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Preparation, structural and thermal studies of 1,1-cyclobutanedicarboxylic acid complexes of cobalt, nickel and copper

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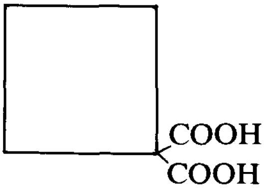
Abstract

Compounds of 1,1-cyclobutanedicarboxylic acid with cobalt, nickel and copper have been prepared in aqueous solution. The compounds have the stoichiometry $M(C_6H_6O_4) \cdot xH_2O$ where $x = 1$ for cobalt and copper, and $x = 3$ for nickel. The cobalt and nickel complexes have octahedral structures while the copper complex has a tetragonal structure. Thermal decomposition studies show that the complexes lose water, followed by the organic ligand, to give the metal oxides.

INTRODUCTION

The compound 1,1-cyclobutanedicarboxylic acid has one type of donor site for forming bonds with metal atoms: the oxygen atoms of the carboxylic acid group.



1,1-Cyclobutanedicarboxylic acid ($C_6H_8O_4$).

This paper reports the complexes formed between 1,1-cyclobutanedicarboxylic acid and the transition metals cobalt, nickel and copper. Information regarding the stereochemistry of the complexes has been obtained using electronic spectra, infrared spectra and magnetic measurements. The thermal decomposition of the complexes has been studied using thermogravimetry and differential thermal analysis.

EXPERIMENTAL

Preparation of the complexes

1,1-Cyclobutanedicarboxylic acid (0.05 mol) was dissolved in boiling water. The resulting solution was then neutralised by the addition of

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cobalt(II) carbonate. The solution was filtered to remove any excess cobalt(II) carbonate and the filtrate was then reduced in volume to yield the metal complex. The procedure was repeated using the carbonates of copper(II) and nickel(II).

Apparatus

The concentration of the metal ions was obtained using a Perkin-Elmer 373 atomic absorption spectrophotometer, and the carbon, hydrogen and nitrogen contents were obtained 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 IR spectrophotometer model 598.

The electronic spectra were obtained on a Beckmann Acta MIV spectrophotometer as solid diffuse reflectance spectra.

Magnetic measurements were carried out by the Gouy method using $Hg[Co(SCN)_4]$ as calibrant.

Thermal analysis studies were carried out on a Stanton-Redcroft model 1500 thermobalance. The thermogravimetry (TG) and differential thermal analysis (DTA) traces were obtained at a heating rate of 6°C min^{-1} in static air, over the temperature range 20–800°C.

RESULTS AND DISCUSSION

The compounds which were prepared are listed in Table 1. The elemental analyses agree with the given formulae of the compounds. All of the compounds have water molecules present.

Table 2 lists the main bands in the infrared spectra together with their descriptions and assignments. The bands in the region 3640–3030 cm^{-1} are assigned to the ν(O–H) vibration of the water molecule and indicate water of crystallisation. The IR spectrum of 1,1-cyclobutanedicarboxylic acid shows a band at 1715 cm^{-1} due to the –COOH group. This band is absent in

TABLE 1

Analyses of the metal complexes in %

Compound		Metal	Carbon	Hydrogen
$Co(C_6H_6O_4) \cdot H_2O$	Found	26.90	32.09	3.67
	Theory	26.57	33.52	3.69
$Ni(C_6H_6O_4) \cdot 3H_2O$	Theory	23.03	28.28	4.74
	Found	22.79	28.04	4.34
$Cu(C_6H_6O_4) \cdot H_2O$	Theory	28.40	32.22	3.60
	Found	28.10	32.38	3.34

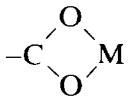
TABLE 2

Infrared spectra (4000–200 cm^{-1})

Compound	ν(O–H) (H_2O)	ν(COOH)	ν(COO^-)	ν(C–O)	ν(M–O)
$C_6H_8O_4$	–	1715 (s)	–	1410 (s)	–
$Co(C_6H_6O_4) \cdot H_2O$	3620–3040 (br, s)	–	1579 (s)	1385 (s)	258 (m)
$Ni(C_6H_6O_4) \cdot 3H_2O$	3640–3060 (br, s)	–	1582 (s)	1383 (s)	260 (m)
$Cu(C_6H_6O_4) \cdot H_2O$	3600–3030 (br, s)	–	1574 (s)	1377 (s)	256 (m)

Key: s, strong; m, medium; br, broad.

the IR spectra of the metal complexes due to the formation of the COO^- group which bonds to the metal ions [1] as shown in Structure 1. Metal–oxygen bands are reported for each of the metal complexes.



