

## Dipicolinate complexes of main group metals with hydrazinium cation

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**Abstract.** Some new coordination complexes of hydrazinium main group metal dipicolinate hydrates of formulae  $(N_2H_5)_2M(dip)_2 \cdot nH_2O$  (where,  $M = Ca, Sr, Ba$  or  $Pb$  and  $n = 0, 2, 4$  and  $3$  respectively and  $dip = dipicolinate$ ),  $N_2H_5Bi(dip)_2 \cdot 3H_2O$  and  $(N_2H_5)_3Bi(dip)_3 \cdot 4H_2O$  have been prepared and characterized by physico-chemical techniques. The infrared spectra of the complexes reveal the presence of tridentate dipicolinate dianions and non-coordinating hydrazinium cations. Conductance measurements show that the mono, di and trihydrazinium complexes behave as 1:1, 2:1 and 3:1 electrolytes respectively, in aqueous solution. Thermal decomposition studies show that these compounds lose water followed by endothermic decomposition of hydrazine to give respective metal hydrogendipicolinate intermediates, which further decompose exothermically to the final product of either metal carbonates ( $Ca, Sr, Ba$  and  $Pb$ ) or metal oxycarbonates ( $Bi$ ). The coordination numbers around the metal ions differ from compound to compound. The various coordination numbers exhibited by these metals are six ( $Ca$ ), seven ( $Ba$ ), eight ( $Sr$ ) and nine ( $Pb$  and  $Bi$ ). In all the complexes the above coordination number is attained by tridentate dipicolinate dianions and water molecules. The X-ray diffraction patterns of these compounds differ from one another suggesting that they are not isomorphous.

**Keywords.** Hydrazinium; dipicolinate; main group metals; thermal analysis.

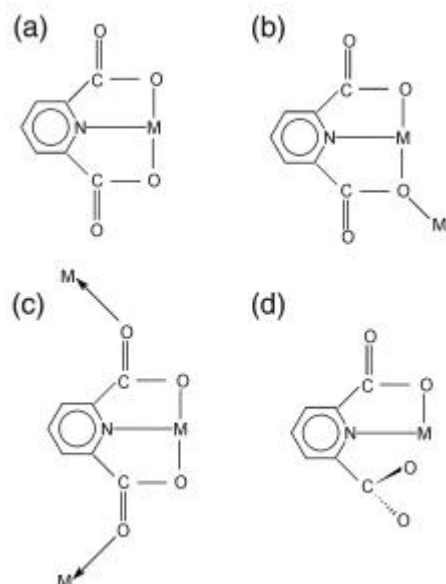
### 1. Introduction

The capacity of pyridine carboxylic acids to act as ligand is an important property, relevant in several areas of chemistry and in other sciences. The pyridine carboxylic acids, which have been by far most studied as ligands, are picolinic, nicotinic, isonicotinic, quinolinic, lutidinic, isocinchomeric, dipicolinic, cinchomeric and dinicotinic acid. Among these acids, the coordination chemistry of dipicolinic acid (pyridine-2,6-dicarboxylic acid,  $H_2 dip$ ) has attracted great attention for long time and significant progress has been made in understanding the structure of its complexes, both in solution<sup>1</sup> and in the solid state<sup>2</sup>.

The interest in this ligand seems to centre on the versatile and unpredictable manner in which it co-ordinates to a variety of metals. The different coordination modes for the dipicolinate dianion are shown in figure 1. Among these modes, the rigid tridentate coordination of this flat chelate ligand (figure 1a) is found for many bivalent or trivalent transition metals<sup>3,4</sup>. There are, however, a few examples of other coordination modes of

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**Figure 1.** Coordination modes for the dipicolinate dianion.

this ligand such as bridging of two metal atoms (figure 1b)<sup>5</sup>, polymerization of chelate complexes by coordination of the carbonyl atom (figure 1c)<sup>6</sup> and bidentate N–O coordination (figure 1d)<sup>7</sup>.

