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THERMAL DECOMPOSITION OF 8-HYDROXYQUINOLINE COMPLEXES WITH ALUMINIUM, COBALT, MANGANESE AND NICKEL

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ABSTRACT

The conditions of thermal decomposition of aluminium(III), cobalt(II), manganese(II) and nickel(II) 8-hydroxyquinoline complexes have been studied by TG–DSC analysis. The thermal decomposition of these complexes has two stages: dehydration and loss of 8-hydroxyquinoline. The final solid product is an oxide.

INTRODUCTION

8-Hydroxyquinoline is a familiar complexing agent for several metal ions. Most papers concerning metal complexes of 8-hydroxyquinoline deal with complex equilibria or various analytical applications, but few with the thermal behaviour of these complexes [1–3].

The present work was conducted to study the thermal behaviour of the 8-hydroxyquinoline complexes of aluminium(III), cobalt(II), manganese(II) and nickel(II) by TG, DSC, IR and MS analyses.

EXPERIMENTAL

All reagents were of analytical grade, obtained from Fluka AG and used without further purification.

The 8-quinolinol chelates were prepared following procedures described elsewhere [4]. The metal contents of the compounds studied were determined by DCP–AES (Spectra Span IIIB), hydrogen contents with an elemental analyser (Leco RH2) and carbon contents by a classical gravimetric method where carbon was burned into CO_2 and the gas released was passed into an adsorption tube containing soda asbestos (ascarite). Analytical data of the compounds are given in Table 1.

Thermogravimetric analyses (TG) were carried out on a Mettler TG 50 thermobalance. Samples of 5–10 mg were used for TG and the heating rate

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TABLE 1

Analytical data

	% C		% H		% M	
	Calcd.	Found	Calcd.	Found	Calcd.	Found
$Al(C_9H_6NO)_3 \cdot 2\,H_2O$	65.5	66.3	4.5	4.37	5.3	5.7
$Co(C_9H_6NO)_2 \cdot 2\,H_2O$	56.4	55.4	4.2	4.58	15.4	15.1
$Mn(C_9H_6NO)_2 \cdot 2\,H_2O$	57.0	57.3	4.3	4.26	14.5	14.5
$Ni(C_9H_6NO)_2 \cdot 2\,H_2O$	56.4	55.8	4.2	4.30	15.3	15.9

was 5 K min^{-1}. DSC curves were obtained in the range 298–873 K with a Mettler DSC-20 at a heating rate of 5 K min^{-1} under a dynamic air atmosphere (50 ml min^{-1}), and with 4–5 mg samples. IR spectra were recorded in KBr matrix on a Perkin-Elmer 457 grating spectrometer in the range 250–4000 cm^{-1}. The mass spectra of the decomposition products were obtained on a Kratos MS 80 RF mass spectrometer using the direct inlet technique with sample heating (pure compound or intermediate product) at a rate of 50 K min^{-1} and using scanning rate of 1 s/decade for recording the spectra.

RESULTS AND DISCUSSION

The IR spectra of the metal complexes studied are shown in Fig. 1. The spectra recorded for the transition metal complexes investigated have almost identical features. The bands at 1418, 1465, 1495 and 1570 cm^{-1} are mainly attributed to C=N and C=C stretching vibration frequencies and those at 740, 785 and 815 cm^{-1} arise from C–H out-of-plane deformation vibrations. The bands at 500 and 1105 cm^{-1} are an M–O vibrational band and a C–O stretching vibration frequency. There are some deviations in the IR spectra of the aluminium complex from those mentioned above. There is a strong C=C stretching vibration band at 1600 cm^{-1}. Also the bands in the region 350–650 cm^{-1} deviate from those for the transition metal chelates.

The initial decomposition temperatures of the complexes indicate an order of thermal stability of Co > Ni > Mn > Al (Fig. 2). The dihydrated Al, Co, Mn and Ni complexes undergo dehydration in the first step (Table 2). Peak dehydration temperatures change in the region 403–423 K. Figure 3 shows isothermal plots of α vs. t for the complexes studied at 408 K. At this temperature and after 2 min, the values of α (fraction decomposed) for Al, Ni, Co and Mn complexes are 0.05, 0.57, 0.58 and 0.92, respectively. This means that the rate of dehydration is strongest in the case of the Mn(II) complex.

The total ion chromatogram and MS spectra of the Co complex represent the second stage in the decomposition of the complexes studied (Fig. 4).