Structure 1.

The position of the bands in the electronic spectra and the magnetic moments suggest that for the cobalt and nickel complexes, the metal ions are in an octahedral environment [2], while for the copper complex the copper ions are in a tetragonal environment [3] (Table 3).

The fact that the cobalt, nickel and copper compounds were isolated as powders and not as single crystals prevents a complete structural determination. However, spectroscopic and magnetic data enable us to predict a possible stereochemistry for the compounds. It is suggested that in these compounds, two molecules of the 1,1-cyclobutanedicarboxylate are attached to each metal ion to give a planar structure. Each metal ion is thus bonded to four oxygen atoms in the plane. It is further suggested that a layer structure exists in each compound and that each metal ion is bonded

TABLE 3

Electronic spectra and magnetic moments

Compound	Band positions/ cm^{-1}	d-d transition	μ/BM
$Co(C_6H_6O_4) \cdot H_2O$	7936	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	4.83
	19048	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	
$Ni(C_6H_6O_4) \cdot 3H_2O$	8620	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	3.08
	14925	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	
	25316	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	
$Cu(C_6H_6O_4) \cdot H_2O$	14925	${}^2B_1 \rightarrow {}^2A_1$	2.11

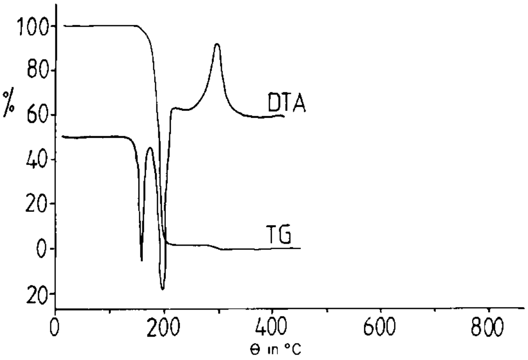


Fig. 1. TG and DTA trace for 1,1-cyclobutanedicarboxylic acid. Sample weight 10.10 mg.

to oxygen atoms in adjacent layers to give a six-coordinate environment for the metal ion.

The TG and DTA traces for 1,1-cyclobutanedicarboxylic acid and its metal complexes are shown in Figs. 1–4. The TG trace for 1,1-cyclobutanedicarboxylic acid shows that the compound is thermally stable in the range 20–156°C. Decomposition starts at 156°C and finishes around 316°C with the total elimination of the sample. The DTA trace displays a sharp

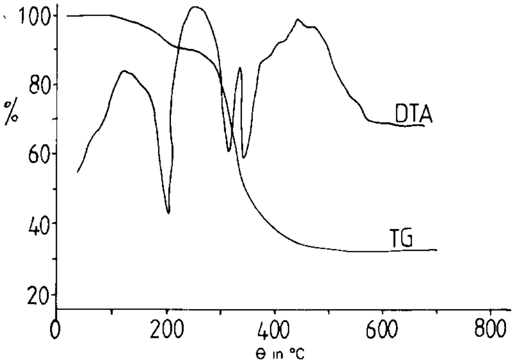


Fig. 2. TG and DTA trace for $Co(C_6H_6O_4) \cdot H_2O$. Sample weight 11.40 mg.

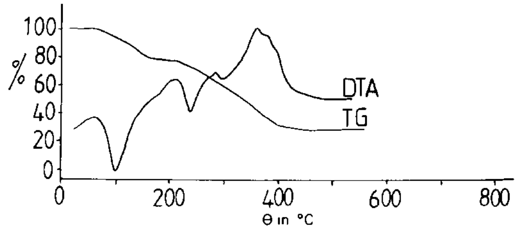


Fig. 3. TG and DTA trace for $Ni(C_6H_6O_4) \cdot 3H_2O$. Sample weight 9.47 mg.