Based upon the coordination number of six to nine, commonly adopted by many main group metals, and the ability of  $\text{dip}^{2-}$  to function as a tridentate ligand, we expect to find anionic complexes of the type  $[\text{M}(\text{dip})_2]^{x-}$  ( $x=1$  or  $2$ ) and  $[\text{M}(\text{dip})_3]^{x-}$  ( $x=3$  or  $4$ ). A number of such complexes has been reported for transition metal ions, lanthanides and actinides, examples being  $\text{Na}[\text{M}(\text{dip})_2] \cdot 2\text{H}_2\text{O}$  ( $\text{M} = \text{Ru}, \text{Ir}$ )<sup>6</sup>,  $\text{Na}[\text{Cr}(\text{dip})_2] \cdot 1.5\text{H}_2\text{O}$ <sup>8</sup>,  $(\text{N}(\text{C}_3\text{H}_7)_4)_2[\text{Fe}(\text{dip})_2] \cdot 7.25\text{H}_2\text{O}$ <sup>9</sup>,  $\text{Na}[\text{Fe}(\text{dip})_2] \cdot 2\text{H}_2\text{O}$ <sup>9</sup>,  $\text{Na}_2[\text{M}(\text{dip})_2] \cdot n\text{H}_2\text{O}$ <sup>10</sup> ( $\text{M} = \text{Mn}, \text{Co}, \text{Ni}, \text{Cu}$  or  $\text{Zn}$ ;  $n=2$  or  $3$ ), some Nd and Yb complexes of the type  $\text{Na}_3[\text{M}(\text{dip})_3] \cdot n\text{H}_2\text{O}$ <sup>11</sup> and few actinide complexes  $(\text{Ph}_4\text{As})_2[\text{U}(\text{dip})_3] \cdot 3\text{H}_2\text{O}$ <sup>12</sup> and  $(\text{Ph}_4\text{As})_2[\text{UO}_2(\text{dip})_2] \cdot 6\text{H}_2\text{O}$ <sup>13</sup>. Apparently similar anionic complexes of main group metal ions have not been studied. This prompted us to study the dipicolinate complexes of main group metals with hydrazinium cation. We have chosen hydrazinium ion ( $\text{N}_2\text{H}_5^+$ ) as cation due to its interesting versatile nature, i.e., it can either act as a coordinating ligand to the metal<sup>14,15</sup> or as an ionic<sup>16</sup> species like  $\text{NH}_4^+$  counterion.

The complexes have been isolated in the solid state and structures have been assigned tentatively on the basis of their analytical, spectral, powder X-ray diffraction and thermal studies. The results of these studies are given in this paper.

## 2. Experimental

All the chemicals used were AnalaR grade and the solvents were freshly distilled before use. Hydrazine hydrate of 99–100% purity was used in all the reactions.

### 2.1 Preparation of $(N_2H_5)_2Ca(dip)_2$ and $(N_2H_5)_2Sr(dip)_2 \cdot 2H_2O$

The respective metal nitrates [ $Ca(NO_3)_2 \cdot 4H_2O$ , 0.4724 g, 0.002 mol and  $Sr(NO_3)_2$ , 0.4232 g, 0.002 mol] dissolved in water (50 ml) was added solid dipicolinic acid (0.6684 g, 0.004 mol). The resulting mixture was heated over a waterbath until the acid dissolved and a clear solution formed. To the clear solution, in the hot condition, 100% hydrazine hydrate (0.35 ml, 0.007 mol) was added with stirring and the pH of the solution was adjusted to 6 by adding a few drops of 10% hydrazine hydrate. This solution was concentrated to a 20 ml volume over a waterbath and then kept for crystallisation at room temperature. After four days, the crystalline solids deposited were collected by filtration and washed with ice-cold water–alcohol (1 : 1) mixture and air-dried.

### 2.2 Preparation of $(N_2H_5)_2Ba(dip)_2 \cdot 4H_2O$

Solid dipicolinic acid (0.6684 g, 0.004 mol) was added to a 50 ml of water containing  $Ba(NO_3)_2$  (0.5228 g, 0.002 mol) at room temperature. On heating, the acid dissolved and the solution became turbid. To this turbid solution, in hot condition, 100% hydrazine hydrate (0.35 ml, 0.007 mol) was added with stirring. Few drops of 10%  $N_2H_4$  was added until all solids had dissolved and the solution pH was 6. The resulting solution was heated on a waterbath for 30 min and then kept for crystallisation at room temperature. White powdered solid formed after 24 h was filtered out and the filtrate was reduced to 25 ml volume and left at room temperature for 4 days. The crystalline complex formed was filtered off and washed with ice-cold water–alcohol (1 : 1) mixture and air-dried.

### 2.3 Preparation of $(N_2H_5)_2Pb(dip)_2 \cdot 3H_2O$

Solid dipicolinic acid (0.6684 g, 0.004 mol) was added to a hot solution of  $Pb(NO_3)_2$  (0.6624 g, 0.002 mol) in water (75 ml). The acid dissolved with a formation of white precipitate. To this, in hot condition, 100% hydrazine hydrate (0.35 ml, 0.007 mol) was added with constant stirring. The pH of the mixture was adjusted to 6 by careful addition of a few drops of 10% hydrazine hydrate. On the addition of base, a large portion of the precipitate dissolved and was heated on a waterbath about an hour, in order to solubilise maximum amount of precipitate. After an hour of heating, the slight insoluble present was filtered off and the filtrate was reduced to 25 ml volume by heating on waterbath and was kept for crystallisation at room temperature. The white crystalline complex formation started after two days and the crystallisation was allowed to continue up to 5 days. After 5 days the complex obtained was filtered off and washed with ice-cold water–alcohol (1 : 1) mixture and air dried. The shiny crystals effloresced the water molecules and became opaque within two days. All the studies were carried out on opaque crystals.

### 2.4 Preparation of $N_2H_5Bi(dip)_2 \cdot 3H_2O$

$Bi(NO_3)_3 \cdot 5H_2O$  (0.98 g, 0.002 mol) and dipicolinic acid (0.6684 g, 0.004 mol) were mixed in 100 ml water and on heating both dissolved and a turbid solution was formed. To this turbid solution in hot condition 100% hydrazine hydrate (0.35 ml, 0.007 mol) was added with stirring, until a clear solution was obtained. Few drops of 10%  $N_2H_4 \cdot H_2O$  was added until the pH of the solution had a value  $\approx 6$ . The solution was heated for 30 min and the negligible amount of solid present was filtered out and the filtrate was reduced to

30 ml volume by heating on waterbath and then kept for crystallisation at room temperature. White solid formation started on the second day onwards and was filtered after four days and, washed and dried as before.