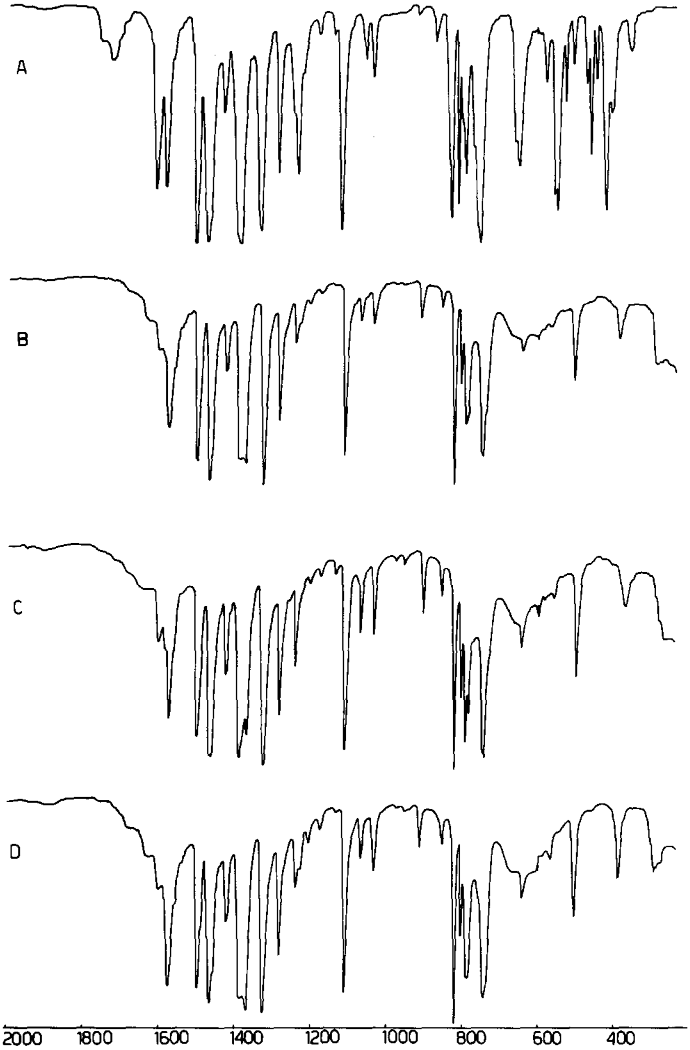

Fig. 1. IR spectra of (A) Al(III); (B) Co(II); (C) Mn(II); and (D) Ni(II) 8-hydroxyquinoline dihydrate complexes.

These results indicate that in this step, the loss of 8-quinolinol molecules occurs ($M/z = 145$). To substantiate this conclusion we have recorded ion chromatograms of peaks from the mass spectra (Fig. 4B), e.g. 28, 44, 57, 63, 71, 90, 103, 117 and 135 (M/z), but the influence of these ions on the total ion chromatogram (TIC) is really very small compared with the ion chromatogram of 8-quinolinol ($M/z = 145$). This means that the main component in this second decomposition stage of the complex is 8-quinolinol and peaks of mass spectra at 28, 44, 57 (M/z), etc., are its fragments. On the basis of IR spectra and the weight of the residue (Table 2), the final

TABLE 2

Data on the decomposition of Al, Co, Mn and Ni 8-hydroxyquinoline complexes

	Temperature range of dehydration (K)	Weight loss (%)		Loss of H_2O (mol)	Temperature range of decomposition (K)	Residue (%)		Temperature of oxide formation (K)
		calcd.	found			calcd.	found	
$Al(C_9H_6NO)_3 \cdot 2\,H_2O$	302–443	7.3	7.4	2	538–873	10.3	5.4	873
$Co(C_9H_6NO)_2 \cdot 2\,H_2O$	346–430	9.4	10.0	2	593–713	21.6	21.8	713
$Mn(C_9H_6NO)_2 \cdot 2\,H_2O$	379–413	9.5	9.5	2	556–680	22.9	21.2	680
$Ni(C_9H_6NO)_2 \cdot 2\,H_2O$	364–423	9.4	8.6	2	573–793	19.5	17.0	793

