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THERMAL ANALYSIS STUDIES ON PYRIDINE CARBOXYLIC ACID COMPLEXES OF ZINC(II)

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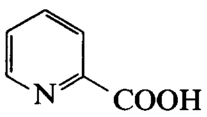
ABSTRACT

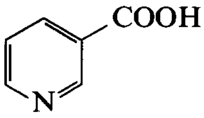
Compounds of zinc with picolinic acid, nicotinic acid and isonicotinic acid have been prepared. The thermal behaviour of these compounds together with that of the free pyridine carboxylic acids has been studied by thermogravimetry and differential thermal analysis. The metal complexes which are all hydrated lose water, followed by loss of the organic ligand to give zinc(II) oxide. The IR spectra of the compounds are also discussed.

INTRODUCTION

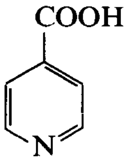
This work is an extension of previous studies on complexes of pyridine monocarboxylic acids with the first-row transition elements [1–3]. The pyridine carboxylic acids, picolinic acid, nicotinic acid and isonicotinic acid, have two different donor sites: the oxygen atoms of the carboxylic acid group and the nitrogen atom in the aromatic ring.



Picolinic acid
(Hpic)



Nicotinic acid
(Hnic)



Isonicotinic acid
(Hisonic)

This paper reports the thermal analysis studies of these pyridine carboxylic acids together with the complexes formed by the acids and zinc(II) ions. The IR spectra of the compounds have also been studied.

EXPERIMENTAL

Preparation of complexes

5 g of the pyridine carboxylic acid was dissolved in hot water and zinc carbonate was added in small amounts, with stirring, until effervescence

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ceased. The solution was filtered and the filtrate evaporated until the volume had decreased and the complex precipitated. The precipitate was filtered, washed with water and dried at room temperature.

Apparatus

The IR spectra were obtained using KBr discs, 4000–600 cm^{-1}, and polyethylene discs, 600–200 cm^{-1}, on a Perkin–Elmer IR spectrophotometer model 598.

The thermal analysis studies were carried out on a Stanton Redcroft model STA 781 thermobalance. Thermogravimetry (TG) and differential thermal analysis (DTA) curves were obtained at a heating rate of 6 °C min^{-1} in static air. In all cases the 20–600 °C temperature range was studied.

The concentration of the zinc ion was obtained using a Perkin–Elmer 373 atomic absorption spectrophotometer. The carbon, nitrogen and hydrogen analyses were determined using a Carlo Erba elemental analyser.

RESULTS AND DISCUSSION

The compounds formed between zinc ions and the pyridine carboxylic acids in aqueous solution have the following stoichiometries: $Zn(pic)_2(H_2O)_4$; $Zn(nic)_2(H_2O)_4$ and $Zn(isonic)_2 0.5H_2O$ (Table 1).

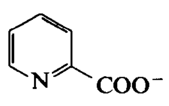
A comparison of the bands in the infrared spectra of the hydrated metal complexes with those of the free pyridine carboxylic acids shows that the spectra are similar in the 2000–650 cm^{-1} region. The complexes $Zn(pic)_2(H_2O)_4$ and Zn $(isonic)_2 0.5H_2O$ have bands in the range 3600–2700 cm^{-1}, ν(OH), and 1630–1580 cm^{-1}, δ(OH), indicating the presence of water which is not coordinated to the zinc. The presence of coordinated

TABLE 1

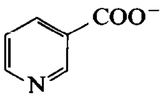
Analysis of compounds

Compounds	Calculated (%)				Experimental (%)			
	Zinc	Carbon	Nitrogen	Hydrogen	Zinc	Carbon	Nitrogen	Hydrogen
$Zn(pic)_2(H_2O)_4$	17.12	37.76	7.34	4.22	17.04	38.10	7.30	3.59
$Zn(nic)_2(H_2O)_4$	17.12	37.76	7.34	4.22	16.92	38.44	7.83	3.09
$Zn(isonic)_2 0.5H_2O$	20.51	45.24	8.79	2.84	20.23	44.54	8.60	2.71

pic,



; nic,



; isonic,

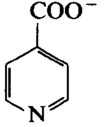


TABLE 2

Infrared spectra (4000–200 cm^{-1})

