

## **PREPARATION AND THERMAL REACTIVITY OF HYDRAZINIUM 2,*n*-PYRIDINEDICARBOXYLATES (*n*=3, 4, 5 and 6)**

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### **Abstract**

Hydrazinium 2,*n*-pyridinedicarboxylates of general compositions  $N_2H_5HA$ ,  $(N_2H_5)_2A \cdot H_2O$  and  $N_2H_5HA \cdot H_2A$ , where  $H_2A=2,n$ -pyridinedicarboxylic acid ( $n=3$ , quinolinic acid;  $n=4$ , lutidinic acid;  $n=5$ , isocinchomeric acid and  $n=6$ , dipicolinic acid) have been prepared by the neutralisation of aqueous solution of hydrazine hydrate with the respective acids, in stoichiometric ratios. Formation of these hydrazinium derivatives has been confirmed by analytical, IR spectral and thermal studies. Among these, the monohydrazinium salts are anhydrous whereas the dihydrazinium salts are monohydrated. While lutidinic and dipicolinic acids form all the three types of salts, the quinolinic and isocinchomeric acids do not form  $N_2H_5HA \cdot H_2A$  and  $N_2H_5HA$ , respectively, except the other two types. Infrared spectra of these salts reveal N–N stretching frequencies of the hydrazinium ion in the region  $970\text{--}950\text{ cm}^{-1}$ . The simultaneous TG and DTA of these salts show that all of them decompose without clear melting and lose hydrazine endothermically between 200 and 280°C, except dihydrazinium isocinchomeric acid monohydrate in which half of the hydrazine molecule is lost exothermically, to give pyridinemono- or dicarboxylic acid intermediate which further decomposes exothermically to gaseous products.

**Keywords:** hydrazinium salts, IR spectra, pyridinedicarboxylic acids, thermal decomposition

### **Introduction**

Hydrazine hydrate is a diacidic base and forms  $N_2H_5HA$ ,  $(N_2H_5)_2A$  and  $N_2H_5HA \cdot H_2A$  types of salts with dicarboxylic acids. Though, a variety of hydrazinium salts of the former two types with mineral [1–3] and carboxylic acids [3–9] have been studied, there appears to be no report on the hydrazinium salts of the third type, viz.,  $N_2H_5HA \cdot H_2A$ , except with oxydiacetic acid [9]. However, such a kind of salts of oxalic acid with ammonium [10] and potassium [10, 11], and dipicolinic acid with sodium [12, 13] and bis-cyclopentadienyl chromium III [14] have been studied in detail, including their crystal structures. These hydrazinium salts have numerous applications, such as a source of anhydrous hydrazine, additives in propellants, drugs to treat cancer and Hodgkin's disease, explosives [3] and also as ligands to prepare

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metal hydrazine complexes [15–18]. A few of these salts are also used as flame retardants [1, 2] and proton conductors [19]. While several hydrazinium dicarboxylates with oxalic [4, 5] to sebacic acids [7], phthalic [6], malic [7], aspartic, glutamic [7], maleic, fumaric [8] and oxydiacetic [9] acids have been characterized, the hydrazinium salts of pyridinedicarboxylic acids are still unknown. Prompted by the need to understand the type of salts formed by pyridinedicarboxylic acids, we have carried out the reaction of 2,*n* – pyridinedicarboxylic acids (*n*=3, H<sub>2</sub>qui; *n*=4, H<sub>2</sub>lut; *n*=5, H<sub>2</sub>iso; and *n*=6, H<sub>2</sub>dip) with hydrazine and the details are described herein.

## Experimental

All these salts reported here have been prepared by the neutralisation of the respective pyridinedicarboxylic acids in aqueous medium with hydrazine hydrate (99–100%) in appropriate molar ratios. All the acids were used as purchased (from Aldrich Chemical Co.) without further purification.