### 2.5 Preparation of $(N_2H_5)_3Bi(dip)_3 \cdot 4H_2O$

$Bi(NO_3)_3 \cdot 5H_2O$  (0.98 g, 0.002 mol) and dipicolinic acid (1 g, 0.006 mol) were mixed in 100 ml of water and on heating both dissolved and turbid solution formed. To this turbid solution in hot condition 100% hydrazine hydrate (0.6 ml, 0.012 mol) was added with stirring and the solution became clear with  $pH = 6$ . The resulting clear solution was concentrated to a 30 ml volume on a waterbath, filtered and then kept for crystallisation at room temperature. The hexagonal-shaped crystals formed, after five days, were collected by filtration and washed with ice-cold water–alcohol (1 : 1) mixture and air dried. The shiny crystals effloresced the water molecules and became opaque within two days and the studies were carried out on opaque crystals.

### 2.6 Analyses

The metal content in all the complexes was determined by EDTA complexometric titration, after decomposing a known weight of the sample with concentrated nitric acid. The hydrazine content was determined volumetrically using 0.025 M  $KIO_3$  solution under Andrews' conditions.

### 2.7 Physicochemical studies

The molar conductances of the complexes in 0.001 M solutions, in water, were measured using Elico CM183 EC-TDS analyser. The IR spectra of the solid samples in the range  $4000\text{--}400\text{ cm}^{-1}$  were recorded on a Shimadzu FTIR 8000 spectrophotometer using KBr pellets. Simultaneous TG-DTA experiments were carried out using STA 1500 systems. The heating rate employed was  $10^\circ\text{C min}^{-1}$  in air. About 10 mg of the sample was used for each experiment. The X-ray powder diffraction patterns of the samples were obtained using a JEOL JDX 8030 X-ray diffractometer using  $CuK_\alpha$  radiation with nickel filter.

## 3. Results and discussion

The reaction of metal nitrates (1 part) with dipicolinic acid (2 or 3 parts) and hydrazine hydrate (3.5 or 6 parts) yielded the hydrazinium metal dipicolinate hydrates of formula  $(N_2H_5)_2M(dip)_2 \cdot nH_2O$ , where  $n = 0$  for  $M = Ca$ ,  $n = 2$  for  $M = Sr$ ,  $n = 4$  for  $M = Ba$  and  $n = 3$  for  $M = Pb$ ,  $N_2H_5Bi(dip)_2 \cdot 3H_2O$  and  $(N_2H_5)_3M(dip)_3 \cdot 4H_2O$ . The chemical analyses (table 1) of these complexes conform to the desired composition.

### 3.1 Molar conductance

The molar conductances of 0.001 M aqueous solutions of the complexes are given in table 1. The calcium, strontium, barium and lead complexes show conductance value in the range  $231\text{--}249\text{ cm}^2\text{ mho mol}^{-1}$ , indicating their 2 : 1 electrolytic nature, for which  $\Lambda_M$  is expected to be in the range  $230\text{--}270\text{ cm}^2\text{ mho mol}^{-1}$ <sup>17</sup>. The monohydrazinium bismuth complex shows conductance value close to 1 : 1 electrolyte (e.g.,

**Table 1.** Analytical and molar conductance data.

Compound	Colour	Hydrazine (%)		Metal (%)		Molar conductance (cm <sup>2</sup> mho mol <sup>-1</sup> )
		Obs.	Calcd.	Obs.	Calcd.	
(N <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Ca(dip) <sub>2</sub>	White	14.10	14.67	9.70	9.19	231
(N <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Sr(dip) <sub>2</sub> .2H <sub>2</sub> O	White	12.20	12.31	17.20	16.85	237
(N <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Ba(dip) <sub>2</sub> .4H <sub>2</sub> O	White	10.30	10.57	21.90	22.68	249
(N <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Pb(dip) <sub>2</sub> .3H <sub>2</sub> O	White	9.70	9.73	32.40	31.52	240
N <sub>2</sub> H <sub>5</sub> Bi(dip) <sub>2</sub> .3H <sub>2</sub> O	White	5.10	5.11	33.90	33.37	126
(N <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> Bi(dip) <sub>3</sub> .4H <sub>2</sub> O	White	10.50	10.59	22.70	23.05	372

