metals form only hemihydrazinate complexes.

The thermal decomposition of the free acid shows a strong single-step endothermic decomposition, while its salts undergo two-step decomposition with an endotherm followed by an exotherm. All the metal complexes undergo two-step decomposition to give metal oxide as an end product through metal imidazoledicarboxylate intermediate. The complexes are obtained only as powders and hence, structural studies could not be carried out.

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