### *Preparation of hydrazinium hydrogenpyridinedicarboxylates, N<sub>2</sub>H<sub>5</sub>HA*

Hydrazinium hydrogenpyridinedicarboxylates were prepared by adding hydrazine hydrate (0.25 mL, 0.005 mol) to an aqueous solution (50 mL) containing respective pyridinedicarboxylic acids (0.84 g, 0.005 mol) in equimolar ratio. The resulting mixture was kept over water bath for a few minutes till a clear solution was obtained. This clear solution (pH=3–4) was concentrated over water bath to one half of its volume and kept aside for crystallization at room temperature. The powdered crystalline salts began to appear after a few hours and the crystallisation was continued for four days. During crystallization, the quinolinate and lutidinate crystals were creeping along the sides of the beaker. After four days, the crystals were filtered off and washed with absolute alcohol and dried in vacuo. In the case of isocinchomeric acid, hydrazinium hydrogen isocinchomeric acid was obtained, instead of the simple salt as in other cases.

### *Preparation of dihydrazinium pyridinedicarboxylate monohydrates, (N<sub>2</sub>H<sub>5</sub>)<sub>2</sub>A·H<sub>2</sub>O*

Hydrazine hydrate (0.5 mL, 0.01 mol) and respective pyridinedicarboxylic acids (0.84 g, 0.005 mol) in 2:1 ratio were mixed in 50 mL of water and heated over water bath to obtain a clear solution. Then, the volume of the clear solution, with pH=5–6, was reduced to half and kept for crystallisation at 27°C. The crystallisation started after two days and was allowed to continue for a week. The polycrystalline substances obtained were separated after a week, washed and dried as before.

### *Preparation of hydrazinium hydrogenpyridinedicarboxylate pyridinedicarboxylic acids, N<sub>2</sub>H<sub>5</sub>HA·H<sub>2</sub>A*

These salts were prepared by adding hydrazine hydrate (0.25 mL, 0.005 mol) to an aqueous solution (50 mL) of respective isomeric pyridinedicarboxylic acids (1.67 g,

0.01 mol) in 1:2 ratios. The resulting mixture was heated over water bath till a clear solution was obtained. In the case of isocinchomeric acid, the slight undissolved acid present was filtered out. The resulting clear solution (pH=2–3) was concentrated and crystallised as before. The salts obtained were separated, washed with absolute alcohol and dried in vacuo. In the case of lutidinic and dipicolinic acids the salts were formed within an hour as a bulky mass, whereas the isocinchomeronate was obtained only after 24 h. But in the case of quinolinic acid, the above isomeric salt was not obtained instead only hydrazinium hydrogenquinolinate was creeping along the sides of the beaker with the deposition of the free acid.

These salts are soluble in cold water except hydrazinium hydrogenisocinchomeronate isocinchomeric acid, which is completely soluble only in hot water. The dihydrazinium quinolinate monohydrate is slightly hygroscopic and hence stored in tightly closed container by keeping it in the desiccator over calcium chloride.

The hydrazine content, in these salts was, determined volumetrically using 0.025 M potassium iodate solution under Andrews' condition [20]. Elemental analyses were performed on Perkin Elmer 240 B CHN analyser. Infrared spectra of the salts in the range of 4000–400  $\text{cm}^{-1}$  were recorded on a Shimadzu FTIR 8000 spectrophotometer using KBr pellets. The simultaneous TG-DTA experiments were carried out using STA 1500 thermal analyser system. The heating rate employed was 10°C  $\text{min}^{-1}$  in air and nearly 4 mg of the sample was used for each experiment.

## Results and discussion

The results of the chemical analysis are given in Table 1. The analytical data agree well with the proposed formulae for the salts. All the monohydrazinium salts are anhydrous, whereas the dihydrazinium salts are monohydrated. Further, it is to be noted here that dipicolinic and lutidinic acids form all the three types of salts, whereas the quinolinic and isocinchomeric acids do not form  $\text{N}_2\text{H}_5\text{Hqui}\cdot\text{H}_2\text{qui}$  and  $\text{N}_2\text{H}_5\text{Hiso}$ , respectively, except the other two types.

### *Infrared spectra*

The important IR absorption bands of the acids and their salts along with the assignments are given in Table 2. The IR spectra of all the hydrazinium salts show bands in the region 3100–2900  $\text{cm}^{-1}$  which is assigned to N–H stretching of  $\text{N}_2\text{H}_5^+$  ions. The broad intense band observed in the region 3390–3320  $\text{cm}^{-1}$ , due to O–H stretching has been assigned to the water of hydration in the dihydrazinium salts. All of these salts show asymmetric and symmetric stretchings of the carboxylate group in the range 1615–1550 and 1470–1350  $\text{cm}^{-1}$  respectively. The sharp band observed between 1736 and 1681  $\text{cm}^{-1}$  for all the monohydrazinium salts except dihydrazinium salts confirms the presence of free acid group in them. The sharp band in the region 970–950  $\text{cm}^{-1}$  for these salts is an indicative of N–N stretching of  $\text{N}_2\text{H}_5^+$  ions [3].

