

THERMAL, SPECTRAL AND MAGNETIC STUDIES ON THE CHLORO COMPOUNDS OF SOME FIRST-ROW TRANSITION METALS WITH TRIETHYLENEDIAMINE

J.R. ALLAN, G.H.W. MILBURN and F. RICHMOND

*Department of Applied Chemical and Physical Sciences, Napier Polytechnic,
Edinburgh (Gt. Britain)*

A.S. WILSON

British Petroleum (Chemicals) Ltd, Penarth, South Glamorgan, Wales (Gt. Britain)

D.L. GERRARD and J. BIRNIE

British Petroleum Research Centre, Sunbury, Middlesex (Gt. Britain)

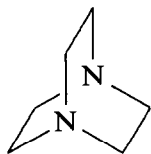
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ABSTRACT

Compounds of triethylenediamine with the chlorides of manganese, iron, cobalt, nickel and copper have been prepared in ethanolic solution. The compounds, which have been characterised by analyses, magnetic moments, and vibrational and electronic spectra, show that for the iron and cobalt compounds the metal ions are in a tetrahedral environment, whereas for the manganese, 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 iron, cobalt, nickel and copper compounds which are hydrated lose water, followed by organic ligand and halogen, to give the metal oxide. The manganese compound loses the organic ligand and halogen to form an oxide of manganese.

INTRODUCTION

Tertiary amines are used as catalysts in the commercial production of polyurethane foam. The study of the thermal stability of tertiary amines is thus an important area of research. This paper reports thermal analysis studies of the tertiary amine triethylenediamine (shown below) and of the metal complexes formed by the amine and the transition metals manganese, iron, cobalt, nickel and copper.



Triethylenediamine (C₆H₁₂N₂)

Spectral and magnetic studies were used to characterise each metal complex and to interpret the type of coordination to the metal ion. A thermal stability study of the triethylenediamine complexes is reported.

EXPERIMENTAL

Preparation of compounds

(A) A saturated ethanolic solution of triethylenediamine was added to a warm ethanolic solution of the hydrated metal halide; the precipitate formed was washed with ethanol and air dried.

(B) This method was similar to (A) except that the preparation was carried out under dry nitrogen.

Apparatus

The concentration of metal ion was determined using a Perkin-Elmer 373 atomic absorption spectrophotometer. The carbon, hydrogen and nitrogen analyses were obtained 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 IR spectrophotometer model 598. The electronic spectra were recorded as solid diffuse reflectance spectra using a Beckman Acta MIV spectrophotometer. Measurements of the magnetic moments were made using the Gouy method, with $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrant. The thermal analysis measurements were made on a Stanton Redcroft model STA 781 thermobalance. Thermogravimetry (TG) and differential thermal analysis (DTA) curves were obtained at a heating rate of 6 $^{\circ}\text{C min}^{-1}$ in static air. The 20–800 $^{\circ}\text{C}$ temperature range was studied in all cases.

RESULTS AND DISCUSSION

The compounds which have been prepared are listed in Table 1. The elemental analyses agree with the given formulae of the compounds. Water molecules are present in all of the compounds except for the manganese compound, which is anhydrous.

The wavenumbers of the IR absorption bands for the metal complexes are given in Table 2, together with the descriptions and assignments. The bands in the region 3650–3150 cm^{-1} are assigned to the $\nu(\text{O-H})$ vibration of water. A comparison of the bands of the metal complexes with those of the triethylenediamine shows that the spectra are similar in the 2000–650 cm^{-1} region except for the bands associated with the $\nu_{\text{N-C}}$ vibrations, which move