Compounds	ν_{O-H} (H_2O)	ν_{COOH}	ν_{COO^-}	ν_{C-O}	Ring vibrations	ν_{Zn-O}	ν_{Zn-N}
Hpic		1704(s)		1442(s)	1588(s) 1510(s)		
Zn(pic)$_2$(H_2O)$_4$	3500–2700(br, m)		1622(s)	1445(s)	1596(s) 1522(s)	294(w) Zn–OH_2 415(m)	449(m)
Hnic		1680(s)		1412(s)	1590(s) 1520(s)		
Zn(nic)$_2$(H_2O)$_4$			1640(s)	1424(s)	1600(s) 1562(s)	Zn–OH_2 410(m)	440(m)
H isonic		1705(s)		1410(s)	1610(s) 1545(s)		
Zn(isonic)$_2$0.5H_2O	3600–2800(br, m)		1590(s)	1408(s)	1625(s) 1562(s)	320(m), 304(m)	454(m)

br, broad; s, strong; m, medium; and w, weak.

water in the compounds $Zn(pic)_2(H_2O)_4$ and $Zn(nic)_2(H_2O)_4$ is shown by bands at 415 cm and 410 cm^{-1} which have been assigned to the $Zn{-}OH_2$ vibration [4]. The $\nu(C{=}O)$ bands in the compounds $Zn(pic)_2(H_2O)_4$ and Zn $(isonic)_2 0.5H_2O$ show a marked shift to lower frequency while in $Zn(nic)_2(H_2O)_4$ a much smaller shift to lower frequency is observed. In all of the complexes the bands due to the ring vibrations show a shift to higher frequency. The bands observed in the far infrared spectra of the metal complexes in the range 290–320 cm^{-1} have been assigned to $\nu(Zn{-}O)$ vibrations while the bands in the range 440–454 cm^{-1} have been assigned to $\nu(Zn{-}N)$ vibrations [5].

In the isonicotinic acid complex, the zinc atom is considered to be in an octahedral environment because bands are observed in the far infrared spectrum at 304 and 320 cm^{-1} [6]. The poor solubility of the compound suggests a polymeric structure [5,7–9]. The compound is thus considered to have a planar arrangement with a nitrogen atom and an oxygen atom of a carboxylate group of each isonicotinate bonded to two different zinc atoms to give a chain-like structure. It is further suggested that each zinc atom is bonded to oxygen atoms in adjacent layers to give the six-coordinate environment for the zinc atom. The water molecules are attached by hydrogen bonding.

In the compound $Zn(nic)_2(H_2O)_4$, the zinc ion has an octahedral environment involving the nitrogen atoms of two nicotinate groups and the oxygen atoms of the four water molecules [10]. The $Zn{-}OH_2$ vibration is observed in the far infrared spectrum of the compound and is reported in Table 2.

In the compound $Zn(pic)_2(H_2O)_4$, the picolinate acts as a simple chelate by coordinating to the zinc through the nitrogen atom of the aromatic ring and an oxygen atom of the carboxylate group. Two of the water molecules are also involved to give a six-coordinate environment for the zinc ion. The remaining two water molecules are involved in hydrogen bonding which exists between molecules in the crystal lattice [11]. The presence of the coordinated and uncoordinated water in the compound is again evident from the bands recorded in the IR spectrum (Table 2).

The TG and DTA curves for picolinic acid, Fig. 1, show that the acid is

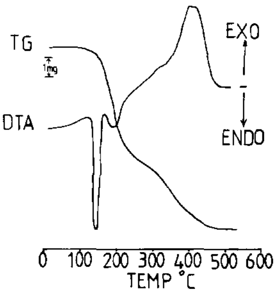


Fig. 1. TG/DTA curves for picolinic acid, sample weight = 9.50 mg.

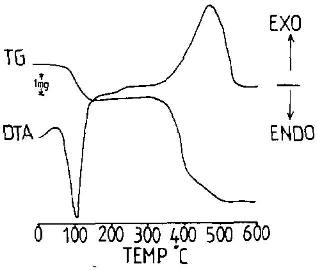


Fig. 2. TG/DTA curves for nicotinic acid, sample weight = 9.28 mg.

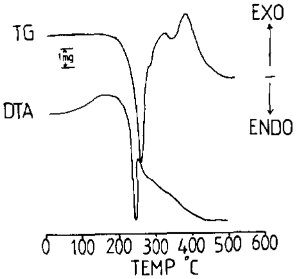


Fig. 3. TG/DTA curves for isonicotinic acid, sample weight = 9.68 mg.