**Table 1** Analytical data

Compound	Colour	Yield/%	Hydrazine/%		Carbon/%		Hydrogen/%		Nitrogen/%	
			obsd.	calcd.	obsd.	calcd.	obsd.	calcd.	obsd.	calcd.
N <sub>2</sub> H <sub>5</sub> Hqui	light yellow	93	16.50	16.07	42.00	42.19	4.46	4.52	20.92	21.09
(N <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> qui·H <sub>2</sub> O	yellow	90	26.10	25.69	33.58	33.72	6.14	6.02	27.83	28.10
N <sub>2</sub> H <sub>5</sub> Hlut	colourless	92	16.10	16.07	42.03	42.19	4.59	4.52	21.27	21.09
(N <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> lut·H <sub>2</sub> O	dull brown	95	25.20	25.69	33.50	33.72	5.93	6.02	27.10	28.10
N <sub>2</sub> H <sub>5</sub> Hlut·H <sub>2</sub> lut	colourless	90	8.70	8.74	45.58	45.87	3.79	3.82	15.11	15.29
(N <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> iso·H <sub>2</sub> O	dirty white	90	25.70	25.69	33.89	33.72	6.10	6.02	28.24	28.10
N <sub>2</sub> H <sub>5</sub> Hiso·H <sub>2</sub> iso	very light yellow	85	8.90	8.74	45.96	45.87	3.86	3.82	15.38	15.29
N <sub>2</sub> H <sub>5</sub> Hdip	colourless	94	15.80	16.07	41.98	42.19	4.60	4.52	21.26	21.09
(N <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> dip·H <sub>2</sub> O	colourless	91	26.30	25.69	33.60	33.72	5.96	6.02	28.33	28.10
N <sub>2</sub> H <sub>5</sub> Hdip·H <sub>2</sub> dip	colourless	95	8.80	8.74	45.71	45.87	3.80	3.82	15.40	15.29

**Table 2** Infrared spectral data/cm<sup>-1</sup>

Compound	O–H Str.	N–H Str.	$\nu_{C=O}$ of COOH	COO Asym. str.	COO Sym. str.	N–N Str.
H <sub>2</sub> qui	3182	–	1705	1614	1469	–
N <sub>2</sub> H <sub>5</sub> Hqui	3297	2994	1709	1554	1365	968
(N <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> qui·H <sub>2</sub> O	3295	2996	–	1557	1364	968
H <sub>2</sub> lut	3364	–	1701	1611	1460	–
N <sub>2</sub> H <sub>5</sub> Hlut	3337	3000	1724	1587	1410	963
(N <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> lut·H <sub>2</sub> O	3335	2998	–	1591	1361	968
N <sub>2</sub> H <sub>5</sub> Hlut·H <sub>2</sub> lut	3078	2910	1681	1552	1356	954
H <sub>2</sub> iso	3096	–	1734	1595	1387	–
(N <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> iso·H <sub>2</sub> O	3323	3038	–	1595	1387	970
N <sub>2</sub> H <sub>5</sub> Hiso·H <sub>2</sub> iso	3119	3057	1736	1599	1390	970
H <sub>2</sub> dip	3074	–	1697	1575	1416	–
N <sub>2</sub> H <sub>5</sub> dip	3339	3082	1726	1566	1375	968
(N <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> dip·H <sub>2</sub> O	3388	3059	–	1578	1379	951
N <sub>2</sub> H <sub>5</sub> dip·H <sub>2</sub> dip	3360	3097	1726	1560	1369	966

*Thermal analysis*

The thermal data of these salts are summarised in Table 3. Generally hydrazinium carboxylates are known [3–9] to melt before decomposition. But it is observed that all the salts reported here decompose without clear melting.

