Thermochimica Acta, 231 (1994) 129–134
Elsevier Science B.V., Amsterdam
SSDI 0040-6031(93)01384-F

Preparation, structural characterisation and thermal analyses studies of the cobalt(II), nickel(II) and copper(II) complexes of benzylmalonic acid

J.R. Allan* and J. Dalrymple

Department of Applied Chemical and Physical Sciences, Napier University, Edinburgh EH10 5DT (UK)

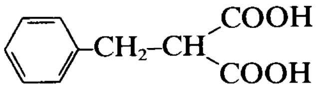
(Received 3 May 1993; accepted 2 June 1993)

Abstract

Compounds of benzylmalonic acid with cobalt, nickel and copper have been prepared in aqueous solution. The compounds have stoichiometry $Co(C_{10}H_8O_4) \cdot 2H_2O$; $Ni(C_{10}H_8O_4) \cdot 3H_2O$ and $Cu(C_{10}H_8O_4)$. The cobalt and nickel complexes have octahedral structures, and the copper complex has a tetragonal structure. Thermal decomposition studies show that the cobalt and nickel complexes decompose with the loss of water followed by the organic ligand to give the metal oxides. The copper compound loses organic ligand to give copper oxide.

INTRODUCTION

The dibasic acid, benzylmalonic acid can bond to metal ions by means of the oxygen(s) of the carboxylate ions. This paper reports the preparation of the complexes formed between benzylmalonic acid and the ions of cobalt, nickel and copper. Spectral and magnetic studies have been used to obtain the sterochemistry of each of the complexes. Thermal analysis studies have been carried out on the benzylmalonic acid and its metal complexes.



Benzylmalonic acid ($C_{10}H_{10}O_4$)

EXPERIMENTAL

Preparation of the complexes

Benzylmalonic acid (0.05 mol) was dissolved in boiling water; the resulting solution was neutralised by the addition of cobalt(II) carbonate. The solution was then filtered to remove any excess cobalt(II) carbonate

---

* Corresponding author.

and the filtrate reduced in volume to yield the metal complex. This procedure was repeated using the carbonates of nickel(II) and copper(II).

Apparatus and measurements

The concentration of the metal ion was obtained by a Perkin-Elmer 373 atomic absorption spectrophotometer and the carbon, hydrogen and nitrogen concentrations 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 10°C min^{-1} in static air, over the range 20–800°C.

RESULTS AND DISCUSSION

The compounds which were prepared are listed in Table 1. The cobalt and nickel complexes are hydrated and have stoichiometry of $M(C_{10}H_8O_4) \cdot nH_2O$ where $n = 2$ for cobalt and $n = 3$ for nickel. The copper complex has stoichiometry $Cu(C_{10}H_8O_4)$.

The main bands in the infrared spectra of benzylmalonic acid and its

TABLE 1

Analyses of the metal complexes in %

Compound[a]	Colour		Metal	Carbon	Hydrogen
$Co(C_{10}H_8O_4) \cdot 2H_2O$	Pink	Theory	20.52	41.83	4.91
		Found	20.29	41.59	4.64
$Ni(C_{10}H_8O_4) \cdot 3H_2O$	Green	Theory	19.25	39.39	4.62
		Found	19.01	39.47	4.39
$Cu(C_{10}H_8O_4)$	Blue	Theory	24.84	46.97	3.15
		Found	24.29	46.49	3.27

[a] $C_{10}H_8O_4$, benzylmalonate.

TABLE 2

Infrared spectra 4000–200 cm^{-1}

Compound	$\nu_{O-H}(H_2O)$/ cm^{-1}	ν(COOH)/ cm^{-1}	$\nu(COO^-)$/ cm^{-1}	ν(C–O)/ cm^{-1}	ν(M–O)/ cm^{-1}
$C_{10}H_{10}O_4$		1689 (s)		1318 (s)	
$Co(C_{10}H_{10}O_4) \cdot 2H_2O$	3660–3140 (br, s)		1561 (s)	1272 (s)	280 (w)
$Ni(C_{10}H_8O_4) \cdot 3H_2O$	3680–3100 (br, s)		1573 (s)	1304 (s)	260 (w)
$Cu(C_{10}H_8O_4)$			1552 (s)	1297 (s)	360 (s)

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

metal complexes are given in Table 2. The cobalt and nickel complexes show a strong broad absorption band in the region 3680–3100 cm^{-1} which is assigned to the ν(O–H) vibration of the water molecule and indicates water of crystallisation. The spectra of the metal complexes confirms the absence of free carboxylic acid groups. A reduction in $\nu(COO^-)$ compared to free $-CO_2H$ is observed which is characteristic of chelation [1]. Metal–oxygen bands for the metal complexes are listed in Table 2.