TABLE I

Analyses and magnetic moments of the compounds

Compound	Method of preparation	Theory (%)			Found (%)			μ (B.M.)
		Metal	Carbon	Nitrogen	Metal	Carbon	Nitrogen	
Mn(C ₆ H ₁₂ N ₂)Cl ₂	A	23.08	30.27	11.76	22.69	29.64	11.07	5.92
Fe(C ₆ H ₁₂ N ₂)Cl ₂ ·0.5H ₂ O	B	22.59	29.16	11.33	22.26	28.76	11.09	5.12
Co(C ₆ H ₁₂ N ₂)Cl ₂ ·0.5H ₂ O	A	23.47	28.70	11.15	23.30	28.56	11.04	4.41
Ni(C ₆ H ₁₂ N ₂)Cl ₂ ·H ₂ O	A	22.59	27.73	10.78	22.02	26.94	10.49	3.17
Cu(C ₆ H ₁₂ N ₂)Cl ₂ ·H ₂ O	A	24.00	27.22	10.58	23.46	26.71	10.33	1.41

TABLE 2

IR spectra (4000–200 cm^{-1})

Compound	$\nu_{\text{O-H}}(\text{H}_2\text{O})$	$\nu_{\text{N-C}}$	$\nu_{\text{M-Cl}}$	$\nu_{\text{M-N}}$
$\text{C}_6\text{H}_{12}\text{N}_2$	—	1155(w)	—	—
$\text{Mn}(\text{C}_6\text{H}_{12}\text{N}_2)\text{Cl}_2$	—	1168(w)	226(w)	270(m)
$\text{Fe}(\text{C}_6\text{H}_{12}\text{N}_2)\text{Cl}_2 \cdot 0.5\text{H}_2\text{O}$	3630–3240 s, br	1165(w)	320(s) 310(s)	280(m)
$\text{Co}(\text{C}_6\text{H}_{12}\text{N}_2)\text{Cl}_2 \cdot 0.5\text{H}_2\text{O}$	3640–3300 s, br	1170(w)	327(s) 318(s)	278(m)
$\text{Ni}(\text{C}_6\text{H}_{12}\text{N}_2)\text{Cl}_2 \cdot \text{H}_2\text{O}$	3640–3180 s, br	1169(w)	238(w)	260(m)
$\text{Cu}(\text{C}_6\text{H}_{12}\text{N}_2)\text{Cl}_2 \cdot \text{H}_2\text{O}$	3650–3220 s, br	1165(w)	232(w)	276(m)

br = Broad; s = strong; m = medium; w = weak.

to higher wavenumbers in the metal complexes. This suggests that in the complexes bonding is taking place between the metal ions and the nitrogen atoms of the triethylenediamine. In the 650–200 cm^{-1} region $\nu(\text{M-Cl})$ and $\nu(\text{M-N})$ bands have been identified for each of the compounds, and are listed in Table 2. They suggest an octahedral environment for the metal ion in the manganese, nickel and copper compounds [1] and a tetrahedral environment for the metal ions in the iron and cobalt compounds [2,3].

In the electronic spectrum of the manganese compound, no bands caused by $d-d$ transitions were observed. The compound has a magnetic moment of 5.92 B.M. The electronic spectra (Table 3) and the magnetic measurement (Table 1) for the nickel compound support the suggestion of an octahedral environment for the nickel ion [1]. From the measured magnetic moments (Table 1) and the electronic spectra (Table 3) there is further evidence that the metal ions in the iron and cobalt compounds are in a tetrahedral environment [3,4]. The broad absorption band observed in the electronic spectra of the copper compound between 10 000 and 15 000 cm^{-1} is a further indication of the copper ions being in an octahedral environment [1]. The magnetic moment for the compound is lower than the spin-only value, which indicates strong copper–copper magnetic interaction.

TABLE 3

Electronic spectra (cm^{-1})

