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The thermal, spectral and magnetic studies of hippuric acid compounds of cobalt(II), nickel(II), copper(II) and zinc(II) ions

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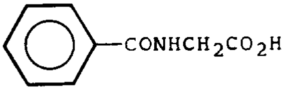
Abstract

Compounds of hippuric acid with cobalt, nickel, copper and zinc have been prepared in aqueous solution. The compounds which have been characterised by analyses, magnetic moments, and vibrational and electronic spectra have their metal ions in an octahedral environment. The thermal behaviour of the compounds has been studied by thermogravimetry and differential thermal analysis. The compounds, which are hydrated, lose their water of crystallisation followed by the organic ligand to give the metal oxide.

INTRODUCTION

Hippuric acid is a monocarboxylic acid with three types of donor site: the nitrogen and oxygen atoms of the amide group, and the oxygen atom of the carboxylic acid group.



Hippuric acid ($C_9H_9O_3N$)

This paper reports the thermal analysis studies of hippuric acid and of its complexes with the transition metals cobalt, nickel, copper and zinc. Spectral and magnetic studies were used to characterise each metal complex and to interpret the type of coordination which takes place to the metal ion.

EXPERIMENTAL

Preparation of the compounds

Hippuric acid (0.05 mol) was dissolved in boiling water; the resulting solution was then neutralised by addition of cobalt(II) carbonate. The solution was then filtered to remove any excess cobalt(II) carbonate and the

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filtrate was reduced in volume to yield the metal complex. This procedure was repeated using the carbonates of zinc(II), copper(II) and nickel(II).

Apparatus

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

The IR spectra were measured using KBr discs (4000–600 cm^{-1}) and polythene discs (600–200 cm^{-1}) on a Perkin–Elmer spectrophotometer model 598.

Magnetic measurements were carried out by the Gouy method using $Hg[Co(SCN)_4]$ as calibrant. Thermal analysis studies were made on a Stanton Redcroft model STA 1500 thermobalance. The thermogravimetry (TG) and differential thermal analysis (DTA) curves were obtained at a heating rate of 10 °C min^{-1} in static air over a temperature range of 20–800 °C.

RESULTS AND DISCUSSION

The analytical results for the complexes are given in Table 1. These analyses agree with the given formula proposed for the complexes. The formulae for the cobalt, nickel, copper and zinc complexes show the presence of water molecules.

The wavenumbers of the IR absorption bands as well as their descriptions and assignments are given in Table 2. The cobalt, nickel, copper and zinc compounds all show a strong broad absorption band in the region 3665–2800 cm^{-1}, due to ν(O–H), indicating the presence of water of crystallisation [1]. These broad bands obscure the bands due to the ν(N–H) vibrations for the

TABLE 1

Analyses and magnetic moments of the compounds

Compound		Metal	Carbon	Nitrogen	Hydrogen	μ (B.M.)
$Co(C_9H_8O_3N)_2 \cdot 4H_2O$	Found	12.09	44.35	5.74	4.95	4.94
	Theory	11.68	44.03	5.32	4.82	
$Ni(C_9H_8O_3N)_2 \cdot 5H_2O$	Theory	11.62	42.80	5.54	5.18	3.08
	Found	11.43	42.66	5.62	5.03	
$Cu(C_9H_8O_3N)_2 \cdot 3H_2O$	Theory	13.40	45.61	5.91	4.67	1.59
	Found	13.24	45.39	5.66	4.22	
$Zn(C_9H_8O_3N)_2 \cdot 4H_2O$	Theory	13.24	43.78	5.67	4.89	–
	Found	13.44	43.62	5.64	4.69	

TABLE 2

Infrared spectra 4000–200 cm^{-1} [a]

Compound	$\nu_{(O-H)}(H_2O)$	$\nu_{(N-H)}(NH)$ [b]	$\nu(COOH)$	$\nu_{(C=O)}(CO)$	$\nu(COO^-)$	ν_{M-O}	ν_{M-N}
$C_9H_8O_3N$	–	3344 (s)	1761 (s)	1601 (s)	– –	–	–
$Co(C_9H_8O_3N)_2 \cdot 4H_2O$	3660–2880 (br,s)	3305 (s)	–	1644 (s)	1579 (s), 1406 (s)	260 (m)	220 (w)
$Ni(C_9H_8O_3N)_2 \cdot 5H_2O$	3664–2905 (br,s)	3300 (s)	–	1626 (s)	1562 (s), 1410 (s)	252 (m)	222 (w)
$Cu(C_9H_8O_3N)_2 \cdot 3H_2O$	3640–2800 (br,s)	3332 (s)	–	1642 (s)	1573 (s), 1416 (s)	268 (m)	236 (w)
$Zn(C_9H_8O_3N)_2 \cdot 4H_2O$	3620–2890 (br,s)	3280 (s)	–	1650 (s)	1579 (s), 1397 (s)	287 (m)	230 (w)

[a] s, strong; br, broad; m, medium; w, weak.

[b] N–H bands obtained from the IR spectra of the compounds after removal of water using the thermobalance.