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

Compound	$\nu(\text{O-H})$	$\nu(\text{N-H})$	Ring vibration	$\nu_{\text{asy}}(\text{COO}^-)$	$\nu_{\text{sy}}(\text{COO}^-)$	$\frac{\Delta\nu[\nu_{\text{asy}}(\text{COO}^-)-\nu_{\text{sy}}(\text{COO}^-)]}{\nu(\text{N-N})}$	$\nu(\text{N-N})$
(N <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Ca(dip) <sub>2</sub>	–	3320 3190 3090	1616	1586	1384	202	957
(N <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Sr(dip) <sub>2</sub> .2H <sub>2</sub> O	3450	3285 3090	1621	1603	1381	222	967
(N <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Ba(dip) <sub>2</sub> .4H <sub>2</sub> O	3446	2982	1629	1602	1374	228	966
(N <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Pb(dip) <sub>2</sub> .3H <sub>2</sub> O	3325	3075 2997	1622	1565	1366	199	951
N <sub>2</sub> H <sub>5</sub> Bi(dip) <sub>2</sub> .3H <sub>2</sub> O	3412 3325	3083	1641	1583	1374	209	947
(N <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> Bi(dip) <sub>3</sub> .4H <sub>2</sub> O	3425 3321	3200 3088 2931	1622	1567	1382	185	957

NaCl – 120 cm<sup>2</sup> mho mol<sup>-1</sup>), whereas trihydrazinium bismuth complex shows conductance value (372) close to 3 : 1 electrolyte<sup>17</sup>.

### 3.2 Infrared spectra

The infrared spectral data of all the complexes are summarised in table 2 and are assigned on the basis of earlier studies<sup>18</sup>. The infrared spectra of calcium and monohydrazinium bismuth complexes are given in figures 2 and 3, as typical examples. Except calcium, all the compounds exhibit strong bands in the range 3450–3325 cm<sup>-1</sup> due to O–H stretching, confirming the presence of water molecule in the compounds. All the compounds show moderately strong bands in the region 3320–2930 cm<sup>-1</sup> due to N–H stretching. The bands in the region 1640–1615 cm<sup>-1</sup> correspond to the ring vibration. The increase in the value of ring vibration (about 20 cm<sup>-1</sup>) from the free ligand shows the coordination of ring nitrogen to the metal<sup>2</sup>. The asymmetric and symmetric stretching frequencies of carboxylate ions are seen in the ranges 1603–1560 and 1384–1360 cm<sup>-1</sup>, respectively with a ( $\nu_{\text{asy}}-\nu_{\text{sym}}$ ) separation of 228–185 cm<sup>-1</sup>, indicating the monodentate linkage of both the carboxylate groups in the dianion. The N–N stretching frequency of the N<sub>2</sub>H<sub>5</sub><sup>+</sup> ion in these complexes, appear in the range 967–947 cm<sup>-1</sup> which is in accordance with the noncoordinated N<sub>2</sub>H<sub>5</sub><sup>+</sup> ion<sup>18</sup>.

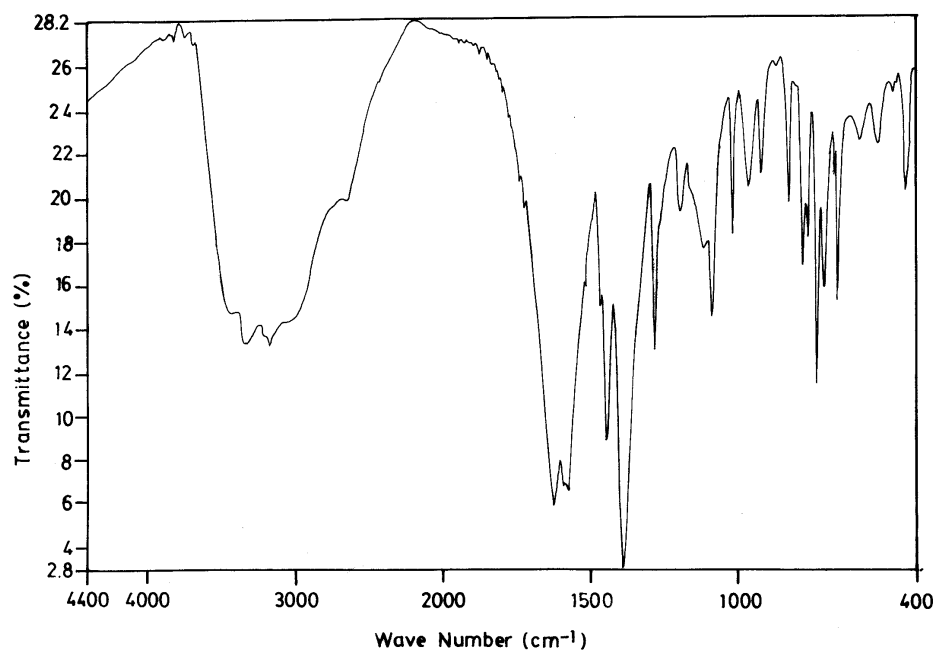


Figure 2. Infrared spectrum of  $(\text{N}_2\text{H}_5)_2\text{Ca}(\text{dip})_2$ .