Compound	Colour	Peak position	d–d Transition
$\text{Mn}(\text{C}_6\text{H}_{12}\text{N}_2)\text{Cl}_2$	White	—	—
$\text{Fe}(\text{C}_6\text{H}_{12}\text{N}_2)\text{Cl}_2 \cdot 0.5\text{H}_2\text{O}$	Brown	4761	${}^5\text{E}(\text{D}) \rightarrow {}^5\text{T}_2(\text{D})$
$\text{Co}(\text{C}_6\text{H}_{12}\text{N}_2)\text{Cl}_2 \cdot 0.5\text{H}_2\text{O}$	Blue	6493	${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{F})$
		15625	${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$
$\text{Ni}(\text{C}_6\text{H}_{12}\text{N}_2)\text{Cl}_2 \cdot \text{H}_2\text{O}$	Green	10526	${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$
		17391	${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$
		20833	${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$
$\text{Cu}(\text{C}_6\text{H}_{12}\text{N}_2) \cdot \text{H}_2\text{O}$	Brown	11049	${}^2\text{E}_g(\text{D}) \rightarrow {}^2\text{T}_{2g}(\text{D})$

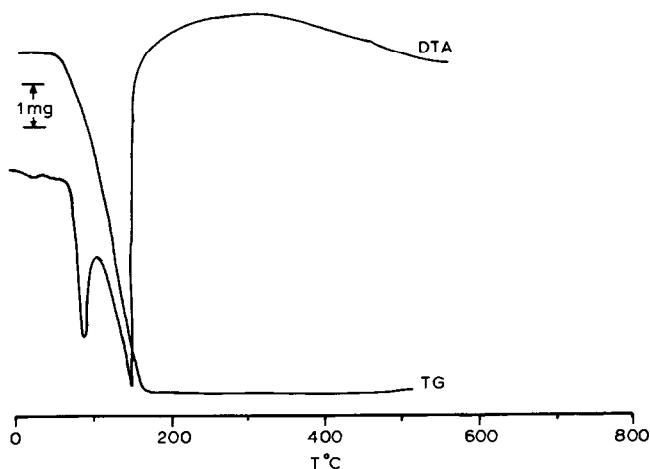


Fig. 1. TG and DTA curves for triethylenediamine. Sample weight = 16.60 mg.

The fact that no suitable single crystals could be obtained from solution for each of the compounds means that no complete structure determination can be made. However, spectroscopic and magnetic data allow possible structures to be postulated. The poor solubility of the manganese, nickel and copper compounds in polar and non-polar solvents indicates that they have polymeric structures [1]. It is suggested that the structure of these compounds consists of parallel chains of metal atoms bonded to halogens with the triethylenediamine molecules acting as bridging units between adjacent chains, this forms a sheet structure which gives a six-coordinate environment for each of the metal ions. In the iron and cobalt compounds it is postulated that the triethylenediamine molecules act as bridging ligands between metal ions. Two terminal chloride ions complete the tetrahedral arrangement around each metal ion.

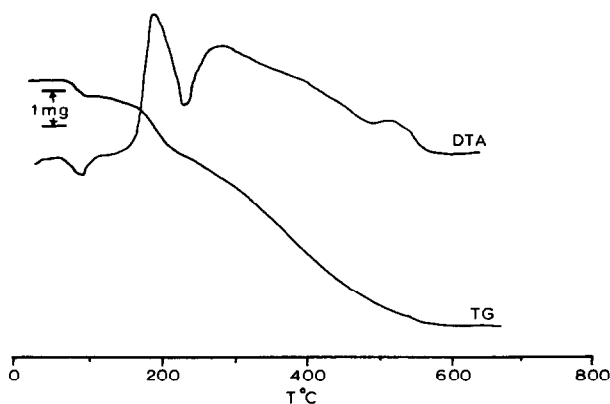


Fig. 2. TG and DTA curves for $\text{Fe}(\text{C}_6\text{H}_{12}\text{N}_2)\text{Cl}_2 \cdot 0.5\text{H}_2\text{O}$. Sample weight = 8.98 mg.

