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THERMAL, SPECTRAL AND MAGNETIC STUDIES OF SOME FIRST-ROW TRANSITION METAL COMPLEXES OF ADIPIC ACID

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ABSTRACT

Some compounds of adipic acid with cobalt, nickel and copper have been prepared in aqueous solution. The thermal behaviour of these compounds, as well as the adipic acid, has been studied by thermogravimetry and differential thermal analysis. The transition metal complexes are all hydrated. Thermal decomposition studies show that they lose water, then the organic ligand, to give the metal oxide.

INTRODUCTION

In this work we describe and discuss the thermal analysis studies of adipic acid, $HO_2C(CH_2)_4CO_2H$, together with the complexes formed by the acid and the transition metals cobalt, nickel and copper.

Spectral and magnetic studies have been used to characterise each complex and to interpret the type of coordination which takes place to the metal ion.

EXPERIMENTAL

Preparation of the complexes

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

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Apparatus

The concentration of the metal ion was obtained using a Perkin–Elmer 373 atomic absorption spectrophotometer, and the carbon and hydrogen analyses were obtained using a Carlo Erba elemental analyser. 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. The thermal analysis studies were carried out on a Stanton Redcroft model STA 781 thermobalance. Thermogravimetry (TG) and differential thermal analysis (DTA) curves were obtained at a heating rate of 10 °C min^{-1} in static air. In all cases, the 20–800 °C temperature range was studied.

RESULTS AND DISCUSSION

The adipate complexes prepared are hydrated and have the stoichiometry $M(C_6H_8O_4)xH_2O$ where $x = 1$ for cobalt, $x = 4$ for nickel and $x = 0.5$ for copper. Table 1 shows that the analytical results for the complexes agree with the given formulae.

The wavenumbers of the IR absorption bands, as well as their descriptions and assignments, are given in Table 2. The IR spectra for the compounds show medium absorption bands present in the region 3660–3000 cm^{-1}, ν(OH), and 1630–1580 cm^{-1}, δ(HOH), confirming the presence of water of crystallisation. The infrared spectrum of adipic acid is almost identical to that of its complexes in the region 2000–625 cm^{-1} except that in the complexes the bands due to the carboxyl group move to lower wavenumbers [1]: this is due to the stretching vibration of the carboxylate groups linked to the metal ions [2,3]. The ν(M–O) vibrations have been identified and are listed in Table 2.

The electronic spectra, Table 3, and the magnetic measurements, Table 1, would suggest that, for the cobalt and nickel compounds, the cobalt atom is

TABLE 1

Analyses and magnetic moments of the compounds

Compound [a]	Colour	Theory (%)			Found (%)			μ (B.M.)
		Metal	Carbon	Hydrogen	Metal	Carbon	Hydrogen	
$Co(C_6H_8O_4)\cdot H_2O$	Violet	26.65	32.59	4.57	26.13	32.14	3.92	3.90
$Ni(C_6H_8O_4)\cdot 4H_2O$	Pale green	21.35	26.21	5.91	20.84	26.66	5.60	3.82
$Cu(C_6H_8O_4)\cdot 0.5H_2O$	Pale green	29.33	33.25	4.19	28.71	33.75	4.23	1.32

[a] $C_6H_8O_4$, Adipate di-anion.

TABLE 2

Infrared spectra (4000–200 cm^{-1})

Compound	$\nu_{O-H}(H_2O)$	ν_{COOH}	ν_{COO^-}	ν_{M-O}
$C_6H_{10}O_4$		1685 (s)		
$Co(C_6H_8O_4)\cdot H_2O$	3660–3000 (br, s)		1526 (s)	315 (s)
$Ni(C_6H_8O_4)\cdot 4H_2O$	3640–2980 (br, s)		1522 (s)	252 (w)
$Cu(C_6H_8O_4)\cdot 0.5H_2O$	3610–3000 (br, s)		1546 (s)	248 (w)

br, Broad; s, strong; w, weak.

in a tetrahedral environment while the nickel atom is in an octahedral environment [4,5]. The position of the band in the electronic spectrum of the copper compound would suggest that the copper atom is in an octahedral environment [5]. The magnetic moment for the copper compound is 1.32 B.M. and this would suggest some copper–copper magnetic interaction [6].

The fact that the compounds were isolated as powders and not as single crystals means that no complete structure determination can be made. However, spectroscopic and magnetic data enable us to predict the environment of the metal ion in the compounds. The cobalt compound has a tetrahedral structure in which the cobalt atom is bonded to the oxygen atoms of the two carboxylate groups. It is suggested that the nickel and copper compounds have a planar arrangement with the carboxylate groups on each molecule of adipic acid bonded to two different metal atoms to give a chain-like structure. It is further suggested that each metal atom is bonded to oxygen atoms in adjacent layers to give a six-coordinate environment for the metal ion. The water molecules are attached by hydrogen bonding in all the compounds.

