Thermochimica Acta, 219 (1993) 159–165
Elsevier Science Publishers B.V., Amsterdam

Structural and thermal studies of the chloro complexes of cobalt, nickel and copper with 1,6-hexanediamine

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(Received 5 November 1992)

Abstract

The preparation and thermal analysis studies of the compounds produced by the reaction of 1,6-hexanediamine with the chlorides of cobalt, nickel and copper in ethanolic solution are reported. Spectral and magnetic studies show that the cobalt and nickel compounds have octahedral structures, whereas the copper compound has a tetragonal structure. The thermal analysis studies of the cobalt, nickel and copper compounds show that one or more intermediate compounds are formed in each case before the metal halide and metal oxide are produced.

INTRODUCTION

The compound 1,6-hexanediamine ($H_2N(CH_2)_6NH_2$) is a primary amine with one type of donor site for bonding to metal ions: the nitrogen atoms of the amine groups. This paper reports the thermal analysis studies of 1,6-hexanediamine and of the complexes formed by the amine with 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 metal complexes

The metal halide (0.05 mol) was dissolved in a minimum of boiling ethanol to which solution was added 0.1 mol of 1,6-hexanediamine with stirring. The resulting solution was heated for a few minutes and then concentrated on a steam bath. The precipitated product was then isolated by filtration, washed with warm ethanol and air-dried.

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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 KBr discs (4000–600 cm^{-1}) and polyethylene discs (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 $Hg[(Co(SCN)_4]$ 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 complexes were isolated for each of the chloro complexes of cobalt, nickel and copper.

RESULTS AND DISCUSSION

The analytical results for the metal complexes are given in Table 1. The elemental analyses agree with the formulae proposed for the metal complexes which are also given in Table 1.

The electronic spectra and magnetic moments, both given in Table 2, would suggest that for the cobalt and nickel complexes, the metal ions are in a octahedral environment [1]. The broad absorption band in the copper compound at 17 390 cm^{-1} is characteristic of compounds having a tetragonal structure [2]. The broadness of the band is due to the Jahn Teller distortion which results from an odd number of electrons in the $d_{x^2-y^2}$ orbital [3]. This band is considered to be a composite band involving transitions from the d_{xy}, d_{yz} and d_{xz} orbitals to the $d_{x^2-y^2}$ orbital. The magnetic moment for this compound is higher than the spin-only value of 1.73 BM, indicating the absence of magnetic copper–copper interaction in the compound.

Table 3 lists the main bands in the IR spectra together with their descriptions and assignments. The IR spectrum of 1,6-hexanediamine is very similar to those of its metal complexes in the 4000–625 cm^{-1} region, except that the bands due the NH_2 vibrations are shifted to lower wavenumbers on formation of the complexes. This suggests that the nitrogen atom in each of the amine groups is coordinated to the metal ions [3]. Further evidence for the octahedral structures of the cobalt and nickel compounds and the tetragonal structure of the copper compound is obtained from the ν(M–Cl) vibrations [1, 4].

The fact that the compounds were isolated from solution as powders and

TABLE 1

Analyses (%) of metal complexes

Compound		M	C	N	H
$Co(C_6H_{16}N_2)_2Cl_2$ [a]	Theory	15.83	38.71	15.05	8.66
	Found	16.02	38.96	15.35	8.92
$Co_3(C_6H_{16}N_2)_5Cl_6$ [b]	Theory	18.21	37.12	14.42	8.29
	Found	17.69	36.86	14.03	7.89
$Co(C_6H_{16}N_2)Cl_2$ [b]	Theory	23.95	29.29	11.38	6.55
	Found	22.66	28.49	10.53	6.01
$Ni(C_6H_{16}N_2)_2Cl$ [a]	Theory	15.77	38.74	15.06	8.66
	Found	15.32	38.63	15.41	8.30
$Ni(C_6H_{16}N_2)Cl_2$ [b]	Theory	23.87	29.31	11.39	6.55
	Found	23.66	29.03	11.04	6.17
$Cu(C_6H_{16}N_2)_2Cl_2$ [a]	Theory	17.36	39.39	15.31	8.81
	Found	17.01	38.96	14.66	8.47
$Cu_2(C_6H_{16}N_2)_3Cl_4$ [b]	Theory	20.57	35.00	13.60	7.82
	Found	19.84	34.77	13.29	7.60
$Cu_2(C_6H_{16}N_2)Cl_4$ [b]	Theory	33.00	18.71	7.27	4.18
	Found	32.72	18.39	6.85	3.94

[a] Initial compound isolated from ethanolic solution.

[b] Intermediate compound produced by heating the initial compound to a fixed temperature determined from the TG trace.

TABLE 2

Electronic spectra and magnetic moments

Compound	Colour	Band position/ cm^{-1}	d–d Transition	μ/BM
$Co(C_6H_{16}N_2)_2Cl_2$	Pink	8475	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	5.01
		18691	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$	
		27700 (sh)	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	
$Ni(C_6H_{16}N_2)_2Cl_2$	Blue	10638	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	3.07
		16393	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	
		26395	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	
$Cu(C_6H_{16}N_2)_2Cl_2$	Purple	17390	$^2B_1 \rightarrow {}^2A_1$	1.77

Key: sh, shoulder.

