Thermochimica Acta, 214 (1993) 243–248
Elsevier Science Publishers B.V., Amsterdam

Preparation, structural characterisation and thermal analysis studies of complexes of cobalt, nickel and copper with nonylamine

J.R. Allan, P.C. Beaumont, G.H.W. Milburn and I. Wood

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

(Received 8 September 1992)

Abstract

Compounds of nonylamine with the chlorides of cobalt, nickel and copper and with the thiocyanate of cobalt, have been prepared in ethanolic solution. The compounds, which have been characterised by analyses, magnetic moments, vibrational and electronic spectra, show that for the cobalt compounds the cobalt ions are in a tetrahedral environment, whereas for the nickel and copper compounds the metal ions are in an octahedral environment. The thermal behaviour of these compounds has been studied by thermogravimetry and differential thermal analysis. The chloro compounds form intermediate compounds during the decomposition process.

INTRODUCTION

Amines are used as catalysts in the polymer industry. The study of the thermal stability of amines and their co-ordination compounds is thus an important area of research. This paper reports the thermal analysis studies of the metal complexes formed by the primary amine nonylamine, $CH_3(CH_2)_8NH_2$, 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 to the metal ion.

EXPERIMENTAL

Preparation of the metal complexes

The metal salt (0.05 mol) was dissolved in a minimum of boiling ethanol. To the boiling ethanol solution was added dropwise with stirring, a solution of nonylamine in ethanol (50:50) until precipitation appeared to be

---

Correspondence to: J.R. Allan, Department of Applied Chemical and Physical Sciences, Napier University, Edinburgh, UK.

complete. The precipitated product was isolated by filtration, washed with a minimum of ethanol and then air dried.

Apparatus and measurements

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

The IR spectra were recorded using KBr discs over the wavenumber range 4000–600 cm^{-1} and polyethylene discs over the wavenumber range 600–200 cm^{-1} on a Perkin-Elmer spectrophotometer model 598. The electronic spectra were recorded as solid diffuse reflectance spectra using a Beckmann Acta MIV spectrophotometer. Measurements of magnetic moments were made using the Gouy method with $HgCo(SCN)_4$ as calibrant.

The thermal analysis measurements were made on a Stanton-Redcroft Model 1500 thermobalance. Thermogravimetry (TG) and differential thermal analysis (DTA) traces were obtained at a heating rate of 6°C min^{-1} in air. The 20–800°C temperature range was studied in all cases. Intermediate compounds were isolated for each of the chloro complexes.

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.

TABLE 1

Analyses (%) of the initial and intermediate compounds

Compound		M	C	N	H
$Co(C_9H_{21}N)_2(NCS)_2$ [a]	Theory	12.76	52.03	12.13	9.17
	Found	12.06	51.23	11.53	8.66
$Co(C_9H_{21}N)_2Cl_2$ [a]	Theory	14.15	51.92	6.72	10.16
	Found	13.44	50.96	6.35	9.57
$Co(C_9H_{21}N)Cl_2$ [b]	Theory	21.57	39.58	5.12	7.75
	Found	20.68	38.88	4.47	7.41
$Ni(C_9H_{21}N)_2Cl_2$ [a]	Theory	14.10	51.95	6.73	10.17
	Found	13.39	51.07	6.29	9.66
$Ni(C_9H_{21}N)Cl_2$ [b]	Theory	21.50	39.61	5.13	7.75
	Found	20.72	38.42	4.62	7.19
$Cu(C_9H_{21}N)_2Cl_2$ [a]	Theory	15.99	51.34	6.65	10.05
	Found	14.43	50.64	6.19	9.61
$Cu(C_9H_{21}N)Cl_2$ [b]	Theory	22.87	38.92	5.04	7.62
	Found	21.81	37.87	4.73	7.22

[a] Initial compound isolated from ethanolic solution. [b] Intermediate compound produced by heating the corresponding initial compound.

TABLE 2

Electronic spectra and magnetic moments

Compound	Colour	Band position (cm^{-1})	d-d transition	μ (BM)
$Co(C_9H_{21}N)_2(NCS)_2$	Dark green	4680 15880	$^4A_2(F) \rightarrow {}^4T_1(F)$ $^4A_2(F) \rightarrow {}^4T_1(P)$	4.30
$Co(C_9H_{21}N)_2Cl_2$	Dark blue	4642 14092	$^4A_2(F) \rightarrow {}^4T_1(F)$ $^4A_2(F) \rightarrow {}^4T_1(P)$	4.58
$Ni(C_9H_{21}N)_2Cl_2$	Yellow	8006 13790 23800	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	3.80
$Cu(C_9H_{21}N)_2Cl_2$	Green	12509	$^2E_g(D) \rightarrow {}^2T_{2g}(D)$	1.83

The position of the bands in the electronic spectra and the magnetic moments listed in Table 2 for the cobalt and nickel compounds would suggest that the cobalt ions are in a tetrahedral environment in each of the compounds, $Co(C_9H_{21}N)_2(NCS)_2$ and $Co(C_9H_{21}N)_2Cl_2$, whereas in the compound $Ni(C_9H_{21}N)_2Cl_2$, the nickel ions are in an octahedral environment [1, 2]. A single broad absorption band in the electronic absorption spectrum of the copper compound indicates that the copper ions are in an octahedral environment [2]. The magnetic moment for this compound is higher than the spin-only value of 1.73 BM and shows the absence of copper–copper magnetic interaction.

