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THERMAL, SPECTRAL AND MAGNETIC STUDIES OF CHLORO COMPLEXES OF COBALT, NICKEL AND COPPER WITH 4-(BUTYLAMINO) BENZOIC ACID

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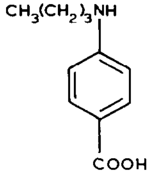
ABSTRACT

The chloro compounds of 4-(butylamino) benzoic acid with cobalt, nickel and copper were prepared in an ethanolic solution from which solid compounds were isolated. The compounds were characterised with analyses, magnetic moments, vibrational and electronic spectra. The cobalt compound has a tetrahedral structure while the nickel and copper compounds have polymeric octahedral structures. The thermal behaviour of these compounds has been studied by thermogravimetry and differential thermal analysis. The cobalt compound, which is hydrated, loses water of crystallisation followed by loss of organic ligand and chlorine to give the metal oxide. The nickel and copper compounds lose organic ligand and chlorine to give the metal oxide.

INTRODUCTION

The compound 4-(butylamino) benzoic acid has two different donor sites for forming bonds with metal ions: the nitrogen atom of the amino group and the oxygen atoms of the carboxylic acid group.



4-(butylamino) benzoic acid ($C_{11}H_{15}NO_2$)

This paper reports the thermal analysis studies of 4-(butylamino) benzoic acid together with some complexes formed by the acid and the transition metals cobalt, nickel and copper. Spectral and magnetic studies have been used to characterise each metal complex and to interpret the type of coordination which takes place to the metal ion.

EXPERIMENTAL

Preparation of the complexes

The metal halide (1 g) was dissolved in 40 cm^3 warm ethanol. To this solution was added 2 g 4-(butylamino) benzoic acid in 60 cm^3 warm ethanol. The volume of solvent was then reduced and the complex precipitated. The precipitated complex was filtered, washed with warm ethanol and dried at room temperature.

Apparatus and measurements

The concentration of metal ion was determined using a Perkin–Elmer 373 atomic absorption spectrophotometer. The carbon, hydrogen and nitrogen analyses were made using a Carlo–Erba elemental analyser.

The IR spectra were recorded using Nujol mulls over the wavenumber range 4000–600 cm^{-1} and polyethylene discs over the range 600–200 cm^{-1} on a Perkin–Elmer IR spectrophotometer model 598.

The electronic spectra were recorded as solid diffuse reflectance spectra using a Beckman Acta MIV spectrophotometer. Measurement of magnetic moments was made using the Gouy method with $Hg[Co(SCN)_4]$ as calibrant.

The thermal analysis measurements were made on a Stanton Redcroft Model STA 1500 thermobalance. Thermogravimetry (TG) and differential thermal analysis (DTA) curves were obtained at a heating rate of 6 °C min^{-1} in static air. The 20–800 °C temperature range was studied in all cases.

RESULTS AND DISCUSSION

The analytical results of the complexes are given in Table 1. These analyses agree with the given formulae proposed for the complexes. The molecular magnetic moments and the bands in the electronic spectra of the complexes are listed in Table 2. The position of the bands in the cobalt and nickel complexes and their magnetic moments suggest that the cobalt atom is in a tetrahedral environment while the nickel atom is in an octahedral environment [1,2]. The copper compound has a broad absorption band

TABLE 1

Analyses of compounds

Compound [a]	Theory (%)				Found (%)			
	Metal	Carbon	Nitrogen	Hydrogen	Metal	Carbon	Nitrogen	Hydrogen
$Co(C_{11}H_{15}NO_2)Cl_2H_2O$	11.02	49.45	5.24	6.03	10.66	49.39	5.18	6.20
$Co(C_{11}H_{15}NO_2)_2Cl_2$ [b]	11.41	51.17	5.42	5.85	11.42	50.12	5.32	5.84
$Ni(C_{11}H_{15}NO_2)_2Cl_2$	11.37	51.19	5.42	5.85	11.56	50.34	5.27	5.66
$Cu(C_{11}H_{15}NO_2)Cl_2$	19.38	40.31	4.27	4.61	19.47	39.07	4.26	4.21

[a] $C_{11}H_{15}NO_2$ = 4-(butylamino) benzoic acid.

[b] Anhydrous compound produced by heating the corresponding hydrated compound.

TABLE 2

Electronic spectra and magnetic measurements

Compound	Colour	Band position (cm^{-1})	$d-d$ Transition	μ (B.M.)
$Co(C_{11}H_{15}NO_2)_2Cl_2$	Blue	6579	$^4A_2(F) \rightarrow 4T_1(F)$	4.32
		15873	$^4A_2(F) \rightarrow {}^4T_1(P)$	
$Ni(C_{11}H_{15}NO_2)_2Cl_2$	Green	7813	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	2.75
		13889	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	
		23256	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	
$Cu(C_{11}H_{15}NO_2)Cl_2$	Green	12738	$^2E_g(D) \rightarrow {}^2T_{2g}(D)$	1.46

between 10000 and 15000 cm^{-1}, indicative of an octahedral environment for the copper atom [1]. The magnetic moment for the copper compound is lower than that expected for the spin-only value and would suggest some copper–copper magnetic interaction in the compound [3].