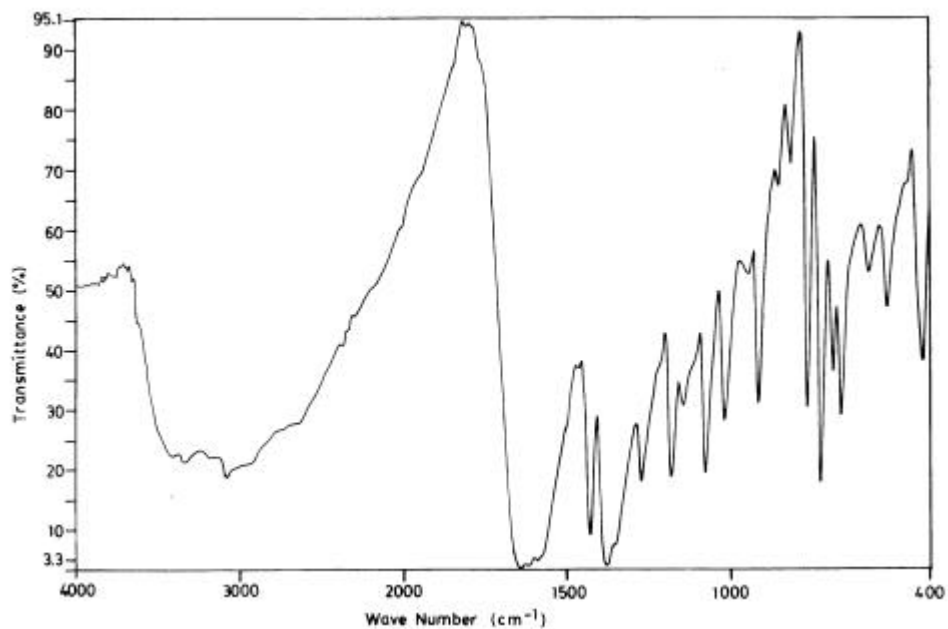


Figure 3. Infrared spectrum of  $\text{N}_2\text{H}_5\text{Bi}(\text{dip})_2 \cdot 3\text{H}_2\text{O}$ .

**Table 3.** Thermal data.

Compound	DTA peak temp. (°C)	Thermogravimetry			Intermediates/ end products
		Temp. range (°C)	Mass loss (%)		
			Obs.	Cald.	
$(N_2H_5)_2Ca(dip)_2$	113 (+)	40–195	7.50	7.33	$N_2H_5[Ca(Hdip)(dip)]$
	216 (+)	195–230	14.50	14.67	$Ca(Hdip)_2$
	289 (-)	230–540	54.00	52.97	$Ca(dip)$
	447 (-)				
	537 (-)				
593 (-)	540–625	73.50	77.06	$CaCO_3$	
$(N_2H_5)_2Sr(dip)_2 \cdot 2H_2O$	190 (+)	85–195	6.80	6.92	$(N_2H_5)_2[Sr(dip)_2]$
	270 (+)	215–270	20.60	19.24	$Sr(Hdip)_2$
	520 (-)	271–560	71.50	71.60	$SrCO_3$
	555 (-)				
$(N_2H_5)_2Ba(dip)_2 \cdot 4H_2O$	67 (+)	45–80	8.50	8.90	$(N_2H_5)_2[Ba(dip)_2(H_2O)]$
	142 (+)	80–145	12.90	11.89	$(N_2H_5)_2[Ba(dip)_2]$
	221 (+)	145–245	22.40	22.46	$Ba(Hdip)_2$
	360 (-)	245–520	50.00	50.06	$Ba(dip)$
	490 (-)				
	565 (-)				
520–570	67.50	67.41	$BaCO_3$		
$(N_2H_5)_2Pb(dip)_2 \cdot 3H_2O$	220 (+)	100–245	8.00	8.21	$(N_2H_5)_2[Pb(dip)_2]$
	385 (+)	245–390	30.00	31.34	$Pb(pic)_2$
	452 (-)	390–515	58.00	59.36	$PbCO_3$
	496(-) <i>sh</i>				
$N_2H_5Bi(dip)_2 \cdot 3H_2O$	270 (+)	75–315	14.00	13.73	$Bi(Hdip)(dip)$
	415 (-)	315–480	58.00	59.28	$Bi_2O_2CO_3$
	441 (-)				
	479 (-) <i>sh</i>				
$(N_2H_5)_3Bi(dip)_3 \cdot 4H_2O$	73 (+)	30–105	8.00	8.23	$(N_2H_5)_3[Bi(dip)_3]$
	262 (+)	105–300	38.00	38.28	$Bi(Hdip)(dip)$
	397 (-)	300–490	69.10	70.87	$Bi_2O_2CO_3$
	426 (-)				
	454 (-)				

(+): Endotherm; (-): exotherm, *sh*: shoulder

### 3.3 Thermal analysis

The thermal data of the complexes are listed in table 3. The compositions of the intermediates and the final products are those, which fit with the observed mass losses in TG. Thermogravimetric results are in good agreement with the DTA data. The simultaneous TG–DTA traces of calcium, barium and monohydrazinium bismuth complexes are shown in figures 4, 5 and 6, respectively, as representative examples.