TABLE 3

Electronic spectra

Compound	Band positions (cm^{-1})	d–d transition
$Co(C_9H_8O_3N)$	8696 19047	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$
$Ni(C_9H_8O_3N)$	8475 18180 25310	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$
$Cu(C_9H_8O_3N)$	14084	$^2E_g(D) \rightarrow {}^2T_{2g}(D)$

cobalt, nickel, copper and zinc complexes. Therefore, each complex was heated on a thermobalance at a fixed temperature until constant weight was obtained to remove the water molecules. The IR spectra were then obtained for each of the anhydrous compounds. The ν(N–H) vibration in the complexes moves to lower wavenumbers when comparison is made between the IR spectra of the complexes and the hippuric acid. These observations indicate that bonding is taking place between the nitrogen atom of the NH group and the metal ions [2]. The IR spectra of the complexes confirm the absence of free carboxylic groups. Bands due to $\nu(COO^-)$ vibrations are observed instead of the band due to free CO_2H vibrations [3]. The band at around 1660 cm^{-1} in hippuric acid and its metal complexes is assigned to the ν(CO) vibration of the amide group. The increase in the absorption frequency in the metal complexes of this carbonyl group suggests that no coordination is taking place through the oxygen to the metal ions [4]. Metal–oxygen and metal–nitrogen bonds are also listed in Table 2 for each of the complexes. The presence of metal–oxygen bands would suggest that the metal ions are in an octahedral environment [5,6].

The electronic spectra (Table 3) and the magnetic measurements (Table 1) for the cobalt and nickel compounds support the suggestion that the metal ions are in an octahedral environment [1]. The single broad absorption band at 14084 cm^{-1} in the electronic spectrum of the copper compound, see Table 3, shows that the copper ions are in an octahedral environment [1]. The magnetic moment of 1.59 B.M. (Table 1) is indicative of some copper–copper interaction in the compound.

The insolubility of the compounds in both polar and non-polar solvents would suggest that they have polymeric structures [1]. The fact that these compounds were isolated as powders and not as single crystals means that no complete structure determination can be made. However, the spectroscopic and magnetic data available enable us to predict that in the complexes, the metal ions are in an octahedral environment. The compounds are considered to have a planar arrangement with the nitrogen atom of the

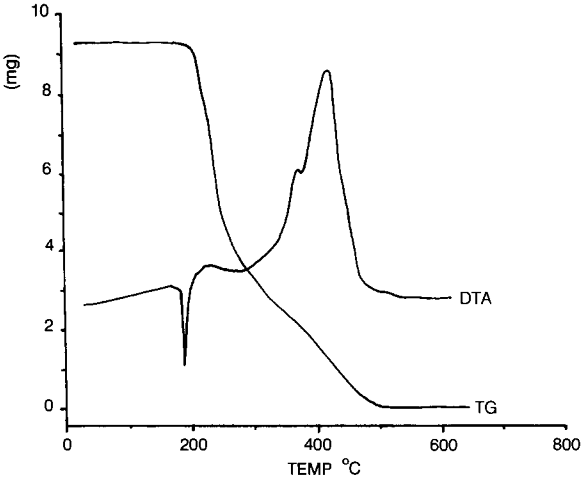

Fig. 1. TG and DTA traces of hippuric acid, sample weight, 9.214 mg.

amide group and the oxygen atom of a carboxylate group of two different hippurate ions bonded to a metal atom to give one layer. It is further suggested that each metal atom is bonded to oxygen atoms in adjacent layers to give a six-coordinate environment for the metal ion and a polymeric structure. The water molecules are attached by hydrogen bonding.

The TG and DTA curves for the hippuric acid, see Fig. 1, show that it is thermally stable in the temperature range 20–192 °C; its pyrolytic decomposition starts at 192 °C and finishes at 512 °C with the total elimination of the sample. The DTA curve of hippuric acid (Fig. 1) shows an endothermic peak at 190 °C corresponding to fusion. The value of the heat of fusion is 33 kJ mol^{-1}. Liquid hippuric acid decomposes immediately with an exothermic peak at 426 °C. The TG and DTA curves for the complexes formed between

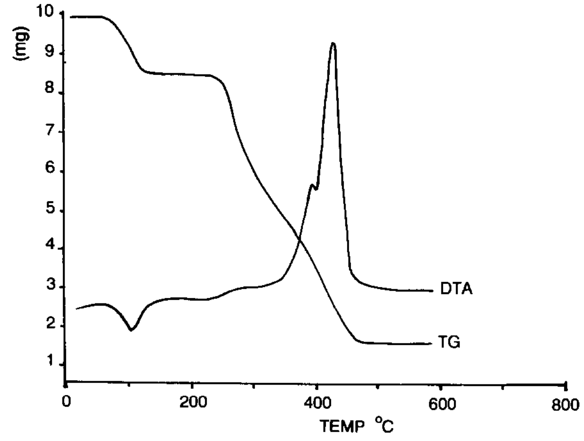

Fig. 2. TG and DTA traces of $\mathrm{Co(C_9H_8O_3N)_2 \cdot 4H_2O}$, sample weight, 9.913 mg.