The wavenumbers of the IR absorption bands as well as their descriptions and assignments are given in Table 3 for the complexes isolated from ethanolic solution. The IR spectrum of nonylamine is almost identical to those of its metal complexes in the 4000–625 cm^{-1} region except for bands due to the $\nu(NH_2)$ vibrations which move to lower wavenumber in the metal complexes. This would suggest that coordination is taking place between the metal and the nitrogen atom of the amine group [3]. In the compound $Co(C_9H_{21}N)_2(NCS)_2$, bands at 2100 and 828 cm^{-1} for the $\nu(NCS)$ vibration show that bonding takes place to the metal through the

TABLE 3

Infrared spectra (4000–200 cm^{-1})

Compound	$\nu(NH_2)$	$\nu(NCS)$	$\nu(M-Cl)$	$\nu(M-N)$
$C_9H_{21}N$	3368(s), 3292(s)	–	–	–
$Co(C_9H_{21}N)_2(NCS)_2$	3346(s), 3220(s)	2100(s), 828(s)	–	432(s), 307(s)
$Co(C_9H_{21}N)_2Cl_2$	3350(s), 3140(s)	–	305(s)	425(s)
$Ni(C_9H_{21}N)_2Cl_2$	3360(s), 3202(s)	–	260(m)	430(s)
$Cu(C_9H_{21}N)_2Cl_2$	3336(s), 3158(s)	–	280(m)	446(m)

Key: s, strong; m, medium.

TABLE 4

Thermal decomposition products

Starting material	Decomp. temp. (°C)	Product	Weight loss (%)	
			Calc.	Found
$Co(C_9H_{21}N)_2(NCS)_2$	137 (endo)	$Co(NCS)_2$	62.1	62.5
	420 (exo)	Co_3O_4	19.4	19.3
$Co(C_9H_{21}N)_2Cl_2$	72 (endo)	$Co(C_9H_{21}N)Cl_2$	34.4	35.0
	398 (endo)	$CoCl_2$	34.4	34.8
	518 (exo)	Co_3O_4	11.9	10.8
$Ni(C_9H_{21}N)_2Cl_2$	139 (endo)	$Ni(C_9H_{21}N)Cl_2$	34.4	34.4
	252 (endo)	$NiCl_2$	34.4	33.8
	410 (exo)	NiO	13.2	11.8
$Cu(C_9H_{21}N)_2Cl_2$	105 (endo)	$Cu(C_9H_{21}N)Cl_2$	34.0	33.2
	278 (endo)	$CuCl_2$	34.0	33.6
	520 (exo)	CuO	13.1	13.4

nitrogen atom of the NCS group [4]. Metal–nitrogen and metal–halogen bands are also assigned in Table 3 for the metal complexes.

The fact that the compounds were isolated from solution as powders means that no complete structure determination could be made. However, spectroscopic and magnetic data enable us to predict that for the cobalt compounds, the cobalt ion is in a tetrahedral environment. In the chloro compound, the cobalt ion is bonded to the nitrogen of the amine group of two molecules of nonylamine and to two chloride ions. In the isothiocyanate compound, a similar structure is proposed with the NCS ions replacing the chloride ions. The poor solubility of the nickel and copper complexes in polar and non-polar solvents would suggest that they have polymeric structures [2]. It is thus postulated that the structure of these compounds is

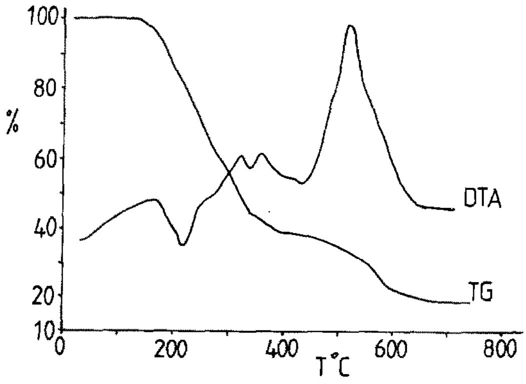

Fig. 1. TG and DTA trace for $Co(C_9H_{21}N)_2(NCS)_2$; sample weight, 10.15 mg.

