

THE THERMAL, SPECTRAL AND MAGNETIC STUDIES OF *p*-TOLYLACETIC ACID COMPOUNDS OF COBALT, NICKEL AND COPPER

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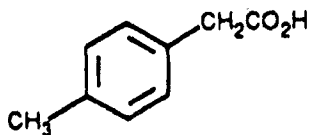
Abstract

The preparation and some properties of complexes of *p*-tolylacetic acid with cobalt, nickel and copper are described. Magnetic measurements, electronic and far infrared spectra show that the metal complexes have octahedral structures. Infrared spectra indicate that coordination takes place through the carboxyl group to the metal ions and that the water molecule in each of the complexes is present as water of crystallisation. Thermogravimetry studies also show that the water molecules in each of the complexes do not form a coordinate bond with the metal ion. Differential thermal analysis show that the dehydration processes are accompanied by endothermic reactions. In each case the anhydrous metal complex undergoes an exothermic reaction to give the metal oxide.

Keywords: complexes

Introduction

In this work we describe the structural properties and some thermal analysis studies of the complexes of *p*-tolylacetic acid



p-tolylacetic acid (C₉H₁₀O₂)

with the first row transition metals cobalt, nickel and copper. The compound *p*-tolylacetic acid has the oxygen atoms of the carboxyl group for bonding to metal ions. No thermal analysis measurements have been previously reported on any of the complexes prepared in this investigation.

Experimental

The complexes were prepared by dissolving the metal carbonate in a hot aqueous solution of *p*-tolylacetic acid. The excess carbonate was removed by filtration. The complex was precipitated by concentrating the solution on a steam bath.

Apparatus

The concentration of the metal ion was obtained by a Perkin Elmer 373 atomic absorption spectrophotometer and the carbon and hydrogen analyses were obtained using a Carlo Erba elemental analyser. The infrared spectra were obtained using KBr discs ($4000\text{--}600\text{ cm}^{-1}$) and polyethylene discs ($600\text{--}200\text{ cm}^{-1}$) 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 $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrant. Thermal analysis studies were carried out on a Stanton Redcroft thermobalance, model 1500. The thermogravimetry (TG) and differential thermal analysis (DTA) traces were obtained at a heating rate of 6°C min^{-1} in static air and over a temperature range of $20\text{--}800^\circ\text{C}$. Sample weights of 7 to 8 mg of the compounds were used.

Results and discussion

In Table 1 the complexes isolated from aqueous solution are listed. The elemental analysis agree with the given formulae for the complexes. The complexes have stoichiometry $\text{M}(\text{C}_9\text{H}_9\text{O}_2)_2 \cdot x\text{H}_2\text{O}$ where $x=1.5$ for cobalt, $x=1$ for nickel and copper.

Table 1 Analysis of complexes

Compound	Colour		Metal	Carbon	Hydrogen
$\text{Co}(\text{C}_9\text{H}_9\text{O}_2)_2 \cdot 1.5\text{H}_2\text{O}$	Pink	Theory	15.33	56.25	5.50
		Found	15.09	56.43	5.11
$\text{Ni}(\text{C}_9\text{H}_9\text{O}_2)_2 \cdot \text{H}_2\text{O}$	Green	Theory	15.65	57.64	5.37
		Found	15.27	56.91	5.21
$\text{Cu}(\text{C}_9\text{H}_9\text{O}_2)_2 \cdot \text{H}_2\text{O}$	Blue	Theory	16.72	56.90	5.31
		Found	16.34	56.39	5.09

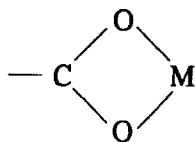
The position of the bands in the electronic spectra of the complexes, Table 2, indicate a six coordinate environment for the metal ions [1]. The magnetic moment for the cobalt complex listed in Table 2 is lower than that normally observed for octahedral cobalt complexes. However Stoufer *et al.* have reported

Table 2 Electronic spectra and magnetic moments of complexes

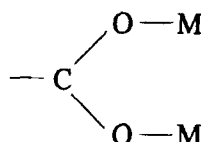
Compound	Band position	<i>d-d</i> transition	μ (B. M.)
Co(C ₉ H ₉ O ₂) ₂ ·1.5H ₂ O	8475	⁴ T _{1g} (F) → ⁴ T _{2g} (F)	3.99
	12500	⁴ T _{1g} (F) → ⁴ A _{2g} (F)	
	20486	⁴ T _{1g} (P) → ⁴ T _{1g} (P)	
Ni(C ₉ H ₉ O ₂) ₂ ·H ₂ O	8333	³ A _{2g} (F) → ³ T _{2g} (F)	2.86
	14706	³ A _{2g} (F) → ³ T _{1g} (F)	
	24390	³ A _{2g} (P) → ³ T _{1g} (P)	
Cu(C ₉ H ₉ O ₂) ₂ ·H ₂ O	14925	² E _{2g} (D) → ² T _{2g} (D)	1.38

complexes which have magnetic moments of around 3.00 B.M. These low magnetic moments have been accounted for in terms of a Boltzmann distribution over thermally accessible levels characterised by different spin multiplicities [2]. The nickel complex has a magnetic moment in the range 2.8–3.4 B.M. which is characteristic of the nickel ion in an octahedral environment [1]. The magnetic moment for the copper complex is 1.38 B.M. Some copper(II) carboxylates [3, 4] and the so-called tri-coordinate copper(II) complexes show subnormal magnetic moments. Copper(II) acetate with three atom carboxylate bridges has a magnetic moment of 1.43 B.M. This value is attributed to spin-spin magnetic interaction between the copper ions.