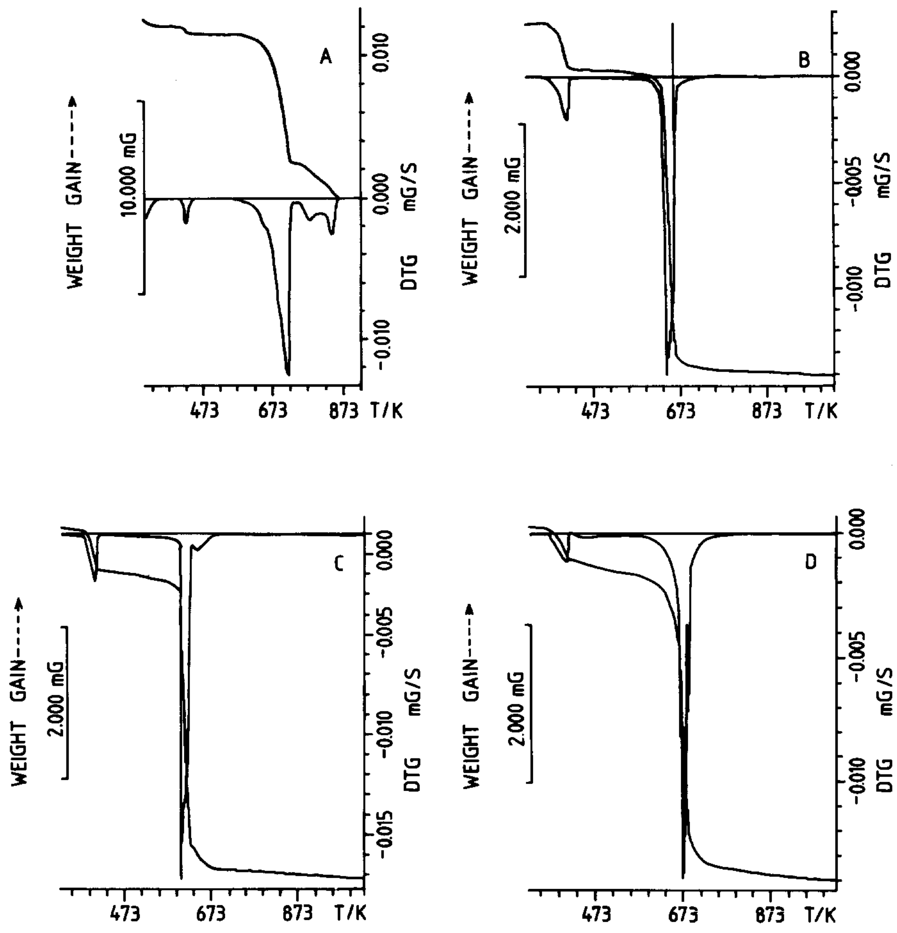

Fig. 2. TG curves for (A) Al(III); (B) Co(II); (C) Mn(II); and (D) Ni(II) complexes.

products are found to be Al_2O_3, Co_2O_3, MnO_2 and NiO. In addition, the colours and metal contents of the residues determined by DCP–AES (59.9, 53.9, 54.0 and 79.6 mass% for Al, Co, Mn and Ni residues) agree with this

TABLE 3

Enthalpy changes, ΔH, for decomposition of the complexes

Compound	Stage I		ΔH (kJ mol^{-1})	Stage II		ΔH (kJ mol^{-1})
	T range (K)	T_p (K)		T range (K)	T_p (K)	
$Al(C_9H_6NO)_3 \cdot 2\,H_2O$	298–443	338	83.1		[a]	[a]
$Co(C_9H_6NO)_2 \cdot 2\,H_2O$	358–443	436	129.6	580–784	703	−7100
$Mn(C_9H_6NO)_2 \cdot 2\,H_2O$	367–422	413	129.5	566–690	685	−6617
$Ni(C_9H_6NO)_2 \cdot 2\,H_2O$	378–441	433	125.8	630–765	731	−6422

[a] Not determined ($T_p >$ upper limit of the DSC-20).

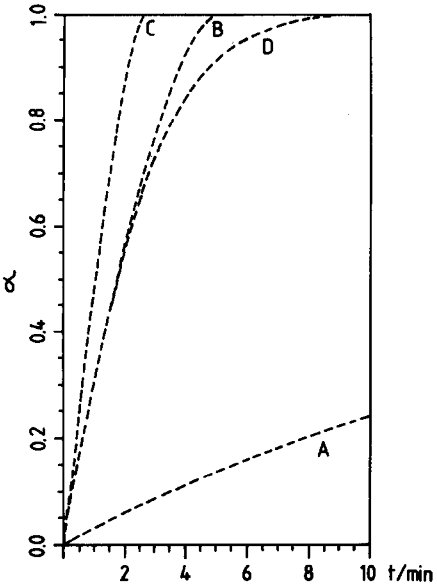

Fig. 3. Plots of α vs. t at 408 K. Letters refer to the same complexes as in Fig. 1.

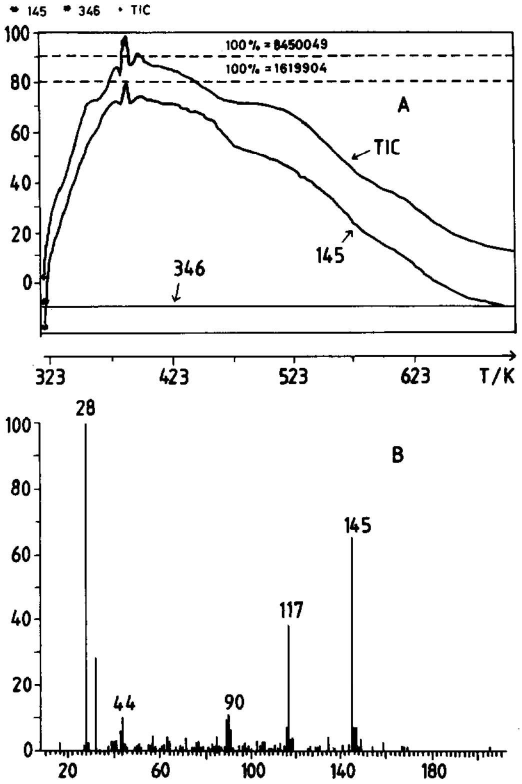

Fig. 4. Total ion chromatogram (A) and MS spectrum (B) of Co(II) 8-hydroxyquinoline at 500 K taken using the straight inlet system of the sample.