TABLE 3

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

Compound	$\nu(NH_2)$		ν(M-Cl)	ν(M-N)
$C_6H_{16}N_2$	3316(s)	3300(s)	–	–
$Co(C_6H_{16}N_2)Cl_2$	3218(s)	3270(s)	276(m)	222(w)
$Ni(C_6H_{16}N_2)Cl_2$	3218(s)	3270(s)	281(m)	230(w)
$Cu(C_6H_{16}N_2)Cl_2$	3200(s)	3110(s)	279(m)	227(w)

Key: s, strong; m, medium; w, weak.

not as single crystals meant that no complete structure determination could be made. However, spectroscopic and magnetic data enable us to postulate structures. As previously concluded, the metal ions in the cobalt and nickel compounds are in an octahedral environment. This is formed by a planar arrangement of two molecules of 1,6-hexanediamine. The four nitrogen atoms thus lie in a plane around the metal ion, which also has chloride ions above and below, completing the octahedral structure. The copper compound has a distorted planar structure of nitrogen atoms (from two molecules of 1,6-hexanediamine) bonded to the copper atom, which has trans bonds to the chloride ions to complete the tetragonal structure.

The TG and DTA traces for 1,6-hexanediamine and its chloro complexes with cobalt, nickel and copper are shown in Figs. 1–4 and the thermal decomposition products are summarised in Table 4.

The TG and DTA trace for 1,6-hexanediamine, see Fig. 1, shows that the pyrolitic decomposition starts at 49°C and finishes at 182°C with the total elimination of the sample. The DTA trace, Fig. 1, shows that this

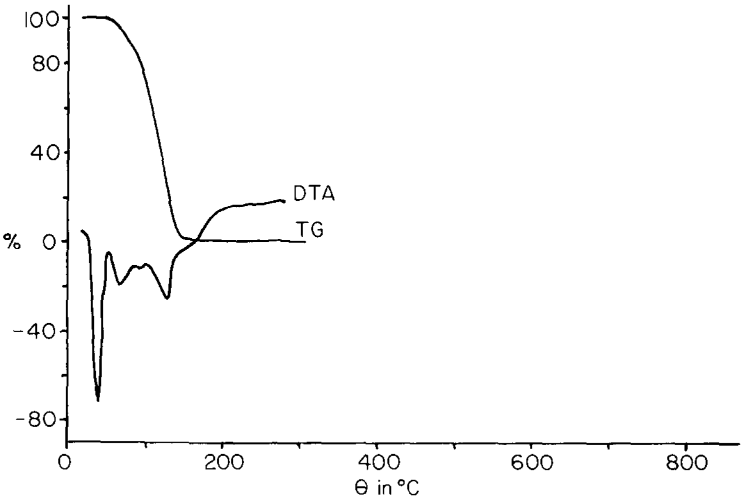

Fig. 1. TG and DTA trace for 1,6-hexanediamine. Sample weight 8.85 mg.

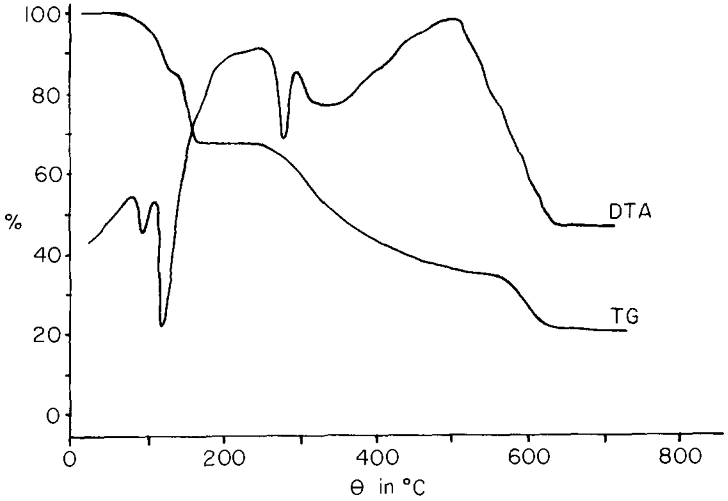

Fig. 2. TG and DTA trace for $Co(C_6H_{12}N_2)_2Cl_2$. Sample weight 11.99 mg.

compound has an endothermic peak at 44°C corresponding to fusion, followed by other endothermic peaks which correspond to the decomposition of the compound.

The TG and DTA traces for the metal complexes are shown in Figs. 2–4. Figure 2 shows that the pink cobalt complex, $Co(C_6H_{16}N_2)_2Cl_2$, undergoes endothermic reactions to give first a blue complex, $Co_3(C_6H_{16}N_2)_5Cl_6$, and then a green complex, $Co(C_6H_{16}N_2)Cl_2$. This is followed by a further endothermic reaction to give cobalt chloride and then an exothermic reaction to give Co_3O_4.