3.3a  $(N_2H_5)_2Ca(dip)_2$ : The TG of the compound shows four steps of decomposition in accordance with DTA showing two endotherms and two exotherms. The first endotherm

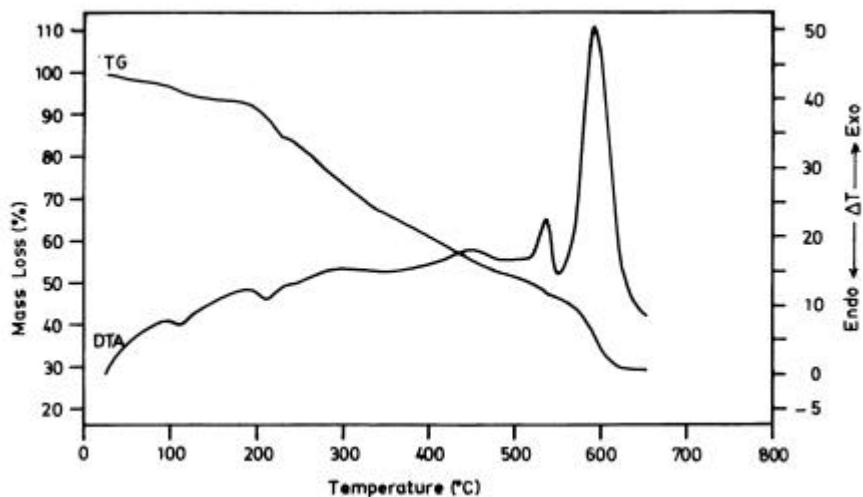


Figure 4. Simultaneous TG–DTA curves of  $(\text{N}_2\text{H}_5)_2\text{Ca}(\text{dip})_2$ .

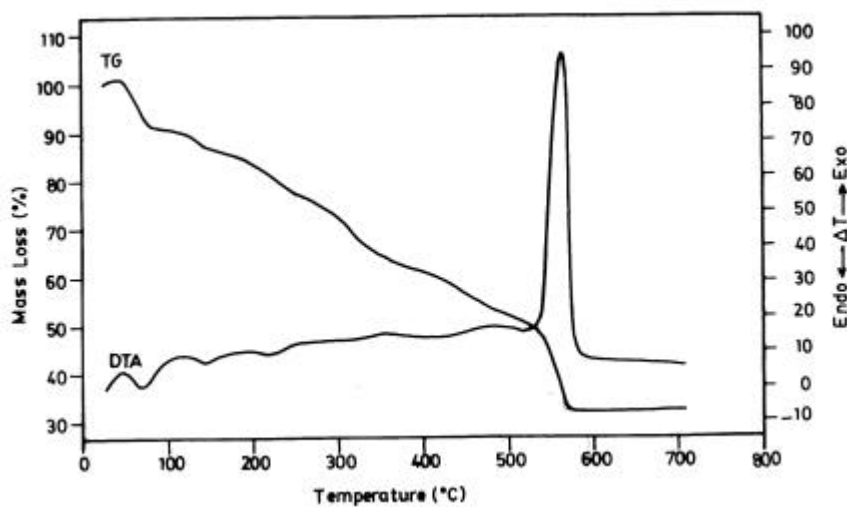
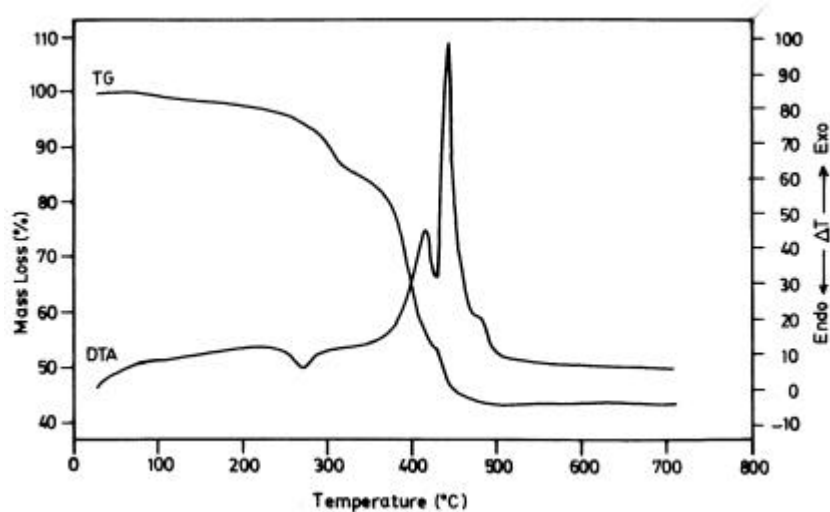


Figure 5. Simultaneous TG–DTA curves of  $(\text{N}_2\text{H}_5)_2\text{Ba}(\text{dip})_2 \cdot 4\text{H}_2\text{O}$ .

observed at 113°C is due to the loss of one molecule of hydrazine to form monohydrazinium calcium dipicolinate as an intermediate, which again loses hydrazine endothermically to form calcium hydrogendipicolinate as an intermediate. This intermediate undergoes a continuous exothermic decomposition with peak temperatures at 289, 447 and 537°C into calcium dipicolinate, which is supported by TG. In the final step, the calcium dipicolinate intermediate decomposes exothermically at 593°C to produce calcium carbonate.





