

THERMAL STUDIES ON PYRIDINE-3,4-DICARBOXYLIC ACID COMPOUNDS OF COBALT, NICKEL AND COPPER

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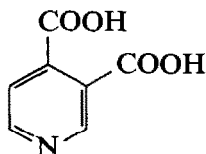
ABSTRACT

Compounds of pyridine-3,4-dicarboxylic acid with cobalt, nickel and copper have been prepared in aqueous solution. Spectral and magnetic studies have shown that in the cobalt and nickel compounds the metal ion is in an octahedral environment, while in the copper compound the copper atom is in a tetrahedral environment. The thermal behaviour of these compounds has been studied by thermogravimetry and differential thermal analysis. The compounds are hydrated, and they decompose thermally by losing water followed by the organic ligand to give the metal oxide.

INTRODUCTION

This work is a continuation of previous studies on the reactions of a pyridine dicarboxylic acid with first-row transition metal ions [1].

Pyridine-3,4-dicarboxylic acid has two different donor sites: the oxygen atoms of the carboxylic acid groups and the nitrogen atom in the aromatic ring.



Pyridine-3,4-dicarboxylic acid (3,4-H₂dpc).

This paper reports the thermal analysis studies of pyridine-3,4-dicarboxylic acid complexes formed with cobalt(II), nickel(II) and copper(II). In addition, spectral and magnetic studies have been used to characterise each metal complex and to determine the geometry of the metal ion in the complex.

EXPERIMENTAL

Preparation of compounds

(A) Pyridine-3,4-dicarboxylic acid (1 g) was dissolved in boiling water and the metal carbonate was added in small amounts, with stirring until effervescence ceased. The solution was filtered and the filtrate was evaporated until the complex precipitated. The precipitate was filtered off and oven dried at 60 °C.

(B) Pyridine-3,4-dicarboxylic acid (8.36 g) was added to 400 cm³ of boiling water, with stirring. To this acid solution was added 2.65 g of sodium carbonate. When the evolution of carbon dioxide was complete 6.24 g of copper sulphate was added to the solution and a precipitate was produced. The precipitate was filtered off and oven dried at 60 °C.

Apparatus

The concentration of the metal ion was obtained using a Perkin-Elmer 373 atomic absorption spectrophotometer, and the carbon, hydrogen and nitrogen analyses were carried out using a Carlo Erba elemental analyser. The infrared spectra were obtained using KBr discs (4000–600 cm⁻¹) and polyethylene discs (600–200 cm⁻¹) on a Perkin-Elmer model 881 IR spectrophotometer. Electronic diffuse reflectance spectra were recorded with a Beckman Acta MIV spectrophotometer. Magnetic measurements were carried out by the Gouy method using Hg[Co(SCN)₄] as calibrant. The thermal analysis studies were carried out on a Stanton Redcroft Model STA 781 thermobalance. Thermogravimetry (TG) and differential thermal analysis (DTA) traces were obtained at a heating rate of 6 °C min⁻¹ in static air. In all cases, the 20–800 °C temperature range was studied.

RESULTS AND DISCUSSION

The compounds prepared are listed in Table 1. The cobalt and nickel complexes have the stoichiometry M(3,4-dpc)(H₂O)₄ and were prepared by method A. The copper complex Cu(3,4-dpc)(H₂O)₂ was prepared using method B (owing to its insolubility in aqueous solution).

TABLE 1

Analyses and magnetic moments of compounds

Compounds ^a	Colour	Theory (%)				Found (%)				μ (B.M.)
		Metal	Carbon	Hydrogen	Nitrogen	Metal	Carbon	Hydrogen	Nitrogen	
Co(3,4-dpc)(H ₂ O) ₄	Pink	19.70	28.39	3.74	4.73	19.62	28.02	3.64	4.66	4.86
Ni(3,4-dpc)(H ₂ O) ₄	Green	19.87	28.41	3.74	4.73	19.41	27.82	3.42	4.70	3.28
Cu(3,4-dpc)(H ₂ O) ₂	Blue	24.76	31.76	2.66	5.29	24.47	32.23	2.42	5.38	1.82

^a dpc, Pyridine-3,4-dicarboxylate anion.