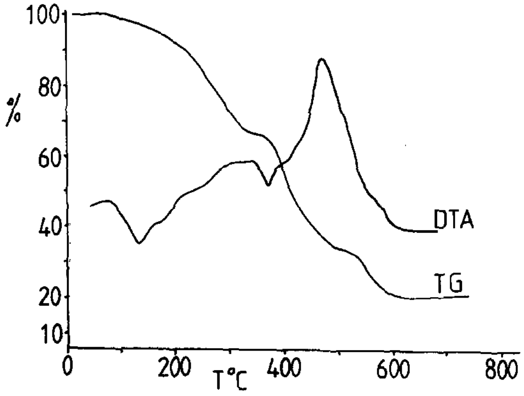

Fig. 2. TG and DTA trace for $Co(C_9H_{21}N)_2Cl_2$; sample weight, 9.17 mg.

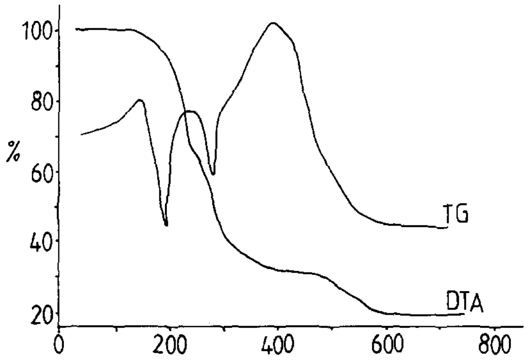

Fig. 3. TG and DTA trace for $Ni(C_9H_{21}N)_2Cl_2$; sample weight, 8.89 mg.

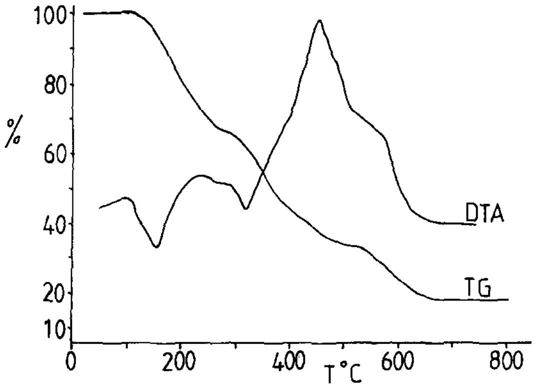

Fig. 4. TG and DTA trace for $Cu(C_9H_{21}N)_2Cl_2$; sample weight, 9.14 mg.

a chain of metal ions bonded to halogens with the nonylamine molecules above and below the plane of the metal–halogen chain.

The results of the TG and DTA studies are given in Figs. 1–4 and Table 4. Figure 1 shows that the compound $Co(C_9H_{21}N)_2(NCS)_2$ undergoes an endothermic reaction with loss of two molecules of nonylamine to give $Co(NCS)_2$, followed by an exothermic reaction to give Co_3O_4. In Figs. 2–4, the TG and DTA traces for $Co(C_9H_{21}N)_2Cl_2$, $Ni(C_9H_{21}N)_2Cl_2$ and $Cu(C_9H_{21}N)_2Cl_2$ are shown. In each case the compounds first undergo an endothermic reaction with loss of one molecule of nonylamine. This is followed by a further endothermic reaction and loss of the other nonylamine molecule to give the metal halide in each case. The metal halides then undergo an exothermic reaction to give metal oxide.

In summary, the decomposition schemes are

$$Co(C_9H_{21}N)_2(NCS)_2 \xrightarrow{\text{endo}} Co(NCS)_2 \xrightarrow{\text{exo}} Co_3O_4$$

$$Co(C_9H_{21}N)_2Cl_2 \xrightarrow{\text{endo}} Co(C_9H_{21}N)Cl_2 \xrightarrow{\text{exo}} CoCl_2 \xrightarrow{\text{exo}} Co_3O_4$$

$$Ni(C_9H_{21}N)_2Cl_2 \xrightarrow{\text{endo}} Ni(C_9H_{21}N)Cl_2 \xrightarrow{\text{exo}} NiCl_2 \xrightarrow{\text{exo}} NiO$$

$$Cu(C_9H_{21}N)_2Cl_2 \xrightarrow{\text{endo}} Cu(C_9H_{21}N)Cl_2 \xrightarrow{\text{exo}} CuCl_2 \xrightarrow{\text{exo}} CuO$$

The observed weight losses for these processes compare favourably with the theoretical values (Table 4).

REFERENCES

1 J.R. Allan and G.M. Baillie, J. Therm. Anal., 14 (1978) 291.
2 J.R. Allan, N.D. Baird and A.L. Kassyk, J. Therm. Anal., 16 (1979) 79.
3 J.R. Allan, B.R. Carson, D.L. Gerrard and S. Hoey, Thermochim. Acta, 153 (1989) 173.
4 S.M. Nelson and T.M. Shepherd, J. Inorg. Nucl. Chem., 27 (1965) 2123.