**Figure 6.** Simultaneous TG–DTA curves of  $N_2H_5Bi(dip)_2 \cdot 3H_2O$ .

3.3b  $(N_2H_5)_2Sr(dip)_2 \cdot 2H_2O$ : This compound undergoes three stages of mass loss. The first stage that occurs in the range 85–195°C is attributed to the loss of two molecules of water. The corresponding DTA peak is observed as an endotherm at 190°C. Such high temperature dehydration is in support of the presence of coordinated water molecules in the compound. The second stage mass loss also takes place endothermically at 270°C as shown by DTA. This mass loss is in accordance with the loss of two molecules of hydrazine to form strontium hydrogendipicolinate intermediate, which finally undergoes exothermic decomposition to give  $SrCO_3$ . In DTA this is observed as an exothermic doublet with peak temperatures at 520 and 555°C.

3.3c  $(N_2H_5)_2Ba(dip)_2 \cdot 4H_2O$ : The barium compound decomposes in five steps. The first weight loss (8.50%) observed endothermically at 67°C can be attributed to the release of three water molecules (calculated 8.90%). Such a low temperature endothermic dehydration indicates that the water molecules are not coordinated to the metal. In the second step the remaining water molecule is lost endothermically at 142°C, suggesting that the water molecule is coordinated to the metal. The anhydrous compound then loses two molecules of hydrazine endothermically at 221°C to form barium hydrogendipicolinate as an intermediate. This intermediate then undergoes exothermic decomposition at 360 and 490°C into barium dipicolinate, which finally decomposes into barium carbonate in an exothermic (565°C) fashion as in other cases.

3.3d  $(N_2H_5)_2Pb(dip)_2 \cdot 3H_2O$ : This compound also shows three clear steps of decomposition. In the first step, three molecules of water are lost endothermically at 220°C. Such a high temperature of dehydration confirms the coordination of water molecules to the metal. In the second step, the anhydrous compound loses two molecules each of hydrazine and carbondioxide endothermically at 385°C to give lead picolinate as an intermediate. The formation of this intermediate is supported by a break around 30%

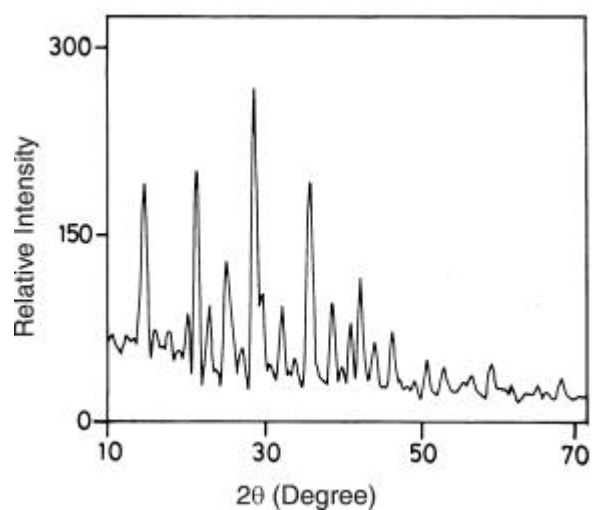
in TG. In the last step, the lead picolinate decomposes sharply at 452°C (exothermic) with a shoulder at 496°C to give PbCO<sub>3</sub>.

3.3e  $N_2H_5Bi(dip)_2 \cdot 3H_2O$ : This monohydrazinium compound shows two steps of decomposition in accordance with DTA showing one endotherm and a exothermic doublet with a shoulder. The first endotherm at 270°C corresponds to the loss of one molecule of hydrazine and three molecules of water to form bismuth dipicolinate as an intermediate. Here also the high temperature dehydration confirms that the water molecules are coordinated to the metal. The bismuth dipicolinate then decomposes into bismuth oxycarbonate. This is seen as a exothermic doublet at 415 and 441°C with a shoulder at 479°C in DTA. Corresponding to this TG also shows a continuous decomposition, but with a break around 46-50%. This may be probably due to the formation of bismuth oxalate, as an intermediate, which further decomposes to bismuth oxycarbonate. The theoretical mass loss for the formation of bismuth oxalate is 45.55%, which coincides with the observed value of 46.50%.

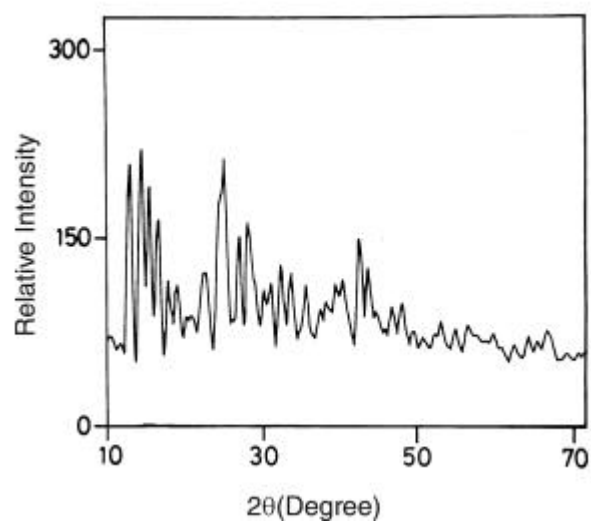
3.3f  $(N_2H_5)_3Bi(dip)_3 \cdot 4H_2O$ : The TG of this trihydrazinium compound shows three steps of decomposition. In the first step, all the four molecules of water are lost endothermically at 73°C suggesting the presence of water molecules as a lattice water. In the second step, three hydrazine molecules and one dipicolinate are lost endothermically in the range 105–300°C to give bismuth dipicolinate as an intermediate. The bismuth dipicolinate intermediate then decomposes as in the previous case.