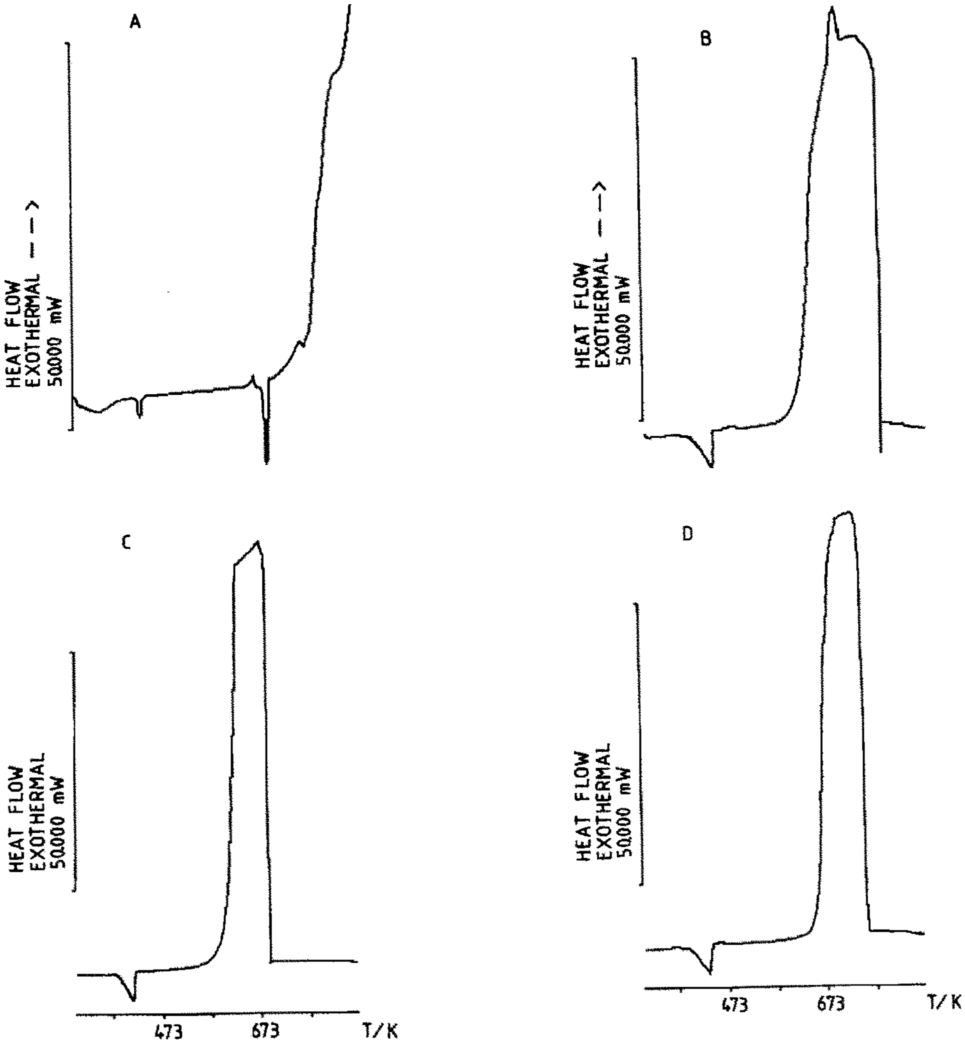

Fig. 5. DSC curves for (A) Al(III); (B) Co(II); (C) Mn(II); and (D) Ni(II) 8-hydroxyquinoline dihydrate complexes.

deduction. The temperatures of oxide formation increase periodically with increasing atomic number.

Table 3 and Fig. 5 show enthalpy changes for the decomposition of Al(III), Co(II), Mn(II) and Ni(II) 8-hydroxyquinoline dihydrate complexes. ΔH values for the dehydration processes are endothermic and nearly in the same order of magnitude for Co, Mn and Ni complexes. The second step involves the very exothermic decomposition of complexes and burning of ligand acid molecules. The ΔH values ($-6422, -6617$ and -7100 kJ mol^{-1}) for Ni, Mn and Co complexes are in the same order of magnitude and agree with MS data that the decomposition process is similar for these complexes.

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