The wavenumbers of the IR absorption bands for 4-(butylamino) benzoic acid and its chloro complexes isolated from ethanolic solution are given in Table 3 together with the description and assignments. The IR spectrum of 4-(butylamino) benzoic acid shows two bands at 3400 and 3362 cm^{-1} which correspond to the N–H vibration. This would indicate the presence of an NH_2 group and not an NH group in 4-(butylamino) benzoic acid [4]. It is thus suggested that the band at 1658 cm^{-1} corresponds to a $\nu(COO^-)$ vibration. The hydrated cobalt complex shows a strong broad adsorption band in the region 3610–3220 cm^{-1}, ν(O–H) indicating the presence of water of crystallisation. The complexes show an absorption band at around 1667 cm^{-1} due to the stretching vibration of the carboxylate group linked to metal ions [5]. Metal–chloride and metal–oxygen bands are reported for the anhydrous complexes. The metal–chloride bands indicate that the cobalt complex has a tetrahedral structure while the nickel and copper complexes have octahedral structures [1,2].

Single crystals of the compounds could not be isolated from ethanolic solution; thus without X-ray analysis no definite structures can be described. However, the spectroscopic and magnetic data enable us to predict possible

TABLE 3

Infrared spectra (4000–200 cm^{-1}) [a]

Compound	ν_s(N–H)	ν(C=O)	ν(M–Cl)	ν(M–O)
$C_{11}H_{15}NO_2$	3396(S), 3359(S)	1658(S)	–	–
$Co(C_{11}H_{15}NO_2)_2Cl_2$	3396(S), 3359(S)	1666(S)	310(S)	390(M)
$Ni(C_{11}H_{15}NO_2)_2Cl_2$	3397(S), 3360(S)	1668(S)	236(S)	291(M)
$Cu(C_{11}H_{15}NO_2)Cl_2$	3395(S), 3361(S)	1668(S)	232(M)	292(M)

[a] S, strong; M, medium.

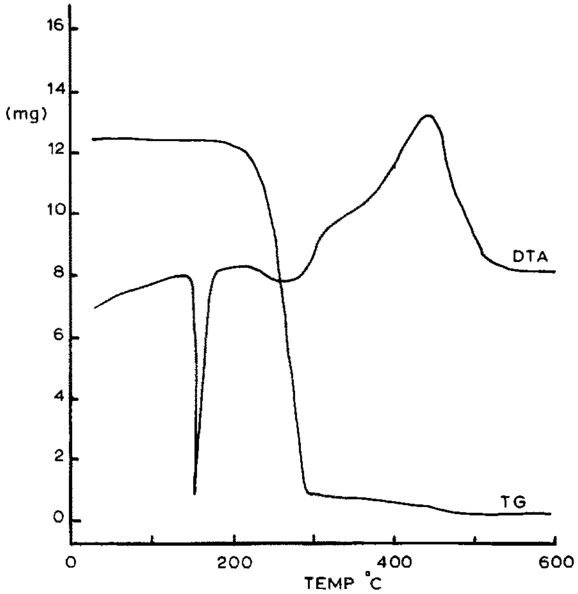


Fig. 1. TG and DTA trace for 4-(butylamino) benzoic acid. Sample mass, 12.40 mg.

structures. The poor solubility of the nickel and copper compounds in both polar and non-polar solvents indicates that they have polymeric structures [1]. It is thus suggested that the nickel complex is a chain of nickel atoms bonded to chloride ions with the 4-(butylamino) benzoic acid molecules

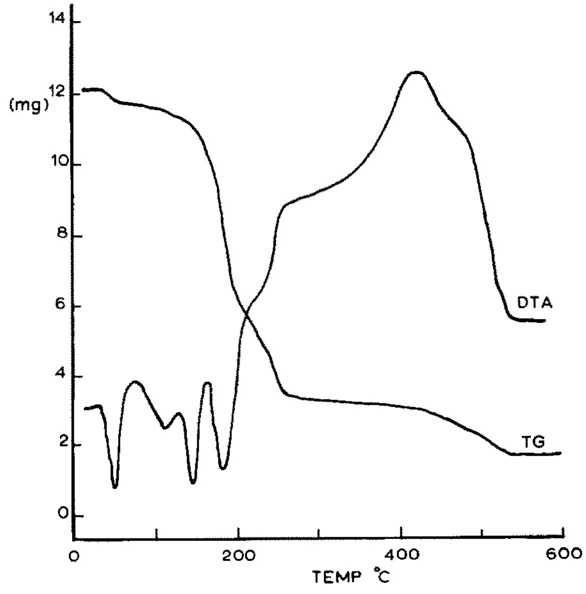


Fig. 2. TG and DTA trace for $Co(C_{11}H_{15}NO_2)_2Cl_2H_2O$. Sample mass, 12.20 mg.

