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A thermal analysis study of hydrogencyclopropane-1,1-carboxylic acid complexes of cobalt, zinc and manganese

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Abstract

Cobalt, zinc, and manganese complexes of cyclopropane-1,1-dicarboxylic acid have been prepared in an aqueous solution from the corresponding metal carbonates. These complexes have 6 mol of water per formula unit and thermally decompose via loss of water, which is followed by a two-stage decomposition of the hydrogencyclopropane-1,1-dicarboxylate ligand with a metal oxide residue.

The metal centre is expected to have octahedral symmetry in accordance with single crystal X-ray diffraction data obtained for the cobalt compound. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Complexes of first row transition metals with organic acids such as substituted acrylic acids or pyrazine–dicarboxylic acids have always been of major interest [1,2]. The importance of cyclic ligands such as cyclobutane-1,1-dicarboxylate arose in the 1980s when [Pt(CBDCA-O,O′)$(NH_3)_2$] was found to be a cancer therapeutic agent [3]. Recently, we reported the synthesis of complexes of cobalt, nickel, and copper with cyclopropane-1,1-dicarboxylic acid [4].

These complexes contain the metal-(II)-cations and the dianions of the acid. Single crystal X-ray investigation of the copper complex show that the structure contains infinite chains of copper–carboxylate units. The chains are linked by [–O–Cu–O] bridges and form a three-dimensional polymeric structure [5].

We now found similar complexes containing again transition metal-(II)-cations (Co^{2+}, Mn^{2+}, Zn^{2+}) and cyclopropane-1,1-carboxylate anions. But this time the complexes consist of one divalent metal cation and two cyclic ligands as the cyclopropane-1,1-dicarboxylic acid is monodeprotonated and therefore will be denoted as hydrogencyclopropane-1,1-carboxylate in this paper. These complexes are found to have an ionic structure which will be discussed in the next chapter.

This paper reports cobalt, zinc, and manganese complexes of cyclopropane-1,1-dicarboxylic acid. The stereochemistry of the complexes has been investigated by IR-spectroscopy and magnetic measurements. The thermal decomposition of the complexes has been studied by thermogravimetry and differential thermal analysis.

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2. Experimental

Preparation of cyclopropane-1,1-dicarboxylic acid Cyclopropane-1,1-dicarboxylic acid ($[C_3H_4(COOH)_2]$) 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) [6].

3. Preparation of the complexes

An aliquot of 0.015 mol of the acid was dissolved in 80 ml hot water. The resulting cloudy solution was then neutralized by adding an equivalent amount of metal-(II)-carbonate in the case of cobalt (II)- and manganese compounds, and basic metal-(II)-carbonate for the zinc (II)-compound.

All three salts $M[C_3H_4(COO)(COOH)]_2{\cdot}6H_2O)$ for M=Co, Zn, Mn are obtained by slow evaporation of the aqueous solutions. Crystals suitable for single crystal X-ray investigations are also obtained by this method [7].

4. Instrumentation

The infrared spectra were obtained over the 4000–300 cm^{-1} range, using KBr discs and a Perkin–Elmer FT–IR spectrometer (Spektrum 1000).

Magnetic investigations were carried out on a Quantum Design's SQUID magnetometer, thermal analyses were carried out on a NETZSCH STA 409 system. Thermogravimetry (TG) and differential thermal analysis (DTA) were performed at a heating rate of 5°C/min in dynamic air (20 cm^3/min), over the 20–1000°C temperature range.

The carbon and hydrogen contents of the metal complexes were determined using a CHN-Rapid (Heraeus), and the metal contents were determined by titration with 0.01 m EDTA using Eriochromblack T as indicator.

5. Results and discussion

The prepared compounds are listed in Table 1. The elemental analyses agree with the given formulae. All complexes are found to have 6 mol of water per formula unit.

Table 1
Metal analysis

Compound	%	Metal	Carbon	Hydrogen
$Co(C_5H_5O_4)_2{\cdot}6H_2O$	Found	13.80	28.18	4.85
	Theory	13.86	28.25	5.22
$Zn(C_5H_5O_4)_2{\cdot}6H_2O$	Found	15.12	27.97	5.22
	Theory	15.15	27.83	5.14
$Mn(C_5H_5O_4)_2{\cdot}6H_2O$	Found	13.01	28.50	5.17
	Theory	13.04	28.50	5.22
$Mn[C_3H_4(COO)_2]$	Found	30.00	32.50	2.56
	Theory	30.02	32.81	2.20

The main bands of the infrared spectra of the complexes are listed in Table 3.

The band with the maximum at 3400 cm^{-1} is assigned to the ν(O–H) stretching vibrations of water. All compounds possess typical ν(C–C) vibrations in the region of 920–1220 cm^{-1} due to the cyclopropane ring [8,9].

Two different kinds of carbonyl stretching vibrations occur. The ν(C=O) stretching vibration of the carboxylic group containing the acidic hydrogen atom occurs at ca. 1650 cm^{-1}, the $\nu(COO^-)$ vibration of the other carboxylic group occurs in the region of 1560–1600 cm^{-1}.