**Table 3** Thermal data ((+) – endo, (–) – exo peak; sh – shoulder)

Compound	DTA peak temp./°C	Thermogravimetry		Decomposition products
		Temp. range/°C	Mass loss/% obsd. calcd.	
N <sub>2</sub> H <sub>5</sub> Hqui	216(+)	201–246	40.00 38.67	nicotinic acid black residue complete decomposition
	311(+)	246–327	80.00 –	
	452(–)	327–580	100.00 100.00	
(N <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> qui·H <sub>2</sub> O	162(+)	133–204	19.50 20.07	N <sub>2</sub> H <sub>5</sub> Hqui nicotinic acid black residue complete decomposition
	211(+)	204–289	50.50 50.58	
	315(+)	289–340	83.50 –	
	454(–) 528(–)	340–600	93.75 100.00	
N <sub>2</sub> H <sub>5</sub> Hlut	260(+)	230–280	36.25 38.67	isonicotinic acid complete decomposition
	545(–)	280–580	93.80 100.00	
(N <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> lut·H <sub>2</sub> O	116(+)	110–270	32.50 32.92	lutidinic acid
	142(+)			
	173(+)			
	256(+)			

**Table 3** Continued

Compound	DTA peak temp./°C	Thermogravimetry			Decomposition products
		Temp. range/°C	Mass loss/%		
			obsd.	calcd.	
N <sub>2</sub> H <sub>5</sub> Hlut·H <sub>2</sub> lut	550(-)	270–620	92.00	100.00	complete decomposition
	243(+)	230–265	33.40	32.77	2 isonicotinic acid
	510(-)	265–545	91.00	100.00	complete decomposition
(N <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> iso·H <sub>2</sub> O	75(+)	57–122	7.00	7.23	(N <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> iso
	148(-)	122–150	13.00	13.65	N <sub>2</sub> H <sub>5</sub> Hiso·1/2N <sub>2</sub> H <sub>4</sub>
	271(+)	227–278	48.30	50.58	nicotinic acid
	542(-)	278–580	92.50	100.00	complete decomposition
N <sub>2</sub> H <sub>5</sub> Hiso·H <sub>2</sub> iso	266(+)	245–277	53.50	54.37	isocinchomeric acid
	524(-)	277–536	92.50	100.00	complete decomposition
N <sub>2</sub> H <sub>5</sub> Hdip	224(+) 237(+)	220–245	37.00	38.67	picolinic acid
	335(-) 383(-)	245–570	98.00	100.00	complete decomposition
	425(-) 546(-)				
	64(+)				
	125(+) 150(+)	121–160	7.0	7.23	(N <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> dip
(N <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> dip·H <sub>2</sub> O	226(+)	218–250	34.00	32.93	dipicolinic acid
	350(-) 381(-)	250–570	96.00	100.00	complete decomposition
	425(-) 520(-)				
	236(+)	228–255	54.00	54.37	dipicolinic acid
N <sub>2</sub> H <sub>5</sub> Hdip·H <sub>2</sub> dip	325(-) 385(-)	255–540	100.00	100.00	complete decomposition
	441(-) 510(-)				

N<sub>2</sub>H<sub>5</sub>Hqui and (N<sub>2</sub>H<sub>5</sub>)<sub>2</sub>qui·H<sub>2</sub>O

The former monohydrazinium salt shows three steps of decomposition in accordance with DTA showing two endotherms and an exotherm. The first endothermic effect at 216°C in DTA and the corresponding mass loss of around 40 per cent in TG agree well for the formation of nicotinic acid after the cleavage of hydrazine and carbon dioxide. The thermally formed nicotinic acid is known [21–23] to decompose endothermically around 300°C to give a black residue (which is not pyrolysed further

in the earlier study). In the present case also the pyrolytically obtained nicotinic acid decomposes endothermically at 311°C giving black residue [23] that further undergoes exothermic (452°C) complete decomposition into gaseous products. The black residue formation is observed as a break around 80 per cent in TG.

The DTA curve of the  $(\text{N}_2\text{H}_5)_2\text{qui}\cdot\text{H}_2\text{O}$  shows an endothermic effect at 162°C and a simultaneous mass loss of 19.5 per cent for the cleavage of one molecule each of water and hydrazine according to the TG. The  $\text{N}_2\text{H}_5\text{Hqui}$ , thus formed, shows almost identical decomposition pattern as that of the above.