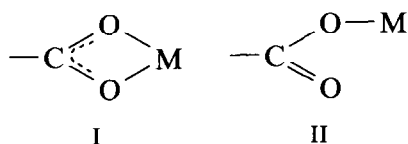
TABLE 2

Infrared spectra (wavenumbers in cm⁻¹)

Compound	$\nu_{\text{O-H}}(\text{H}_2\text{O})$	$\nu(\text{COOH})$	$\nu(\text{COO}^-)$	$\nu_{\text{C-O}}$	Ring vibration	$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}$
3,4-H ₂ dpc	—	1701 (s)	—	1355 (s)	1640 (s)	—	—
Co(3,4-dpc)(H ₂ O) ₄	3630–2960 (br, s)	—	1620 (s)	1396 (s)	1660 (s)	314 (s) Co-OH ₂ 378 (s)	230 (w)
Ni(3,4-dpc)(H ₂ O) ₄	3640–2910 (br, s)	—	1622 (s)	1395 (s)	1655 (s)	381 (s) Ni-OH ₂ 343 (s)	258 (w)
Cu(3,4-dpc)(H ₂ O) ₂	—	—	1602 (s)	1400 (s)	—	308 (s) Cu-OH ₂ 365 (s)	—

Key: br, broad; s, strong; w, weak.

In Table 2, the main bands in the infrared spectra are listed. The cobalt and nickel compounds show strong absorption bands in the region 3650–2880 cm^{-1} , $\nu_{\text{O-H}}(\text{H}_2\text{O})$ and 1640–1620 cm^{-1} , $\delta(\text{HOH})$, indicating the presence of water of crystallisation [2]. The spectra of all the complexes confirm the absence of free carboxylic acid groups. The usual reduction in $\nu(\text{COO})$ compared with free $-\text{CO}_2\text{H}$ is observed, characteristic of bonding types I and II in the complexes [3].



A change to higher frequency of the bands due to the ring vibrations of the pyridine ring is observed in the cobalt and nickel complexes, suggesting that co-ordination to the metal takes place through the nitrogen atom of the pyridine ring [2]. Metal–nitrogen bands are listed for these compounds. Metal–oxygen bands are also reported for each of the complexes, and it is suggested that the bands between 310 and 318 cm^{-1} are due to the M-OH_2 stretching mode [4].

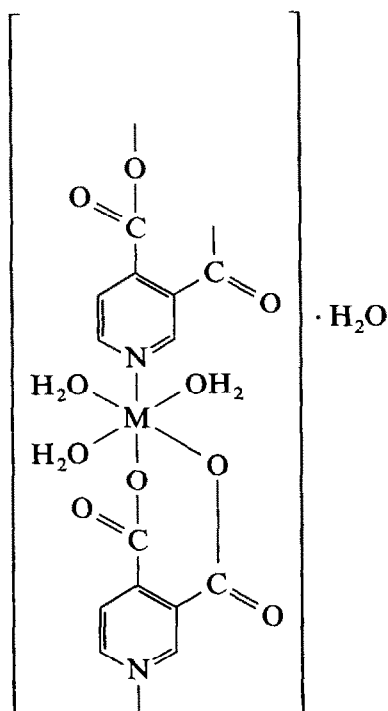
The positions of the bands in the electronic spectra and the values for Dq of the cobalt and nickel complexes, Table 3, clearly indicate a six co-ordinate environment for the cobalt and nickel atoms [2]. The values reported for B and β (Table 3) indicate a high degree of ionic character in the metal–ligand bond [5]. The magnetic moment for each of the compounds is in the expected ranges of 4.8–5.2 BM and 3.2–3.8 BM for octahedral cobalt and nickel compounds respectively [2]. The copper compound has bands at 7463 and 13 820 cm^{-1} in its electronic spectrum. It is suggested that these bands are analogous to those observed for the compound bis(*N*-isopropylsalicylideneaminato)copper(II), which has a pseudo-tetrahedral structure [6]. The

TABLE 3
Electronic spectra (wavenumbers in cm^{-1})

Compound	Band position	Dq	B	β
$\text{Co}(3,4\text{-dpc})(\text{H}_2\text{O})_4$	7693	879	869	0.89
	19608			
$\text{Ni}(3,4\text{-dpc})(\text{H}_2\text{O})_4$	8929	892	860	0.83
	14815			
	24875			
$\text{Cu}(3,4\text{-dpc})(\text{H}_2\text{O})_2$	7463	—	—	—
	12820			

value obtained for the magnetic moment of the compound shows strong distortion towards a planar structure [6].

Single crystals of the compounds could not be isolated from the solution. Therefore, without X-ray analysis, no definite structures can be described. However, the spectroscopic and magnetic data suggest that in the cobalt and nickel compounds the metal is octahedrally co-ordinated by one nitrogen atom and five oxygen atoms, two of which belong to the carboxylate group and three of which belong to co-ordinated water molecules.



Proposed stereochemistry for $[M(3,4\text{-dpc})(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$.

The remaining water molecule is attached by hydrogen bonding. In the copper compound the copper atom is tetrahedrally co-ordinated by the two oxygen atoms from one carboxylate group and the oxygen atoms from two water molecules, one carboxylate group remaining unco-ordinated to the metal atom.