In Table 3, the main bands in the infrared spectra of the *p*-tolylacetic acid and its complexes are reported. The complexes all show a strong absorption band in the region 3700–2850 cm⁻¹ indicating the presence of water of crystallisation [1]. The spectra of the complexes confirm the absence of free carboxylic acid groups. The usual reduction in $\nu(\text{COO}^-)$ compared to free-CO₂H is observed, and is characteristic of bonding type I rather than type II [5]



I



II

Metal–oxygen bands, reported for each of the complexes, indicate a six coordinate environment for the metal ions [6].

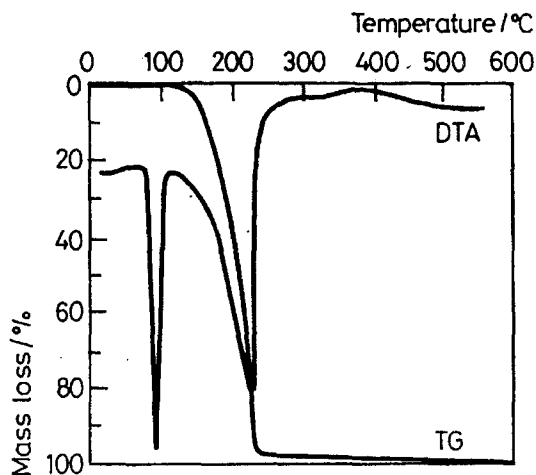
As the complexes were isolated as powders from aqueous solution their structures cannot be determined by X-ray single crystal studies. However, the spectroscopic and magnetic data enable us to predict a possible stereochemistry for the complexes. It is suggested that the complexes have a planar arrangement with the carboxylate groups of two different *p*-tolylacetic acid ions bonded to a

Table 3 Infrared spectra (4000–200 cm^{-1})

Compound	$\nu(\text{H}_2\text{O})$	$\nu(\text{COOH})$	$\nu(\text{COO}^-)$	$\nu(\text{M-O})$
$\text{C}_9\text{H}_{10}\text{O}_2$	—	1698 (s)	—	—
$\text{Co}(\text{C}_9\text{H}_9\text{O}_2)_2 \cdot 1.5\text{H}_2\text{O}$	3398–3200 (br, s)	—	1559 (s)	256 (m)
$\text{Ni}(\text{C}_9\text{H}_9\text{O}_2)_2 \cdot \text{H}_2\text{O}$	3682–2854 (br, s)	—	1543 (s)	264 (m)
$\text{Cu}(\text{C}_9\text{H}_9\text{O}_2)_2 \cdot \text{H}_2\text{O}$	3690–3220 (br, s)	—	1592 (s)	280 (m)

br: broad; s: strong; m: medium

metal atom to give a layer. It is further suggested that each metal is bonded to oxygen atoms in adjacent layers to give a six coordinate environment for the metal ions and a polymeric structure. The water molecules are attached by hydrogen bonding.

**Fig. 1** TG and DTA trace for *p*-tolylacetic acid

The TG and DTG traces for *p*-tolylacetic acid and the complexes with cobalt, nickel and copper are given in Figs 1–4. The *p*-tolylacetic acid, Fig. 1, is thermally stable in the temperature range 20–76°C. Pyrolytic decomposition begins

Table 4 Dehydration processes of metal complexes

Process	$T_{\text{peak}}/^\circ\text{C}$	Thermal nature of process	Weight loss		Enthalpy/ kJ mol^{-1}
			calc.	found	
$\text{Co}(\text{C}_9\text{H}_9\text{O}_2)_2 \cdot 1.5\text{H}_2\text{O} \rightarrow \text{Co}(\text{C}_9\text{H}_9\text{O}_2)_2$	48	Endo	6.0	6.2	119
$\text{Ni}(\text{C}_9\text{H}_9\text{O}_2)_2 \cdot \text{H}_2\text{O} \rightarrow \text{Ni}(\text{C}_9\text{H}_9\text{O}_2)_2$	66	Endo	4.8	4.6	28
$\text{Cu}(\text{C}_9\text{H}_9\text{O}_2)_2 \cdot \text{H}_2\text{O} \rightarrow \text{Cu}(\text{C}_9\text{H}_9\text{O}_2)_2$	52	Endo	4.7	4.6	12

Endo: Endothermic

at 76°C and finishes at 462°C with total elimination of the sample. The DTA trace shows an endothermic peak at 89°C owing to melting. The enthalpy of fusion is 14 kJ mol⁻¹. The liquid *p*-tolylacetic acid then decomposes immediately by means of an endothermic reaction. The TG and DTA traces for the complexes are given in Figs 2–4. The dehydration processes for the complexes is a one stage process. The observed weight losses for these processes compare favourably with the theoretical values, Table 4. The endothermic peak observed in the DTA trace for each of these processes is as expected for a dehydration process associated with this type of compound. The dehydration enthalpies have been calculated and are given in Table 4. Decomposition of the anhydrous com-