#### $\text{N}_2\text{H}_5\text{Hlut}$ , $\text{N}_2\text{H}_5\text{Hlut}\cdot\text{H}_2\text{lut}$ and $(\text{N}_2\text{H}_5)_2\text{lut}\cdot\text{H}_2\text{O}$

A similar mode of decomposition has been observed for former two salts. Both of them undergo dehydrazination followed by partial decarboxylation to form isonicotinic acid as an intermediate at 260 and 243°C, respectively. Then, similar to the decomposition of the nicotinic acid discussed above, the isonicotinic acid also decomposes exothermically at 545 and 510°C, respectively, into gaseous products.

Unlike the monohydrazinium lutidates, the dihydrazinium salt shows multiple endothermic signals at 116, 142, 173 and 256°C corresponding to the elimination of water and two hydrazine molecules to give lutidinic acid. This pyrolytically obtained acid is not stable and hence undergoes continuous decomposition into gaseous products.

#### $(\text{N}_2\text{H}_5)_2\text{iso}\cdot\text{H}_2\text{O}$ and $\text{N}_2\text{H}_5\text{Hiso}\cdot\text{H}_2\text{iso}$

The TG of the former salt shows a four-step decomposition in accordance with DTA showing two endotherms and two exotherms. The first endotherm at 75°C is assigned to dehydration and is supported by the TG mass loss (found: 7.00%; calcd.: 7.23%). Then, the anhydrous salt loses one half of the molecule of hydrazine exothermically at 148°C to give  $\text{N}_2\text{H}_5\text{Hiso}\cdot\frac{1}{2}\text{N}_2\text{H}_4$  as an intermediate. This intermediate undergoes endothermic decomposition at 271°C to give nicotinic acid, which finally decomposes exothermically as expected.

The TG of  $\text{N}_2\text{H}_5\text{Hiso}\cdot\text{H}_2\text{iso}$  shows two-stage decomposition in relation to DTA showing a sharp endotherm followed by an exotherm. The endotherm at 266°C is assigned to decomposition of the salt to form isocinchomeric acid that further decomposes exothermically at 524°C to gaseous products.

#### $\text{N}_2\text{H}_5\text{Hdip}$ , $(\text{N}_2\text{H}_5)_2\text{dip}\cdot\text{H}_2\text{O}$ and $\text{N}_2\text{H}_5\text{Hdip}\cdot\text{H}_2\text{dip}$

The DTA of  $\text{N}_2\text{H}_5\text{Hdip}$  shows an endotherm and a broad complex exothermic multiplet. In the first endothermic decomposition at 237°C with a weak shoulder at 224°C one molecule each of hydrazine and carbon dioxide are lost with a formation of picolinic acid as an intermediate that is supported by the mass loss in TG (found: 37% and calcd.: 38.67%). The broad exotherm with peak temperatures at 335, 383, 425 and 546°C is ascribed to complete decomposition of the acid intermediate into gaseous products.

The TG of the dihydrazinium salt shows four steps of decomposition in accordance with DTA showing three endotherms and a broad exotherm. The first endotherm at 64°C is due to the loss of one half of the molecule of water and is supported by the mass loss in

TG (found: 3.5%; calcd.: 3.61%). The second endotherm observed as a doublet at 125 and 150°C is due to the loss of remaining 1/2H<sub>2</sub>O to give anhydrous dihydrazinium dipicolinate. However, TG shows a single step of decomposition for this loss of 1/2H<sub>2</sub>O in the temperature range 121–160°C. The anhydrous salt then decomposes sharply at 226°C with a loss of two molecules of hydrazine giving dipicolinic acid that further decomposes completely with the evolution of gaseous products. This is seen as a broad exotherm with complex multiplets in DTA.

The N<sub>2</sub>H<sub>5</sub>Hdip·H<sub>2</sub>dip also undergoes similar decomposition pattern as that of the former two salts showing a sharp endotherm at 236°C for the decomposition of the salt giving dipicolinic acid, which again decomposes exothermically as above.

Our effort to isolate the intermediates was unsuccessful due to their continuous decomposition. Hence, we have tried to assign the possible intermediates as observed from the TG mass losses, which are well consistent with the calculated mass losses (Table 3).