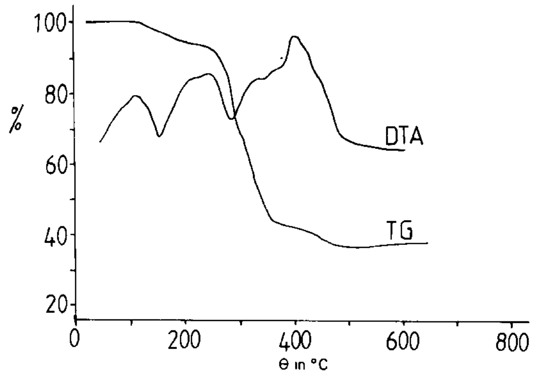


Fig. 4. TG and DTA trace for $Cu(C_6H_6O_4) \cdot H_2O$. Sample weight 9.18 mg.

endothermic peak at 160°C corresponding to fusion. Liquid 1,1-cyclobutanedicarboxylic acid decomposes immediately with an endothermic peak at 196°C. This reaction would appear to be complete by 224°C. However, slight decomposition is observed in the TG trace between 286 and 316°C. It is possible that at 286°C a small amount of tar exists and the decomposition between 286 and 316°C may be due to that tar. The TG and DTA traces for the cobalt, nickel and copper complexes of 1,1-cyclobutanedicarboxylic acid are shown in Figs. 2–4. The dehydration process in each of the complexes takes place in one step. The observed weight losses for these processes compare favourably with the theoretical values, see Table 4. The first endothermic peak observed in the DTA for each of the metal complexes is due to the dehydration process. Decomposition of the anhydrous metal complexes follows after the dehydration and the weight loss observed for the organic ligand in each case is in good agreement with the theoretical values, see Table 5. In the DTA traces, these decomposition processes correspond to endothermic and exothermic effects for the complexes. The decomposition scheme for each metal complex can be

TABLE 4

Dehydration processes of the metal complexes

Process	Peak temperature/ °C	Thermal nature of transformation	Weight loss/%	
			Calc.	Found
$Co(C_6H_6O_4) \cdot H_2O \rightarrow Co(C_6H_6O_4)$	208	Endo	8.2	8.3
$Ni(C_6H_6O_4) \cdot 3H_2O \rightarrow Ni(C_6H_6O_4)$	99	Endo	21.2	21.3
$Cu(C_6H_6O_4) \cdot H_2O \rightarrow Cu(C_6H_6O_4)$	149	Endo	8.1	8.0

Key: Endo, endothermic.

TABLE 5

Decomposition processes of 1,1-cyclobutanedicarboxylic acid and the anhydrous complexes

Process	Temperature range/°C	Thermal nature of transformation	Residue/%	
			Calc.	Found
$C_6H_8O_4 \rightarrow$ pyrolytic process	156–316	Endo/Exo	–	–
$Co(C_6H_6O_4) \rightarrow Co_3O_4$	246–532	Endo/Exo	36.6	36.8
$Ni(C_6H_6O_4) \rightarrow NiO$	192–470	Endo/Exo	31.5	31.7
$Cu(C_6H_6O_4) \rightarrow CuO$	240–512	Endo/Exo	35.6	35.7

Key: Endo, endothermic; Exo, exothermic (obtained from DTA trace).

represented as

$$Co(C_6H_6O_4) \cdot H_2O \xrightarrow{\text{Endo}} Co(C_6H_6O_4) \xrightarrow{\text{Endo/Exo}} Co_3O_4$$

$$Ni(C_6H_6O_4) \cdot 3H_2O \xrightarrow{\text{Endo}} Ni(C_6H_6O_4) \xrightarrow{\text{Endo/Exo}} NiO$$

$$Cu(C_6H_6O_4) \cdot H_2O \xrightarrow{\text{Endo}} Cu(C_6H_6O_4) \xrightarrow{\text{Endo/Exo}} CuO$$

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