Figure 3 shows that the blue nickel complex, $Ni(C_6H_{16}N_2)_2Cl_2$, undergoes

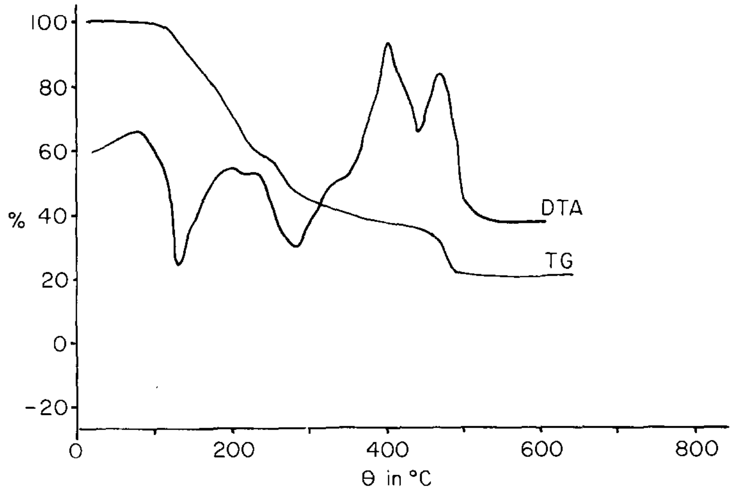

Fig. 3. TG and DTA trace for $Ni(C_6H_{12}N_2)_2Cl_2$. Sample weight 8.63 mg.

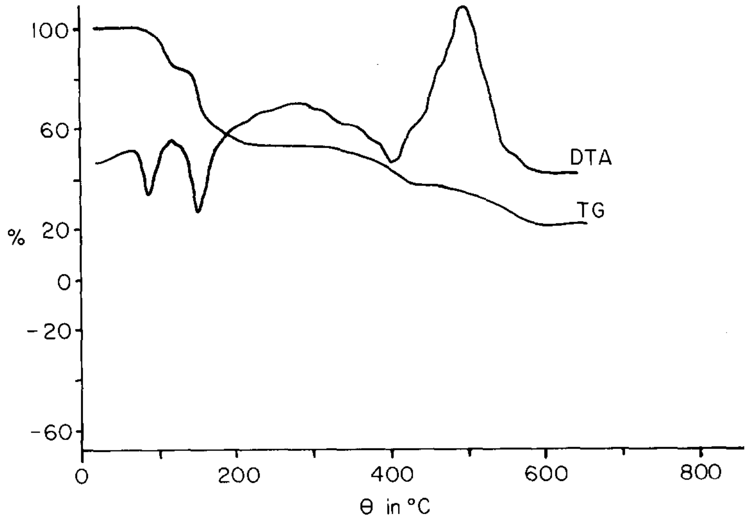

Fig. 4. TG and DTA trace for $Cu(C_6H_{12}N_2)_2Cl_2$. Sample weight 5.81 mg.

an endothermic reaction to give a green complex, $Ni(C_6H_{16}N_2)Cl_2$. A subsequent endothermic reaction then takes place, followed by exothermic reactions to give nickel chloride and NiO respectively. Figure 4 shows that the purple complex $Cu(C_6H_{16}N_2)_2Cl_2$ decomposes by means of endothermic reactions to give a blue complex, $Cu_2(C_6H_{16}N_2)_3Cl_4$, and then a green complex, $Cu_2(C_6H_{16}N_2)Cl_4$. A further endothermic reaction then takes place, followed by an exothermic reaction to give copper chloride

TABLE 4

Thermal decomposition products

Starting material	Decomp. temp./°C	Resulting compound	Weight loss/%	
			Calc.	Found
$Co(C_6H_{16}N_2)_2Cl_2$	76(endo)	$Co_3(C_6H_{16}N_2)_5Cl_6$	10.4	10.6
	132(endo)	$Co(C_6H_{16}N_2)Cl_2$	20.8	21.3
	248(endo)	$CoCl_2$	31.2	31.6
	520(exo)	Co_3O_4	16.0	15.0
$Ni(C_6H_{16}N_2)_2Cl_2$	89(endo)	$Ni(C_6H_{16}N_2)Cl_2$	31.2	31.2
	241(endo)	$NiCl_2$	31.2	31.1
	412(exo)	NiO	17.5	17.0
$Cu(C_6H_{16}N_2)_2Cl_2$	85(endo)	$Cu_2(C_6H_{16}N_2)_3Cl_4$	15.8	15.7
	139(endo)	$Cu_2(C_6H_{16}N_2)Cl_4$	31.8	31.7
	310(endo)	$CuCl_2$	15.8	15.7
	453(exo)	CuO	14.9	15.6

Key: endo, endothermic; exo, exothermic (from DTA trace).

and CuO respectively. The stoichiometry of the residues of the pyrolytic decomposition of the metal complexes was established by metal analysis of the residues.

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