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A thermal analysis study of cyclopropane-1,1-dicarboxylic acid complexes of cobalt, nickel and copper

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Abstract

Complexes of cyclopropane-1,1-dicarboxylic acid with cobalt, nickel and copper have been prepared in aqueous solution from cobalt carbonate and the hydroxides of copper and nickel. Only the copper compound is not hydrated. The complexes show the loss of water (except for copper) which is followed by the decomposition of the cyclopropane-1,1-dicarboxylate to give the metal oxides. The Co^{2+} and the Ni^{2+} ions are expected to have octahedral environment and the Cu^{2+} ion to have a square planar environment, which corresponds to the data obtained by single crystal X-ray investigations of copper cyclopropane-1,1-dicarboxylate. © 1998 Elsevier Science B.V.

Keywords: Cyclopropane-1,1-dicarboxylic acid; Transition metal complexes; Thermal and magnetic studies

1. Introduction

Thermal and spectroscopic studies of complexes of first row transition metals with small organic acids such as adipic or maleic acid are numerous [1,2]. Additionally, there have been previous studies on complexes of cyclobutane-1,1-dicarboxylic acid with transition metals [3]. The platinum compound [Pt(CBDCA-O,O′)(NH₃)₂] has been thoroughly investigated because of its application in cancer therapy [4].

This paper reports a study of with the complexes formed between cyclopropane-1,1-dicarboxylic acid and the transition metals cobalt, nickel and copper. Information regarding the stereochemistry of these complexes has been obtained using IR-spectra and magnetic measurements. The thermal decomposition of the complexes has been studied by thermogravimetry and differential thermal analysis.

2. Experimental

2.1. Preparation of cyclopropane-1,1-dicarboxylic acid

Cyclopropane-1,1-dicarboxylic acid ($[C_3H_4(CO-OH)_2]$) is easily prepared by phase transfer alkylation of diethyl malonate ($CH_2(COOC_2H_5)_2$) with 1,2-dibromethane ($Br(CH_2)_2Br$) catalyzed by triethylbenzylammonium hydroxide (generated from the reaction of triethylbenzylammonium chloride ($[C_6H_5CH_2N-(CH_3)_2]^+Cl^-$) and 50% sodium hydroxide) [5].

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2.2. Preparation of the complexes

0.015 mol of the acid was dissolved in 80 ml hot water. The resulting cloudy solution was then neutralized by adding the equivalent amount of metal(II)-carbonate in the case of the cobalt(II) compound and metal(II)hydroxide for the nickel(II) and copper(II) compound [6]. The copper salt ($Cu[C_3H_4(COO)_2]$) precipitated immediately, the analogous nickel ($Ni[C_3H_4(COO)_2]\cdot5H_2O$) and cobalt salt ($Co[C_3H_4(COO)_2]\cdot5H_2O$) were obtained by evaporation of the aqueous solutions.

3. Experimental

The infrared spectra were obtained using KBr pellets (4000–300 cm^{-1}) on a Perkin Elmer FT-IR spectrometer (Spektrum 1000).

Magnetic investigations were performed with on a Quantum Design's SQUID magnetometer. Thermal analyses were carried out on a NETZSCH STA 409 model. Thermogravimetry (TG) and differential thermal analyses (DTA) were obtained at a heating rate of 5°C/min in dynamic air (20 cm^3/min), over the temperature range 20–1000°C. The carbon and hydrogen contents were obtained using a CHN-Rapid (Heraeus), and the metal contents by titration with 0.01 m EDTA using EriochromeBlack T as indicator.

4. Results and discussion

The prepared compounds are listed in Table 1. The elemental analyses agree with the given formulae of the compounds. The copper compound is found to have no water present whereas the cobalt and nickel

Table 1
Analyses of the metal complexes in %

Compound		Metal	Carbon	Hydrogen
$Co(C_5H_4O_4)\cdot5H_2O$	Found	21.20	21.66	4.99
	Theory	21.27	21.67	5.09
$Ni(C_5H_4O_4)\cdot5H_2O$	Found	21.18	21.68	5.08
	Theory	21.20	21.69	5.10
$Cu(C_5H_4O_4)$	Found	33.10	31.26	2.23
	Theory	33.16	31.34	2.10

complex both have five moles of water per formula unit.

The main bands of the infrared spectra of the acid an the complexes are listed in Table 2. The bands in the region of the 3400–3100 cm^{-1} are assigned to the (O–H) stretching vibrations of water. The most characteristic band for the cyclopropane-1,1-dicarboxylic acid is the ν(C=O) stretching vibration at 1714 cm^{-1} due to the COOH-groups. This band is absent in the metal complexes where the $\nu(COO^-)$ vibration can be observed in the region 1560–1600 cm^{-1}.