Magnetic measurements, Table 4, were determined with a magnetic induction of 1 T (10 kG) in the 5–300 K temperature range. The cobalt and manganese complexes show paramagnetic behaviour whereas the zinc compound is diamagnetic. The magnetic moments are in good agreement with the theoretical data [10,11]. The values of the magnetic moments for all three compounds suggest a metal octahedral environment which is in accordance with single crystal X-ray diffraction data [5].

The title compounds are found to have an ionic structure. The asymmetric unit consists of the metal cation which is surrounded by six water molecules forming an elongated octahedron in the axial direction. The acidic hydrogen forms an angular hydrogen bond with two oxygen atoms of the carboxylic groups [7].

The results of differential thermal analysis are listed in Table 2, the TG/DTA traces are shown in Figs. 1–3.

The dehydration process takes place in one step and corresponds to the first endothermic peak in the

Table 2
Thermal analysis data

Process	Peak temp. (°C)	Thermal nature of transformation	Mass loss (%)	
			calculated	found
$Co(C_5H_5O_4)_2{\cdot}6H_2O{\rightarrow}Co(C_5H_5O_4)_2{+}6H_2O$	99.3	endo	25.4	26.3
$Co(C_5H_5O_4)_2{\rightarrow}Co(C_5H_4O_4)$	ca. 240	(endo)	30.6	29.8
$Co(C_5H_4O_4){\rightarrow}Co_3O_4$	356.9	exo	25.1	26.2
$Zn(C_5H_5O_4)_2{\cdot}6H_2O{\rightarrow}Zn(C_5H_5O_4)_2{+}6H_2O$	91.6	enddo	25.0	23.2
$Zn(C_5H_5O_4)_2{\rightarrow}Zn(C_5H_4O_4)$	ca. 225	endo	30.1	28.1
$Zn(C_5H_4O_4){\rightarrow}ZnO$	389.6	exo	26.0	26.2
$Mn(C_5H_5O_4)_2{\cdot}6H_2O{\rightarrow}Mn(C_5H_5O_4)_2{+}6H_2O$	87.4	enddo	25.7	26.3
$Mn(C_5H_5O_4)_2{\rightarrow}Mn(C_5H_4O_4)$	245.8	enddo	30.9	30.2
$Mn(C_5H_4O_4){\rightarrow}Mn_xO_y$	367.3	exo	26.6	24.9

DTA. The observed mass loss is consistent with the theoretical values.

The three compounds decompose in two steps. Initially, one cyclic ligand is removed with the intermediate formation of the corresponding metal-(II)-carboxylates $M[C_3H_4(COO)_2]$. This process corresponds to a DTA small endothermic peak in the 225–246°C temperature range.

The existence of this intermediate product $M[C_3H_3(COO)_2]$ was proved for the manganese complex by infrared spectroscopy and elemental analysis. The results are listed in Table 1 and Table 3. The complex $Mn[C_3H_4(COO)(COOH)]_2{\cdot}6H_2O$ was heated to 280°C. At this temperature, the dehydration process is completed but the metal carboxylate is not yet fully decomposed (see Fig. 3). The colour of the obtained powder changed from light red to white and the compound is no longer soluble in water which is typical for metal complexes with the formula $M[C_3H_4(COO)_2]$. The elemental analysis agrees with the theoretical value.Table 4

In general, the differentiation between a cyclopropane-1,1-dicarboxylate and a hydrogencyclopropane-1,1-carboxylate by means of infrared spectro-

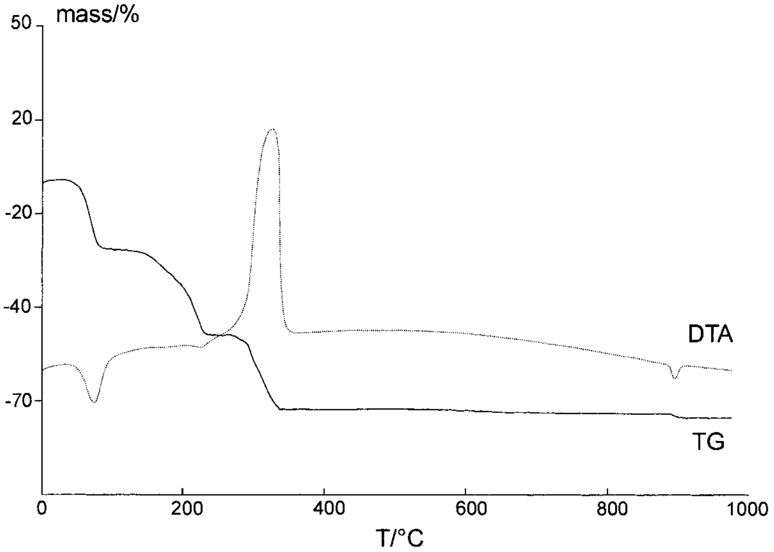

Fig. 1. TG and DTA trace for $Co(C_5H_5O_4)_2{\cdot}6H_2O$.