The TG and DTA curves for adipic acid show that the acid is thermally stable in the temperature range 20–149 °C. Its pyrolytic decomposition starts at 149 °C and finishes at 460 °C with the total elimination of the sample. The DTA curve of the adipic acid, Fig. 1, shows an endothermic

TABLE 3

Electronic spectra (cm^{-1})

Compound	Band position	d–d transition
$Co(C_6H_8O_4)\cdot H_2O$	17094 | 18796	$^4A_2(F) \rightarrow {}^4T_1(P)$
	8772	$^4A_2(F) \rightarrow {}^4T_1(F)$
$Ni(C_6H_8O_4)\cdot 4H_2O$	25510	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$
	13889	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$
	9019	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$
$Cu(C_6H_8O_4)\cdot 0.5H_2O$	13520	$^2E_g(D) \rightarrow {}^2T_{2g}(D)$

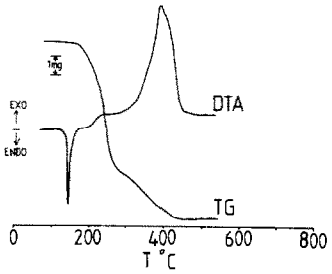

Fig. 1. TG and DTA curves for adipic acid: sample weight, 9.20 mg.

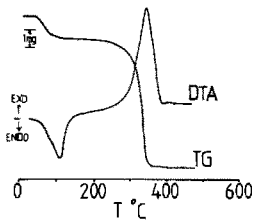

Fig. 2. TG and DTA curves for $Co(C_6H_8O_4)\cdot H_2O$: sample weight, 12.70 mg.

peak at 152°C corresponding to fusion. The value of the fusion enthalpy is 38.34 kJ mol^{-1}. Liquid adipic acid decomposes immediately with an exothermic peak at 412°C. The TG and DTA curves for the complexes formed between adipic acid and cobalt, nickel and copper are shown in Figs. 2–4. The TG and DTA curves are similar. The dehydration of the complexes takes place in one step. The observed weight losses for these processes compare favourably with the theoretical values, see Table 4. The expected endothermic peak for the dehydration processes associated with these compounds was observed in the DTA curves. The dehydration enthalpies have been calculated and are given in Table 4. Decomposition of the anhydrous complexes follows immediately after the dehydration process and the residual weights are in good agreement with the values required for the metallic

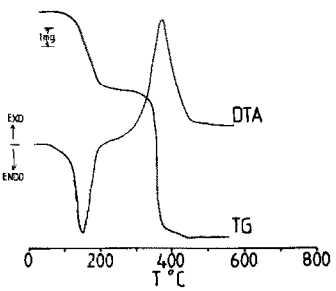

Fig. 3. TG and DTA curves for $Ni(C_6H_8O_4)\cdot 4H_2O$: sample weight, 15.95 mg.

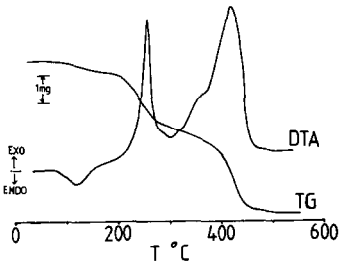

Fig. 4. TG and DTA curves for $Cu(C_6H_8O_4)\cdot 0.5H_2O$: sample weight, 8.6 mg.

TABLE 4

Dehydration processes of the adipic acid–metal complexes

Process	Peak temperature (°C)	Thermal nature of transformation	Weight loss (%)		Enthalpy (kJ mol^{-1})
			Calc.	Found	
$Co(C_6H_8O_4)\cdot H_2O \rightarrow Co(C_6H_8O_4)$	103	Endo	8.21	9.44	19
$Ni(C_6H_8O_4)\cdot 4\,H_2O \rightarrow Ni(C_6H_8O_4)$	150	Endo	26.98	26.33	200
$Cu(C_6H_8O_4)\cdot 0.5\,H_2O \rightarrow Cu(C_6H_8O_4)$	116	Endo	4.15	4.65	37

TABLE 5

Decomposition processes of adipic acid and anhydrous metal complexes

Process	Temperature range (°C)	Thermal nature of transformation	Residue (%)	
			Calc.	Found
$C_6H_{10}O_4 \rightarrow$ pyrolytic process	149–460	Exo	–	–
$Co(C_6H_8O_4) \rightarrow Co_3O_4$	175–418	Exo	36.69	36.22
$Ni(C_6H_8O_4) \rightarrow NiO$	220–464	Exo	28.01	28.21
$Cu(C_6H_8O_4) \rightarrow CuO$	158–518	Exo	36.70	36.04

oxides (Table 5). In the DTA curves, these decomposition processes correspond to exothermic effects for the complexes.

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