All compounds, the acid and the metal complexes, possess typical ν(C–C) vibrations in the region of 920–1220 cm^{-1} due to the cyclopropane ring [7,8], Magnetic measurements (Table 3) were carried out with a magnetic induction of 1 T (10 kG) in the temperature range of 5–300 K. The cobalt and the nickel complex exactly obey the Curie–Weiss law whereas the copper compound shows antiferromagnetic behaviour with a Neel temperature at about 7 K. The magnetic moments are in good agreement with the theoretical results [9,10]. The value for the copper compound suggests a planar environment for the cation which corresponds to the results obtained by single crystal X-ray investigations [11]. However, the environment of the cobalt and nickel species appears

Table 2
Infrared spectra (4000–300 cm^{-1}) for isolated compounds

Compound	ν(O–H)(H_2O)	ν(C=O)	$\nu(COO^-)$	ν(C–C) ring
$C_3H_4(COOH)_2$	–	1714 (s)	–	947, 1219 (s)
$Cu(C_5H_4O_4)$	–	–	1602 (s)	952, 1223 (m)
$Co(C_5H_4O_4)\cdot5H_2O$	3400–3100 (br,s)	–	1560 (s)	927, 1209 (m)
$Ni(C_5H_4O_4)\cdot5H_2O$	3400–3100 (br,s)	–	1569 (s)	933, 1210 (m)

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

Table 3
Magnetic moments for isolated compounds compared with the literature [9,12]

	$Cu(C_5H_4O_4)$	$Co(C_5H_4O_4)\cdot5H_2O$	$Ni(C_5H_4O_4)\cdot5H_2O$
μ_{BM}			
Found	2.3	5.2	3.2
Literature	1.8–2.1	4.3–5.2	2.8–3.5

Table 4
Decomposition of cyclopropane-1,1-dicarboxylic acid complexes

Process	Peak temperature (°C)	Thermal nature of transformation	Mass loss (%)	
			Calculated	Found
$Co(C_5H_4O_4)\cdot5H_2O \rightarrow Co(C_5H_4O_4) + 5H_2O$	104	Endo	32.5	32.3
$Co(C_5H_4O_4) \rightarrow Co_3O_4$	364	Exo	38.5	38.1
$Co_3O_4 \rightarrow CoO$	916	Endo	1.9	1.8
$Ni(C_5H_4O_4)\cdot5H_2O \rightarrow Ni(C_5H_4O_4) + 5H_2O$	125	Endo	32.5	32.5
$Ni(C_5H_4O_4) \rightarrow NiO$	368	Exo	40.5	40.5
$Cu(C_5H_4O_4) \rightarrow CuO$	353	Exo	58.5	56.7

to be octahedral, because the measured μ_B values agree quite well with earlier studied compounds where cobalt and nickel are in octahedrally coodinated [12]. Due to their insolubility, a polymeric structure is more sensible than an ionic structure which is present in the hydrogen-cyclopropane-1,1-carboxylate complex of cobalt [13]. Unfortunately, the above mentioned complexes of cobalt and nickel are only available as powders. Therefore, a complete structure determination is not possible.

The results of the differential thermal analyses are listed in Table 4, the TG/DTA curves are shown in Figs. 1–4.