**Table 4.** X-ray powder diffraction data ( $d$  spacings in Å and relative intensities in parentheses).

$(N_2H_5)_2M(dip)_2 \cdot nH_2O$				$N_2H_5Bi$	$(N_2H_5)_3Bi$
$M = Ca, n = 0$	$M = Sr, n = 2$	$M = Ba, n = 4$	$M = Pb, n = 3$	$(dip)_2 \cdot 3H_2O$	$(dip)_3 \cdot 4H_2O$
8.26 (54)	6.80 (100)	6.06 (68)	6.41 (41)	6.80 (92)	8.26 (100)
6.46 (56)	6.23 (62)	5.60 (26)	5.90 (38)	6.15 (100)	6.06 (73)
5.34 (37)	5.71 (46)	5.04 (26)	5.34 (66)	5.71 (83)	5.15 (46)
4.37 (40)	5.30 (47)	4.44 (31)	3.97 (41)	5.37 (73)	4.87 (42)
4.06 (43)	4.44 (50)	4.21 (76)	3.75 (51)	4.98 (50)	4.57 (39)
3.62 (37)	4.21 (61)	3.95 (32)	3.52 (100)	4.64 (48)	4.29 (59)
3.73 (100)	4.00 (65)	3.59 (46)	3.12 (51)	3.95 (53)	3.93 (62)
3.12 (32)	3.78 (64)	3.15 (100)	3.00 (49)	3.68 (72)	3.60 (48)
2.82 (37)	3.55 (69)	3.03 (35)	2.77 (50)	3.53 (78)	3.39 (80)
2.42 (31)	3.39 (88)	2.80 (33)	2.54 (41)	3.31 (69)	3.18 (45)
2.15 (29)	3.07 (61)	2.53 (71)	2.33 (48)	3.18 (73)	2.85 (44)
	2.87 (52)	2.35 (34)		2.99 (46)	2.66 (48)
	2.78 (54)	2.22 (29)		2.77 (55)	2.38 (49)
	2.61 (86)	2.16 (44)		2.67 (53)	
	2.43 (55)	2.07 (22)		2.53 (48)	
	2.35 (64)	1.97 (26)		2.29 (47)	
	2.28 (56)	1.81 (18)		2.13 (68)	
	2.17 (59)	1.57 (17)		2.07 (56)	
	2.11 (60)			1.94 (41)	
	1.74 (48)			1.89 (43)	



**Figure 7.** X-ray powder diffraction pattern of  $(\text{N}_2\text{H}_5)_2\text{Ba}(\text{dip})_2 \cdot 4\text{H}_2\text{O}$ .



**Figure 8.** X-ray powder diffraction pattern of  $\text{N}_2\text{H}_5\text{Bi}(\text{dip})_2 \cdot 3\text{H}_2\text{O}$ .

#### 3.4 X-ray powder diffraction

The X-ray diffraction patterns of these compounds differ from one another suggesting that the structures of the compounds are not same and the X-ray powder diffraction data of the complexes are summarised in table 4. The X-ray powder diffractograms of barium and monohydrazinium bismuth compounds are given in figures 7 and 8 respectively as references.

#### 4. Conclusions

New dipicolinate complexes of main group metals (Ca, Sr, Ba, Pb and Bi) with hydrazinium cation have been prepared and characterised. Attempt to prepare similar type of complexes with other main group metals such as Mg, Sn and Sb was unsuccessful due to the formation of insoluble dipicolinates. Bismuth forms both 1:2 and 1:3 (metal:dipicolinic acid) complexes whereas other metals form only 1:2 complexes.

The physico-chemical studies suggest that in these complexes the metal ions are coordinated by tridentate dipicolinate dianion and some water molecules, and the hydrazinium ions are present only as charge compensating counter ions. Accordingly six, seven and eight coordination has been proposed for calcium, barium and strontium, respectively, and nine coordination for lead and bismuth complexes. Such a kind of higher coordination number has been reported for lead (ten) in lead nitrate semicarbazone<sup>19</sup> and for bismuth (eight and nine) in EDTA<sup>20</sup> and DTPA<sup>20</sup> complexes. In the present cases also the higher coordination number is not highly improbable due to the multidonor ability of the dipicolinate dianion.

Though these compounds show multiple steps of decomposition, all of them lose hydrazine endothermically (> 200°C), to give the respective metal hydrogendipicolinates. These intermediates further decompose with exothermic multiplets to give the corresponding metal carbonates except bismuth giving oxycarbonate as the end product. The compounds are not isomorphous, as evidenced from the X-ray powder diffraction data.

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