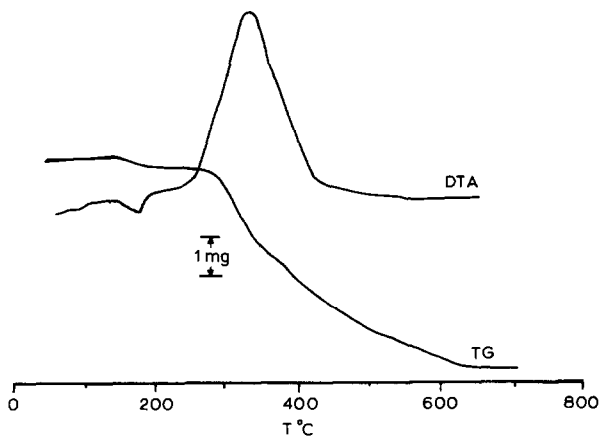


Fig. 3. TG and DTA curves for $\text{Co}(\text{C}_6\text{H}_{12}\text{N}_2)\text{Cl}_2 \cdot 0.5\text{H}_2\text{O}$. Sample weight = 8.56 mg.

The TG curve for triethylenediamine (Fig. 1) shows that the amine is thermally stable in the 20–58°C range. Its pyrolytic decomposition starts at 58°C and finishes around 300°C with the total elimination of the sample. The DTA curve for triethylenediamine (Fig. 1) displays an endothermic peak at 86°C related to decomposition and a sharp endothermic peak at 158°C which corresponds to fusion. The value of the fusion enthalpy calculated from the area of the peak is 18 kJ mol⁻¹. The TG and DTA curves for the complexes formed between triethylenediamine and the chlorides of iron, cobalt, nickel and copper are given in Figs. 2–5. The dehydration of the hydrated complexes takes place in one step. The observed weight losses for these processes compare favourably with the theoretical values (Table 4). The expected endothermic peak for the dehydration processes associated with these compounds is observed in the DTA curves. The dehydration enthalpies have been calculated from the area of the peaks and

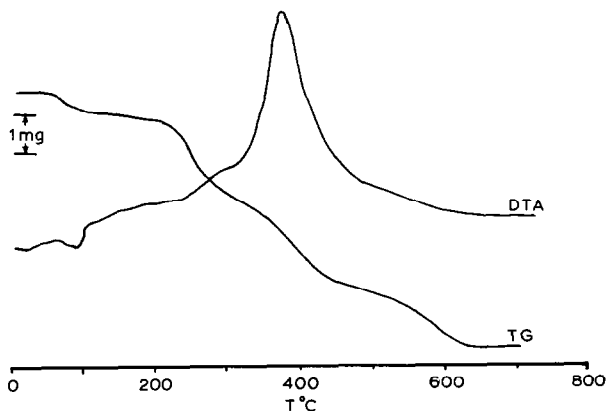


Fig. 4. TG and DTA curves for $\text{Ni}(\text{C}_6\text{H}_{12}\text{N}_2)\text{Cl}_2 \cdot \text{H}_2\text{O}$. Sample weight = 9.21 mg.

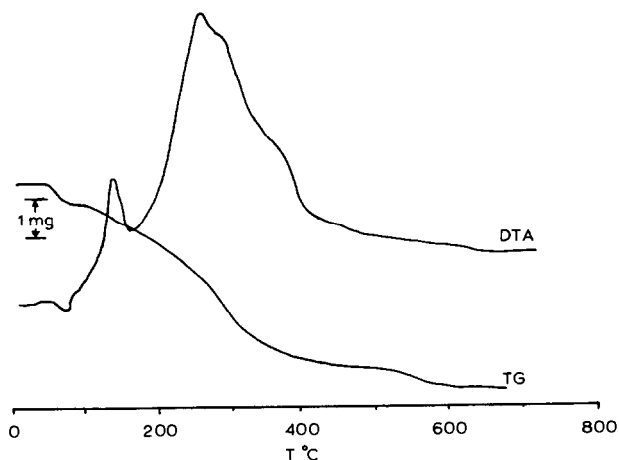


Fig. 5. TG and DTA curves for $\text{Cu}(\text{C}_6\text{H}_{12}\text{N}_2)\text{Cl}_2 \cdot \text{H}_2\text{O}$. Sample weight = 8.10 mg.

