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Structural characterisation of bis(suberate) cobalt(II) 1.5 hydrate and a thermal analysis study of suberic acid and bis(suberate) cobalt(II) 1.5 hydrate

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Abstract

A metal complex of suberic acid with cobalt of stoichiometry $Co(C_8H_{12}O_4) \cdot 1.5H_2O$ has been prepared. The compound has a tetrahedral structure. Thermal decomposition studies of suberic acid and of $Co(C_8H_{12}O_4) \cdot 1.5H_2O$ show that the suberic acid melts at 143°C, while the metal complex loses water and then the organic ligand, to give Co_3O_4.

INTRODUCTION

This investigation is concerned with the complex formed between suberic acid $HOOC(CH_2)_6COOH$ and cobalt carbonate in aqueous solution. Information regarding the stereochemistry of the complex has been obtained using magnetic measurements, and electronic and infrared spectra. The thermal decompositions of the complex and of suberic acid were studied using thermogravimetry and differential thermal analysis.

EXPERIMENTAL

Preparation of the compounds

Suberic acid (0.05 mol) was dissolved in boiling water, and the resulting solution was neutralised by the addition of cobalt(II) carbonate. The solution was then filtered to remove any excess cobalt(II) carbonate and the filtrate was reduced in volume to yield the metal complex; calculated contents: Co, 22.83%; C, 37.22%; H, 5.85%; found: Co, 22.49%; C, 36.64%; H, 5.96%.

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Apparatus

The concentration of the cobalt 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 obtained using KBr discs (4000–600 cm^{-1}) and polythene discs (600–200 cm^{-1}) on a Perkin-Elmer spectrophotometer model 598.

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

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 STA 1500 thermobalance. The thermogravimetry (TG) and differential thermal analysis (DTA) curves were obtained at heating rate of 10°C min^{-1} in static air over the range 20–800°C.

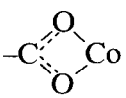
RESULTS AND DISCUSSION

The elemental analyses of the pink cobalt complex indicated that the complex has the stoichiometry $Co(C_8H_{12}O_4) \cdot 1.5H_2O$.

In the infrared spectrum of the cobalt complex, the broad strong band in the region 3670–3100 cm^{-1} is due to the ν(O–H) vibration of the water molecule and indicates the presence of water of crystallisation [1]. The IR spectrum of the suberic acid shows a band at 1696 cm^{-1} due to the –COOH group. This band is absent in the IR spectrum of the cobalt complex. The band at 1552 cm^{-1} in the IR spectrum of the metal complex is due to the COO^- group. The position of this band indicates that the COO^- group bonds to the cobalt ion as shown [2] in Scheme 1. The band at 424 cm^{-1} has been assigned to the Co–O vibration.

In the electronic spectrum of the cobalt complex, bands are observed at 4761, 14598 and 18348 cm^{-1}. The position of these bands would suggest that the cobalt ions are in a tetrahedral environment [3]. The bands have been assigned to the transitions $^4A_2(F) \rightarrow {}^4T_2(F)$, $^4A_2(F) \rightarrow {}^4T_1(F)$ and $^4T_1(F) \rightarrow {}^4T_1(P)$. The magnetic moment of the cobalt complex, which is 4.63 BM, also shows that the cobalt ions are in a tetrahedral environment [3].

The cobalt complex was obtained as a powder, and without single crystals no complete structure determination could be made. However,



Scheme 1.

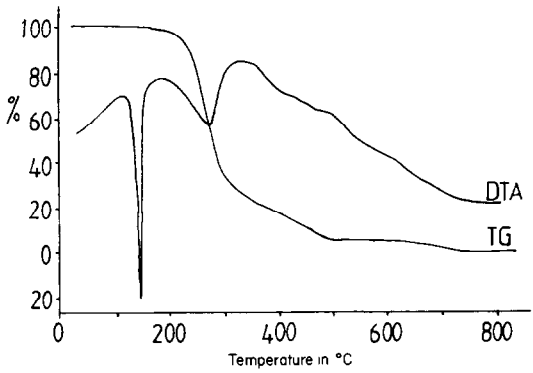


Fig. 1. TG and DTA traces of suberic acid; sample weight = 9.49 mg.

spectroscopic and magnetic data enable us to predict a possible stereochemistry for the cobalt complex. It is suggested that in the cobalt complex the carboxylate groups of the suberate ion are attached to a cobalt ion to give a tetrahedral structure. Each cobalt ion is bonded to the four oxygen atoms of the carboxylate groups. The water molecules are attached by hydrogen bonding.

The TG and DTA traces for suberic acid (Fig. 1) show that it is thermally stable in the range 20–148°C. Decomposition commences at 148°C and ends at 744°C with total elimination of the sample. The DTA trace shows an endothermic peak at 143°C corresponding to fusion. Liquid suberic acid decomposes immediately with an endothermic peak at 270°C. This reaction would appear to be complete by 480°C. However, slight decomposition is still observed between 480 and 744°C. It is possible that at 480°C a small amount of tar exists, and the decomposition between 480 and 744°C is due to the tar. The TG and DTA traces for $Co(C_8H_{12}O_4) \cdot 1.5H_2O$ are shown in Fig. 2. The TG trace shows that the cobalt complex decomposes at 60°C with loss of water. The dehydration process takes place in one step. The

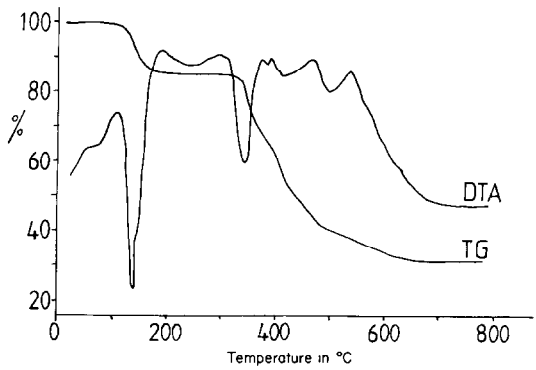


Fig. 2. TG and DTA traces of $Co(C_8H_{12}O_4) \cdot 1.5H_2O$); sample weight = 11.24 mg.

endothermic peak observed in the DTA trace is as expected for the dehydration process associated with this type of compound. The TG trace shows that the anhydrous compound then decomposes to give Co_3O_4. The DTA trace shows that this decomposition process is accompanied by endothermic and exothermic effects.

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