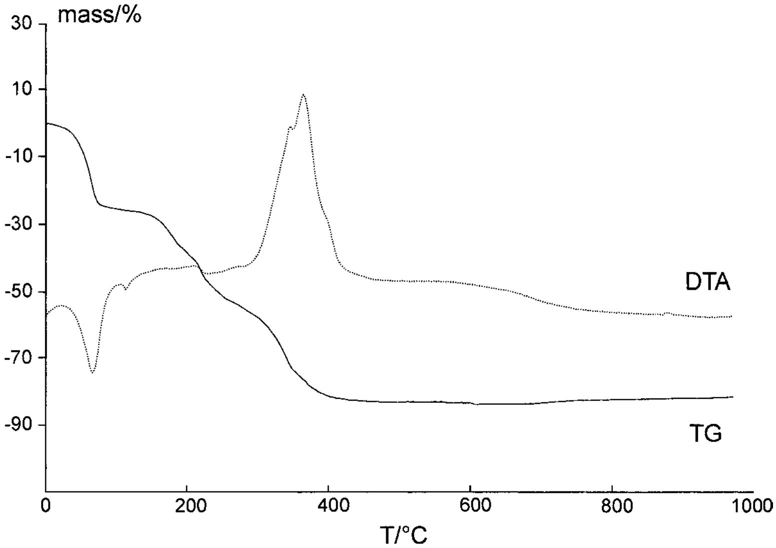

Fig. 2. TG and DTA trace for $Zn(C_5H_5O_4)_2{\cdot}6H_2O$.

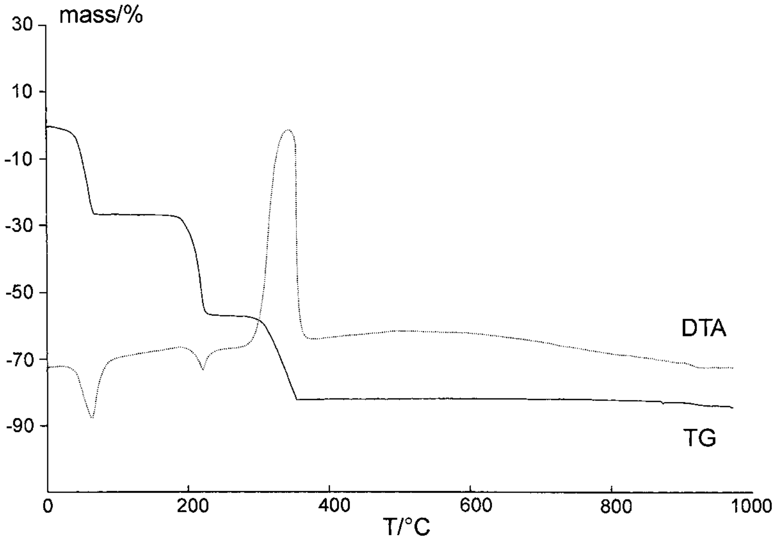

Fig. 3. TG and DTA trace for $Mn(C_5H_5O_4)_2{\cdot}6H_2O$.

scopy is very easy. The highest vibration which can be a ssigned to a stretching vibration of the carboxylic groups occurs in the region of 1560–1600 cm^{-1} for the dicarboxylates [4] and in the region of 1650–1700 cm^{-1} (which is typical for a ν(C=O) vibration) for the hydrogencarboxylates (see Table 3).

Subsequently, the metal carboxylates decompose between 350–390°C exhibiting strong exothermic peaks in the DTA. Finally, Co_3O_4, ZnO and a mixture of manganese oxides [12] are obtained, respectively. The zinc and manganese oxides are stable within the temperature range (20–1000°C), the cobalt oxide Co_3O_4 finally transforms to CoO at ca. 900°C [3].

Table 3
Infrared spectra (4000–300 cm^{-1})

Compound	ν(OH)(H_2O)	ν(C=O)	ν(COO^-)	ν(C–C) ring
$Co(C_5H_5O_4)_2 \cdot 6H_2O$	3100–3500 (br,s)	1654 (s)	1609 (s)	976, 1216 (m)
$Zn(C_5H_5O_4)_2 \cdot 6H_2O$	3100–3500 (br,s)	1651 (s)	1565 (m)	977, 1217 (m)
$Mn(C_5H_5O_4)_2 \cdot 6H_2O$	3100–3500 (br,s)	1656 (s)	1577 (s)	978, 1217 (m)
$Mn[C_3H_4(COO)_2]$	3100–3500 (br,s)		1583 (s)	968, 1218 (m)

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

Table 4
Magnetic moment data

	$Co(C_5H_5O_4)_2 \cdot 6H_2O$	$Zn(C_5H_5O_4)_2 \cdot 6H_2O$	$Mn(C_5H_5O_4)_2 \cdot 6H_2O$
μ(BM) found	5.2	0.0	5.8
μ(BM) lit.	4.3–5.2	0.0	5.7–6.1

The observed mass loss for the cyclic ligand is in good agreement with the theoretical values.

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