TABLE 4

Dehydration processes of the metal complexes

Processes	Peak temp. ($^{\circ}\text{C}$)	Thermal nature of transformation	Weight loss (%)		Enthalpy (kJ mol^{-1})
			Calculated	Found	
$\text{Fe}(\text{C}_6\text{H}_{12}\text{N}_2)\text{Cl}_2 \cdot 0.5\text{H}_2\text{O} \rightarrow \text{Fe}(\text{C}_6\text{H}_{12}\text{N}_2)\text{Cl}_2$	92	Endothermic	3.50	3.34	52
$\text{Co}(\text{C}_6\text{H}_{12}\text{N}_2)\text{Cl}_2 \cdot 0.5\text{H}_2\text{O} \rightarrow \text{Co}(\text{C}_6\text{H}_{12}\text{N}_2)\text{Cl}_2$	166	Endothermic	3.59	2.92	20
$\text{Ni}(\text{C}_6\text{H}_{12}\text{N}_2)\text{Cl}_2 \cdot \text{H}_2\text{O} \rightarrow \text{Ni}(\text{C}_6\text{H}_{12}\text{N}_2)\text{Cl}_2$	88	Endothermic	6.93	6.51	36
$\text{Cu}(\text{C}_6\text{H}_{12}\text{N}_2)\text{Cl}_2 \cdot \text{H}_2\text{O} \rightarrow \text{Cu}(\text{C}_6\text{H}_{12}\text{N}_2)\text{Cl}_2$	79	Endothermic	6.80	6.79	42

TABLE 5

Decomposition processes of triethylenediamine and the metal complexes

Processes	Temp. range ($^{\circ}\text{C}$)	Thermal nature of transformation	Residue (%)	
			Calculated	Found
$\text{C}_6\text{H}_{12}\text{N}_2 \rightarrow$ pyrolytic process	58–300	Endothermic	–	–
$\text{Mn}(\text{C}_6\text{H}_{12}\text{N}_2)\text{Cl}_2 \rightarrow \text{Mn}_2\text{O}_3$	169–670	Exothermic	33.16	32.74
$\text{Fe}(\text{C}_6\text{H}_{12}\text{N}_2)\text{Cl}_2 \rightarrow \text{Fe}_2\text{O}_3$	126–624	Exothermic	31.07	31.18
$\text{Co}(\text{C}_6\text{H}_{12}\text{N}_2)\text{Cl}_2 \rightarrow \text{Co}_3\text{O}_4$	206–662	Exothermic	31.97	31.54
$\text{Ni}(\text{C}_6\text{H}_{12}\text{N}_2)\text{Cl}_2 \rightarrow \text{NiO}$	122–670	Exothermic	28.75	29.31
$\text{Cu}(\text{C}_6\text{H}_{12}\text{N}_2)\text{Cl}_2 \rightarrow \text{CuO}$	101–645	Exothermic	30.04	29.62

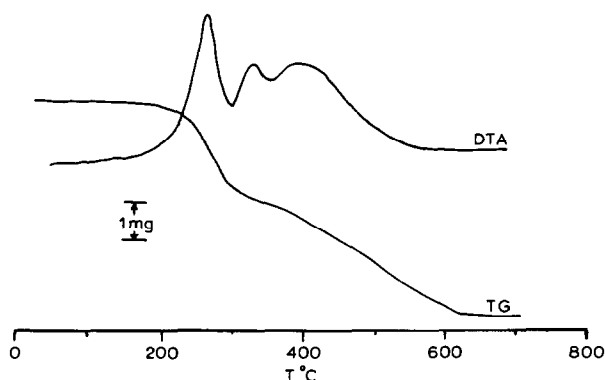


Fig. 6. TG and DTA curves for $\text{Mn}(\text{C}_6\text{H}_{12}\text{N}_2)\text{Cl}_2$. Sample weight = 9.01 mg.

are listed 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 oxides (Table 5). In the DTA curves these decomposition processes correspond to exothermic effects for the complexes and these have been indicated in Table 5. The manganese complex (Fig. 6), which is anhydrous, undergoes an exothermic reaction with loss of the organic ligand and halogen to give Mn_2O_3 .

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