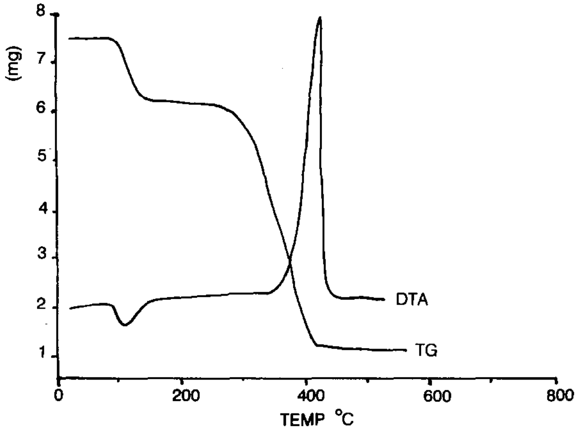

Fig. 3. TG and DTA traces of $Ni(C_9H_8O_3N)_2 \cdot 5H_2O$, sample weight, 7.528 mg.

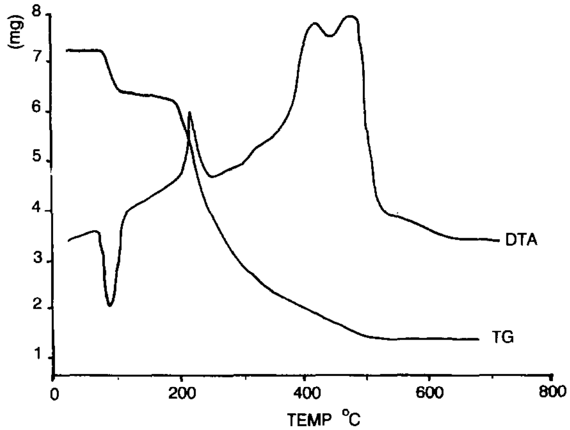

Fig. 4. TG and DTA traces of $Cu(C_9H_8O_3N)_2 \cdot 3H_2O$, sample weight, 7.269 mg.

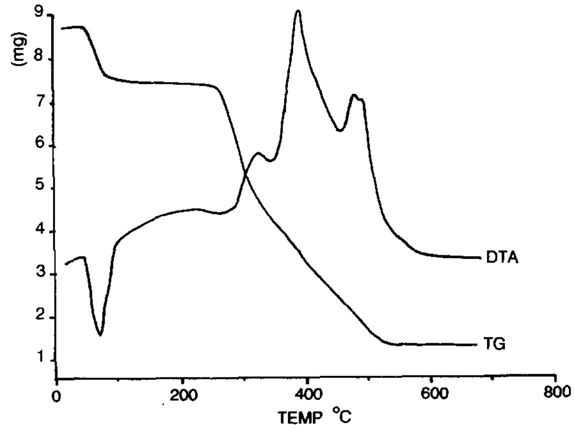

Fig. 5. TG and DTA traces of $Zn(C_9H_8O_3N)_2 \cdot 4H_2O$, sample weight, 8.738 mg.

TABLE 4

Dehydration processes of the hippuric acid

Process	Peak temperature (°C)	Thermal nature of transformation	Weight loss (%)		Enthalpy (kJ mol^{-1})
			Calc.	Found	
$Co(C_9H_8O_3N)_2 \cdot 4H_2O \rightarrow Co(C_9H_8O_3N)_2$	108	Endo	14.78	15.16	133
$Ni(C_9H_8O_3N)_2 \cdot 5H_2O \rightarrow Ni(C_9H_8O_3N)_2$	118	Endo	17.82	17.26	257
$Cu(C_9H_8O_3N)_2 \cdot 3H_2O \rightarrow Cu(C_9H_8O_3N)_2$	86	Endo	11.39	11.65	245
$Zn(C_9H_8O_3N)_2 \cdot 4H_2O \rightarrow Zn(C_9H_8O_3N)_2$	74	Endo	14.58	14.16	192

TABLE 5

Decomposition processes of hippuric acid and the anhydrous complexes

Process	Temperature range (°C)	Thermal nature of transformation	Residue (%)	
			Calc.	Found
$Co(C_9H_8O_3N)_2 \rightarrow Co_3O_4$	230–482	Exo	16.46	16.14
$Ni(C_9H_8O_3N)_2 \rightarrow NiO$	200–512	Exo	14.78	15.14
$Cu(C_9H_8O_3N)_2 \rightarrow CuO$	170–550	Exo	16.78	16.50
$Zn(C_9H_8O_3N)_2 \rightarrow ZnO$	190–546	Exo	16.48	16.02

hippuric acid and cobalt, nickel, copper and zinc are shown in Figs. 2–5. The TG and DTA curves are similar. The dehydration of the compounds takes place in one step; the observed weight losses for the dehydration processes compare favourably with the theoretical values, see Table 4. The dehydration enthalpies have been calculated and are given in Table 4. The decomposition of the anhydrous complexes follows immediately after the corresponding dehydration process and the residual weights are in good agreement with the values required for the metal oxide, see Table 5. In the DTA curves, these decomposition processes correspond to exothermic effects for the complexes.

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