## Conclusions

Apart from the commonly known simple mono- and dihydrazinium salts, (N<sub>2</sub>H<sub>5</sub>HA and (N<sub>2</sub>H<sub>5</sub>)<sub>2</sub>A) of dicarboxylic acids, the some what rare type of salt, viz., N<sub>2</sub>H<sub>5</sub>HA·H<sub>2</sub>A (H<sub>2</sub>A=dicarboxylic acid) is also obtained with lutidinic, isochomeronic and dipicolinic acids with the exception of quinolinic acid, probably due to the internal hydrogen bonding between the adjacent carboxyl groups, which prevents the salt formation.

The dehydrazination is endothermic in all the cases, except (N<sub>2</sub>H<sub>5</sub>)<sub>2</sub>iso·H<sub>2</sub>O in which half of the hydrazine molecule is lost exothermically and remaining hydrazines endothermically. All the monohydrazinium salts show two steps of decomposition in TG, whereas the dihydrazinium salts exhibit multiple steps of decomposition. However, all of them decompose via., the respective pyridinemono- or dicarboxylic acid intermediate that further decomposes exothermically, proving the cleavage of the CO<sub>2</sub> group, which is located in the 2-position of the parent acid as reported [22, 23]. Further, the hydrazinium salts of the respective acids show similar mode of decomposition.

## References

- 1 K. C. Patil, J. P. Vittal and C. C. Patel, *Thermochim. Acta*, 43 (1981) 213.
- 2 K. C. Patil, J. P. Vittal and C. C. Patel, *J. Fire Retard. Chem.*, 7 (1980) 3.
- 3 E. W. Schmidt, *Hydrazine and its derivatives - Preparation, Properties and Applications*, Wiley, New York 1984.
- 4 D. Gajapathy, S. Govindarajan and K. C. Patil, *Thermochim. Acta*, 60 (1983) 87.
- 5 J. O. Thomas, *Acta Cryst.*, B29 (1973) 1767.
- 6 K. Kuppusamy, B. N. Sivasankar and S. Govindarajan, *Thermochim. Acta*, 259 (1995) 251.
- 7 S. Yasodhai and S. Govindarajan, *Thermochim. Acta*, 338 (1999) 113.
- 8 S. Govindarajan, S. U. Nasrin Banu, N. Saravanan and B. N. Sivasankar, *Proc. Indian Acad. Sci. (Chem. Sci.)*, 107 (1995) 559.

- 9 S. Yasodhai and S. Govindarajan, *J. Therm. Anal. Cal.*, 62 (2000) 737.
- 10 M. Currie, J. C. Speakman and N. A. Curry, *J. Chem. Soc. (A)*, (1967) 1862.
- 11 D. J. Haas, *Acta Cryst.*, 17 (1964) 1511.
- 12 K. Browning, K. A. Abboud and G. J. Palenik, *J. Chem. Cryst.*, 25 (1995) 851.
- 13 P. Laine, A. Gourdob and J.-P. Launay, *Inorg. Chem.*, 34 (1995) 5129.
- 14 D. Braga, C. Bazzi, L. Maini and F. Grenioni, *Cryst. Eng. Comm.*, 5 (1999).
- 15 S. Govindarajan, K. C. Patil, M. D. Poojary and H. Manohar, *Inorg. Chim. Acta*, 120 (1986) 103.
- 16 D. Gajapathy, S. Govindarajan, K. C. Patil and H. Manohar, *Polyhedron*, 2 (1983) 865.
- 17 B. N. Sivasankar and S. G. Govindarajan, *J. Therm. Anal. Cal.*, 48 (1997) 1401.
- 18 K. Kuppusamy and S. Govindarajan, *Thermochim. Acta*, 274 (1996) 125.
- 19 S. Chandra and N. Singh, *J. Phys. Chem.*, 16 (1983) 3081.
- 20 A. I. Vogel, *A Text Book of Quantitative Inorganic Analysis*, Longmans, London 1975, p. 380.
- 21 J. R. Allan, M. Barron and A. R. Werninck, *Thermochim. Acta*, 153 (1989) 249.
- 22 H. Briehl and J. Butenuth, *Thermochim. Acta*, 167 (1990) 249.
- 23 H. Briehl and J. Butenuth, *Thermochim. Acta*, 211 (1992) 121.