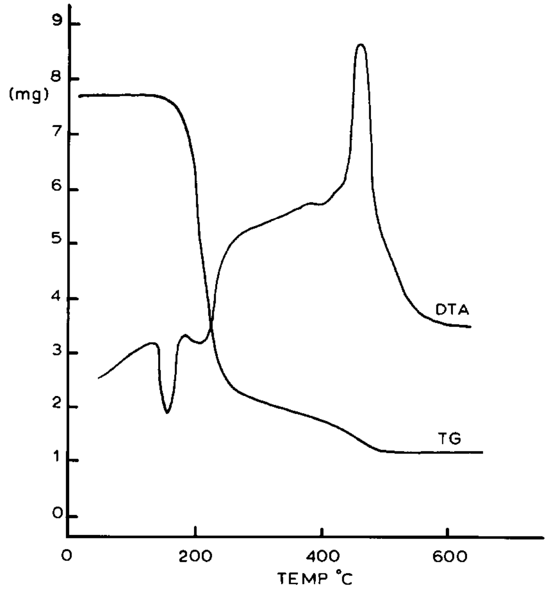


Fig. 3. TG and DTA trace for $Ni(C_{11}H_{15}NO_2)_2Cl_2$. Sample mass, 7.66 mg.

above and below the plane of the metal–chloride chain and bonded to the nickel ions by an oxygen atom of the carboxylate group. The copper compound is considered to have a double chain of copper atoms bonded to chloride ions and the 4-(butylamino) benzoic acid molecules attached in a

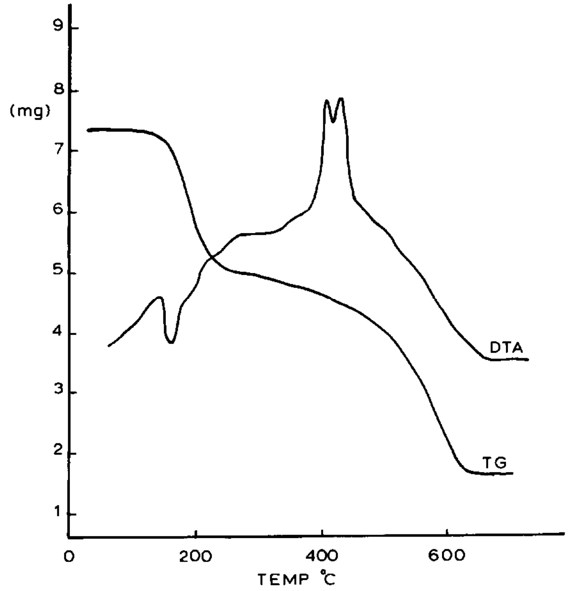


Fig. 4. TG and DTA trace for $Cu(C_{11}H_{15}NO_2)Cl_2$. Sample mass, 7.37 mg.

TABLE 4

Dehydration processes of the metal complexes

Process	Peak temp. (°C)	Thermal nature of transformation	Mass loss (%)		Enthalpy (kJ mol^{-1})
			Calc.	Found	
$Co(C_{11}H_{15}NO_2)_2Cl_2H_2O \rightarrow Co(C_{11}H_{15}NO_2)_2$	48	Endo	3.20	3.26	36

similar way to the nickel complex. The cobalt compound has a tetrahedral structure with two chloride ions and two 4-(butylamino) benzoic acid molecules bonded to the cobalt atom.

The TG and DTA traces for the 4-(butylamino) benzoic acid, (Fig. 1) show that it is thermally stable in the temperature range 20–174°C. Its pyrolytic decomposition starts at 174°C and finishes at 486°C with the total elimination of the sample. The DTA trace of the 4-(butylamino) benzoic acid (Fig. 1), shows an endothermic peak at 152°C corresponding to fusion. The value of the fusion enthalpy is 29 kJ mol^{-1}. Liquid 4-(butylamino) benzoic acid decomposes immediately with an exothermic peak at 442°C. The TG and DTA traces for the compounds formed between 4-(butylamino) benzoic acid and cobalt, nickel and copper are given in Figs. 2–4. The dehydration of the cobalt compound takes place in one step. The observed mass loss for this process compares favourably with the theoretical value given in Table 4. The expected endothermic peak for the dehydration process associated with this compound is observed in the DTA trace. The dehydration enthalpy has been calculated and is listed in Table 4. The anhydrous nickel and copper compounds decompose with loss of the organic ligand and chlorine to give the corresponding metal oxide (Table 5). The residual masses of these compounds are in good agreement with the values required for their metallic oxides. In the DTA traces, these decomposition

TABLE 5

Decomposition processes of 4-(butylamino) benzoic acid and its metal complexes

Process	Temp. range (°C)	Thermal nature of transformation	Residue (%)	
			Calc.	Found
$C_{11}H_{15}NO_2 \rightarrow$ pyrolytic process	174–486	Exo	–	–
$Co(C_{11}H_{15}NO_2)_2Cl_2 \rightarrow Co_3O_4$	108–538	Endo/exo	14.29	14.19
$Ni(C_{11}H_{15}NO_2)_2Cl_2 \rightarrow NiO$	160–502	Endo/exo	14.47	14.32
$Cu(C_{11}H_{15}NO_2)Cl_2 \rightarrow CuO$	126–634	Endo/exo	24.26	23.86

processes correspond to endothermic and exothermic effects for the compounds.

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