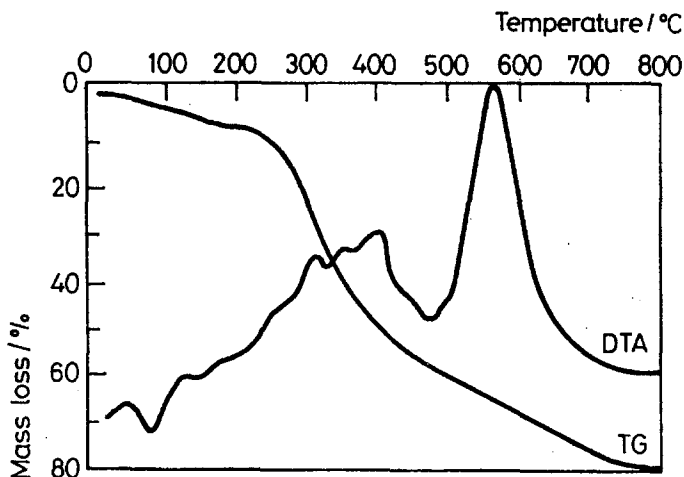


Fig. 2 TG and DTA trace for $\text{Co}(\text{C}_9\text{H}_9\text{O}_2)_2 \cdot 1.5\text{H}_2\text{O}$

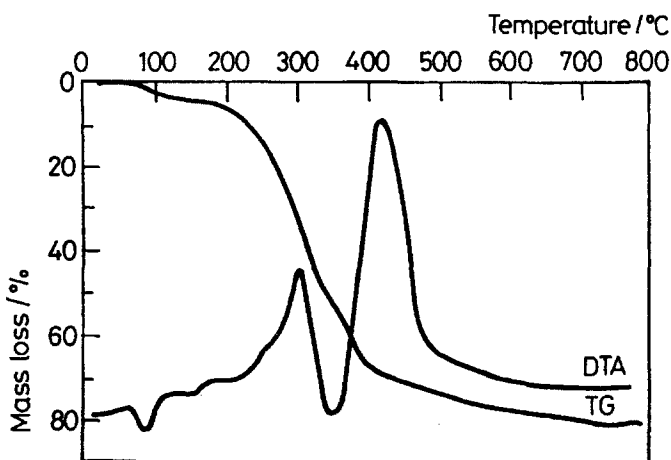


Fig. 3 TG and DTA trace for $\text{Ni}(\text{C}_9\text{H}_9\text{O}_2)_2 \cdot \text{H}_2\text{O}$

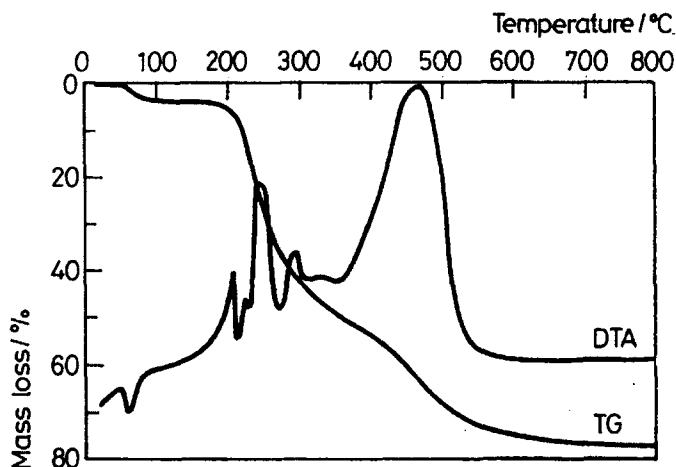


Fig. 4 TG and DTA trace for $\text{Cu}(\text{C}_9\text{H}_9\text{O}_2)_2 \cdot \text{H}_2\text{O}$

Table 5 Decomposition processes of *p*-tolylacetic acid and its metal complexes

Process	$T_{\text{range}}/$ °C	Thermal nature of process	Residue/%	
			calc.	found
$\text{C}_9\text{H}_9\text{O}_2 \rightarrow$ Pyrolytic process	76-462	Endo	-	-
$\text{Co}(\text{C}_9\text{H}_9\text{O}_2)_2 \rightarrow \text{Co}_3\text{O}_4$	189-766	Exo	20.9	21.1
$\text{Ni}(\text{C}_9\text{H}_9\text{O}_2)_2 \rightarrow \text{NiO}$	146-752	Exo	19.9	19.6
$\text{Cu}(\text{C}_9\text{H}_9\text{O}_2)_2 \rightarrow \text{CuO}$	136-757	Exo	20.9	21.9

Endo: Endothermic; Exo: Exothermic

plexes follows immediately after the dehydration processes and the residual weights are in good agreement with the values reported in Table 5 for the metal oxides. In the DTA traces these decomposition processes are exothermic.

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