TABLE 3

Dehydration processes of the zinc complexes

Process	Peak temperature (°C)	Thermal nature of transformation	Weight loss (%)		Enthalpy ($kJ\ mol^{-1}$)
			Calc.	Found	
$Zn(pic)_2(H_2O)_4 \rightarrow Zn(pic)_2$	114	Endo	18.89	18.68	282
$Zn(nic)_2(H_2O)_4 \rightarrow Zn(nic)_2$	93	Endo	18.89	19.76	214
$Zn(isonic)_2 0.5H_2O \rightarrow Zn(isonic)_2$	104	Endo	2.82	2.62	55

TABLE 4

Decomposition process of each acid and zinc complex

Process	Temp. range (°C)	Thermal nature of transformation	Residue (%)	
			Calc.	Found
pic → pyrolytic process	96–456	Endo/exo	–	–
nic → pyrolytic process	140–426	Endo/exo	–	–
isonic → pyrolytic process	150–472	Endo/exo	–	–
$Zn(nic)_2 \rightarrow ZnO$	312–530	Exo	21.31	22.52
$Zn(nic)_2 \rightarrow ZnO$	210–502	Exo	21.31	20.93
$Zn(isonic)_2 \rightarrow ZnO$	350–470	Exo	25.54	26.26

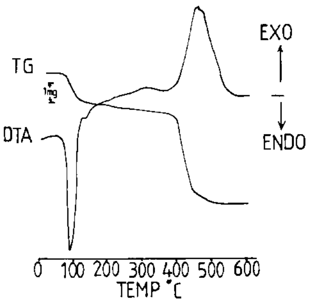


Fig. 4. TG/DTA curves for $Zn(pic)_2(H_2O)_4$, sample weight = 9.10 mg.

thermally stable in the range 20–96 °C. Its pyrolytic decomposition begins at 96 °C and finishes at 456 °C with total elimination of the sample. The DTA curve shows an endothermic peak at 138 °C due to fusion. The value for the fusion enthalpy is 30 kJ mol^{-1}. The acid then decomposes immediately producing an exothermic peak at 415 °C. The TG and DTA curves for zinc picolinate tetrahydrate, Fig. 2, show that the four water molecules are removed in one step and an endothermic peak is observed in the DTA trace at 114 °C. The observed weight loss for this process compares favourably with the theoretical values, Table 3. The dehydration enthalpy has been calculated and is given in Table 3. The anhydrous complex is stable over the temperature range 125–315 °C. The complex then decomposes at 315 °C with loss of the organic ligand and the residual weights are in good agreement with the values required for ZnO, Table 4. In the DTA curve this decomposition process corresponds to an exothermic peak for the complex.

The TG and DTA curves for nicotinic acid, Fig. 3, show that the acid is stable in the range 20–140 °C. Its pyrolytic decomposition begins at 140 °C and finishes at 426 °C. The DTA curve shows an endothermic peak at 237 °C due to fusion. The value of the fusion enthalpy is 30 kJ mol^{-1}. The acid then decomposes immediately producing an exothermic peak at 397 °C. The TG and DTA curves for zinc nicotinate tetrahydrate complex, Fig. 4, show that the four water molecules are removed in one step and an

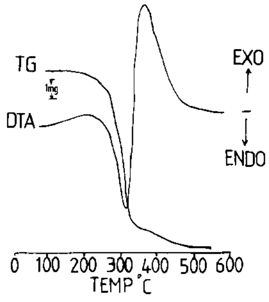


Fig. 5. TG/DTA curves for $Zn(nic)_2(H_2O)_4$, sample weight = 8.60 mg.

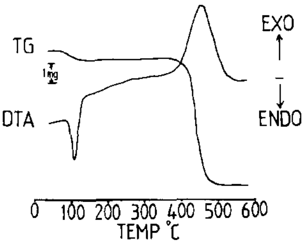


Fig. 6. TG/ DTA curves for Zn(isonic)$_2$0.5H$_2$O, sample weight = 9.52 mg.

endothermic peak for the dehydration process is observed at 93 °C in the DTA trace. The observed weight loss for the process compares favourably with the theoretical value, Table 3. The dehydration enthalpy has been calculated and is given in Table 3. The complex then decomposes at 140 °C with loss of the organic ligand and the formation of zinc oxide. The residual weight is in good agreement with the value required for ZnO, Table 4. In the DTA curve this decomposition process corresponds to an exothermic peak for the complex.

The TG and DTA curves for isonicotinic acid, Fig. 5, show that the acid is thermally stable in the range 20–150 °C. Its pyrolytic decomposition begins at 150 °C and finishes at 427 °C with total elimination of the sample. The DTA curve shows an endothermic peak at 320 °C due to fusion. The value for the fusion enthalpy is 135 kJ mol^{-1}. The acid then decomposes immediately producing an exothermic peak at 382 °C. The TG and DTA curves for the hydrated zinc isonicotinate, Fig. 6, shows that the half molecule of water is removed in one step and an endothermic peak is produced. The observed weight loss for this process compares favourably with the theoretical values, Table 3. The dehydration enthalpy has been calculated and is given in Table 3. The anhydrous complex is stable over the temperature range 107–350 °C. The complex then decomposes at 350 °C with loss of the organic ligand and the residual weights are in good agreement with the values required for ZnO, Table 4. In the DTA curve this decomposition process corresponds to an exothermic peak for the complex.

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