The TG and DTA curves for pyridine-3,4-dicarboxylic acid, in Fig. 1, show that the acid is thermally stable in the temperature range 20–169°C. Its pyrolytic decomposition begins at 169°C and finishes at 565°C with the total elimination of the sample. The DTA curve of pyridine-3,4-dicarboxylic

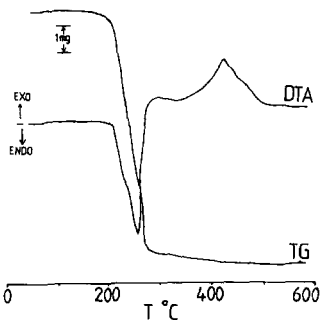


Fig. 1. TG and DTA curves for pyridine-3,4-dicarboxylic acid. Sample weight, 9.89 mg.

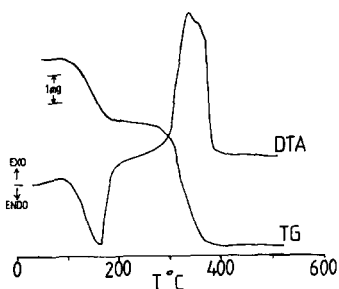


Fig. 2. TG and DTA curves for $\text{Co}(3,4\text{-dpc})(\text{H}_2\text{O})_4$. Sample weight, 9.78 mg.

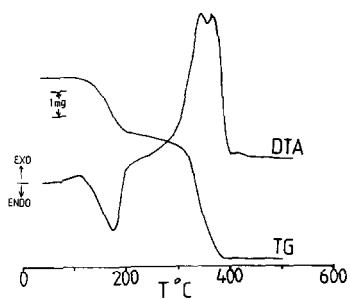


Fig. 3. TG and DTA curves for $\text{Ni}(3,4\text{-dpc})(\text{H}_2\text{O})_4$. Sample weight, 9.30 mg.

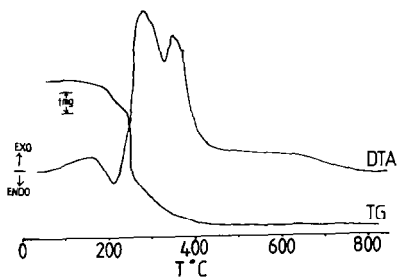


Fig. 4. TG and DTA curves for $\text{Cu}(3,4\text{-dpc})(\text{H}_2\text{O})_2$. Sample weight, 9.35 mg.

TABLE 4

Dehydration processes for the metal complexes

Process	Peak temp. (°C)	Thermal nature of transformation	Weight loss (%)		Enthalpy (kJ mol ⁻¹)
			Calc.	Found	
Co(3,4-dpc)(H ₂ O) ₄ → Co(3,4-dpc)	162	Endo	24.32	24.33	221
Ni(3,4-dpc)(H ₂ O) ₄ → Ni(3,4-dpc)	174	Endo	24.33	23.65	230
Cu(3,4-dpc)(H ₂ O) ₂ → Cu(3,4-dpc)	204	Endo	13.66	13.30	130

acid shows an endothermic peak at 260 °C due to melting. The value of the fusion enthalpy calculated from the area of this peak is 64 kJ mol⁻¹. The acid then decomposes immediately, producing an exothermic peak at 428 °C, possibly due to the presence of impurity. The TG and DTA curves for the complexes formed between pyridine-3,4-dicarboxylic acid and cobalt, nickel and copper are shown in Figs. 2–4.

The TG and DTA curves show that the dehydration of the complexes takes place in one step. The observed weight losses for these processes compare favourably with the theoretical values, as shown in Table 4. The expected peak for the dehydration processes associated with these compounds has been observed in the DTA curves. The dehydration enthalpies have been calculated and are given in Table 4. In the case of the cobalt and nickel complexes, samples of the anhydrous complexes were isolated by keeping the thermobalance at a fixed temperature until the required constant weight was obtained. Examination of the IR spectra for each of the samples showed that the $\nu(\text{COO})$ band was now at 1600 cm⁻¹, instead of ~ 1620 cm⁻¹ in the hydrated complexes. This indicates that the carboxylate groups are now functioning as bidentate ligands in the anhydrous complexes. For the copper complex, decomposition of the anhydrous complex followed immediately after the dehydration process. The residual weights are compared with those calculated theoretically for the metal oxides in Table 5.

TABLE 5

Decomposition processes of pyridine-3,4-dicarboxylic acid and the metal complexes

Process	Temp. range (°C)	Thermal nature of transformation	Residue (%)	
			Calc.	Found
3,4-H ₂ dpc pyrolysis	169–565	Exo	–	–
Co(3,4-dpc) → Co ₃ O ₄	248–420	Exo	27.11	26.58
Ni(3,4-dpc) → NiO	218–396	Exo	25.25	25.80
Cu(3,4-dpc) → CuO	204–404	Exo	30.05	29.95

In the DTA curves these decomposition processes correspond to exothermic effects for the complexes.

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