The acid is thermally stable up to 138°C. Decomposition starts at 138°C and ends at 360°C with almost total elimination of the sample. The DTA curve of the
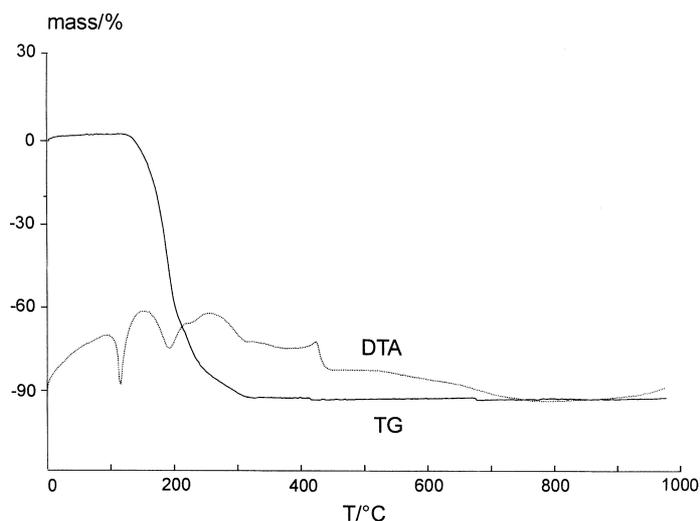
Fig. 1. TG and DTA curves for $C_5H_6O_4$. Sample mass 22.50 mg.
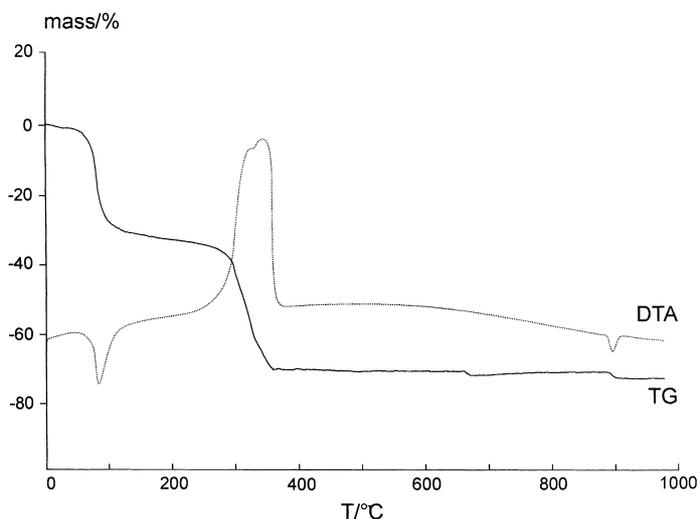
Fig. 2. TG and DTA curves for CoC$_5$H$_4$O$_4$·5H$_2$O. Sample mass 22.30 mg.
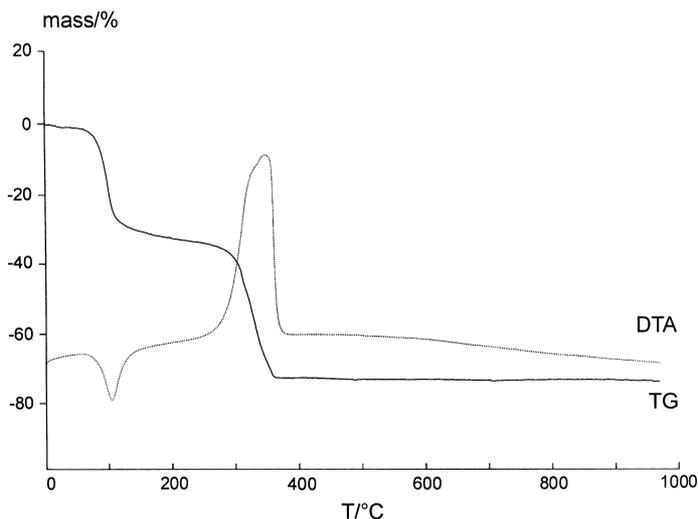
Fig. 3. TG and DTA curves for NiC$_5$H$_4$O$_4$·5H$_2$O. Sample mass 24.40 mg.

sample shows an endothermic peak at 138°C due to melting. The liquid cyclopropane-1,1-dicarboxylic acid decomposes immediately producing an endothermic peak at 215°C.

The TG and DTA curves of the cobalt, nickel, and copper complexes are similar.

The dehydration process takes place in one step. The observed loss in mass is consistent with the theoretical values, as given in Table 4.

This dehydration corresponds to the first endothermic peak in the DTA for the nickel and cobalt salt. All three compounds start to decompose at about 350°C. This process, which can be observed in the DTA as an exothermic peak, finally leads to the metal oxides CoO, NiO and CuO. For the cobalt complex the decomposition proceeds via Co$_3$O$_4$, Fig. 2, resulting in a mixture of Co$_3$O$_4$ and CoO. All three oxides MeO are thermally stable within the measured temperature
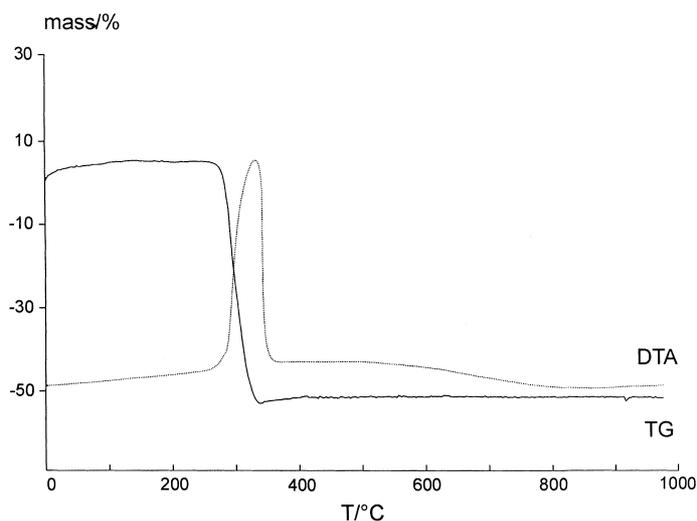
Fig. 4. TG and DTA curves for $CuC_5H_4O_4$. Sample mass 20.00 mg.

range (20–1000°C). The observed mass loss for the cyclic ligand is again in very good agreement with the theoretical values.

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