The position of the bands in the electronic spectra of the compounds and their magnetic moments are listed in Table 3. The metal atoms in the cobalt and nickel compounds are observed to be in an octahedral environment [2]. In the copper compound the band at 14 925 cm^{-1} and a magnetic moment of 1.88 BM would suggest that the copper compound has a tetragonal structure [3].

Because the compounds were isolated as powders rather than single crystals, no complete structural determination using X-ray crystallography was carried out. However, the spectroscopic and magnetic data enable us to predict a possible sterochemistry for the metal complexes. The compounds $Co(C_{10}H_8O_4) \cdot 2H_2O$ and $Ni(C_{10}H_8O_4) \cdot 3H_2O$ are considered to have a planar arrangement with the carboxylate groups on each benzylmalonate dianion bonded to two different metal atoms to give a chain-like structure. Each metal atom is bonded to four oxygen atoms in the plane. It is further

TABLE 3

Electronic spectra and magnetic moments

Compound	Band position/cm^{-1}	d–d transition	μ/BM
$Co(C_{10}H_8O_4) \cdot 2H_2O$	7407	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	5.18
	18587	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	
$Ni(C_{10}H_8O_4) \cdot 3H_2O$	8403	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	3.28
	14492	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	
	25252	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	
$Cu(C_{10}H_8O_4)$	14925	$^2B_1 \rightarrow {}^2A_1$	1.88

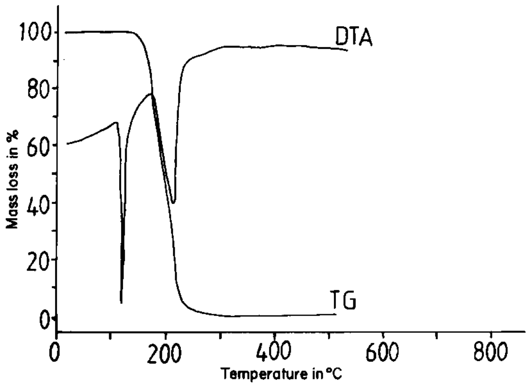


Fig. 1. TG and DTA traces for benzylmalonic acid. Sample mass, 10.58 mg.

suggested that the compounds consist of a layer structure in which each metal atom is bonded to oxygen atoms in adjacent layers, giving a six coordinate environment for the metal atoms. The water molecules are attached by hydrogen bonding in each of the compounds. The compound $Cu(C_{10}H_8O_4)$ has a pseudo-planar structure with long bonds from the copper atoms to the oxygen atoms of carboxylate groups in adjacent planes to give a tetragonal structure.

The TG and DTA traces for benylmalonic acid and its metal complexes are shown in Figs. 1–4. Benzylmalonic acid (Fig. 1) is thermally stable in the temperature range 20–125°C. Pyrolytic decomposition begins at 125°C and finishes at 326°C. The DTA trace shows an endothermic peak at 122°C due to melting. A further endothermic peak is observed at 216°C in the DTA trace for the decomposition of the acid. The TG traces for the cobalt (Fig. 2) and the nickel (Fig. 3) complexes which are hydrated show that the dehydration of each complex takes place in one step. The observed mass losses for these processes compare favourably with the theoretical values

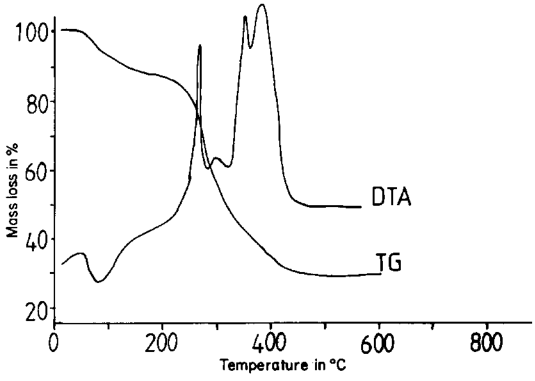


Fig. 2. TG and DTA traces for $Co(C_{10}H_8O_4) \cdot 2H_2O$. Sample mass, 8.84 mg.

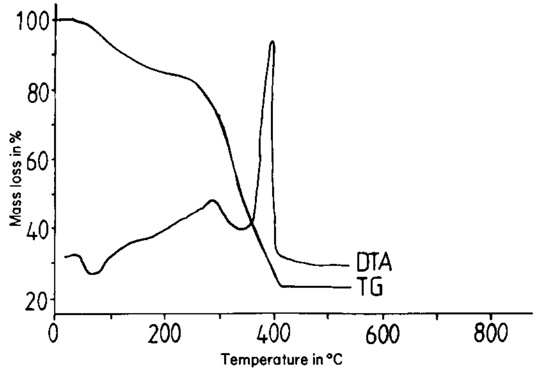


Fig. 3. TG and DTA traces for $Ni(C_{10}H_8O_4) \cdot 3H_2O$. Sample mass, 9.69 mg.

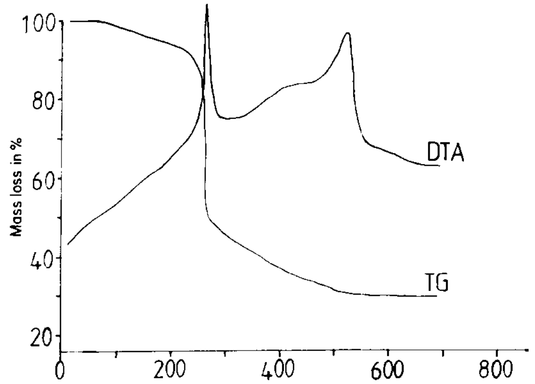


Fig. 4. TG and DTA traces for $Cu(C_{10}H_8O_4)$. Sample mass, 5.56 mg.

(Table 4). The endothermic peaks observed in each case in the DTA traces are as expected for the dehydration processes associated with these compounds. Decomposition of the anhydrous complexes follows immediately after the dehydration process and the actual mass losses reported in

TABLE 4

Dehydration processes of the metal complexes

Process	Decomposition temperature/°C	Thermal nature of transformation	Mass loss/%	
			Calc.	Found
$Co(C_{10}H_8O_4) \cdot 2H_2O \rightarrow Co(C_{10}H_8O_4)$	35	ENDO	12.5	12.4
$Ni(C_{10}H_8O_4) \cdot 3H_2O \rightarrow Ni(C_{10}H_8O_4)$	29	ENDO	17.7	17.5

TABLE 5

Decomposition processes of the metal complexes

Process	Temperature range/°C	Thermal nature of transformation	Mass loss/%	
			Calc.	Found
$Co(C_{10}H_8O_4) \rightarrow Co_3O_4$	189–484	EXO	59.6	59.4
$Ni(C_{10}H_8O_4) \rightarrow NiO$	207–418	EXO	57.8	57.5
$Cu(C_{10}H_8O_4) \rightarrow CuO$	72–532	EXO	68.9	68.6

Table 5 are in good agreement with the calculated values. The DTA traces show that these decomposition processes are accompanied by exothermic reactions. The copper compound (Fig. 4, Table 5), undergoes exothermic reactions with loss of the organic ligand to give CuO.

In summary the decomposition scheme for the metal complexes can be represented as

$$Co(C_{10}H_8O_4) \cdot 2H_2O \xrightarrow{\text{Endo}} Co(C_{10}H_8O_4) \xrightarrow{\text{Exo}} Co_3O_4$$

$$Ni(C_{10}H_8O_4) \cdot 3H_2O \xrightarrow{\text{Endo}} Ni(C_{10}H_8O_4) \xrightarrow{\text{Exo}} NiO$$

$$Cu(C_{10}H_8O_4) \xrightarrow{\text{Exo}} CuO$$

REFERENCES

1 J.R. Allan, B.R. Carson, D.L. Gerrard and S. Hoey, Thermochim. Acta, 158 (1990) 91.
2 J.R. Allan, N.D. Baird and A.L. Kassyk, J. Therm. Anal., 16 (1979) 79.
3 J.R. Allan and K. Turvey, Thermochim. Acta, 176 (1991) 89.