Thermochimica Acta, 122 (1987) 403–412
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL AND ELECTRICAL STUDIES ON QUINOXALINE COMPOUNDS OF SOME FIRST ROW TRANSITION METAL IONS

J.R. ALLAN and A.D. PATON

Department of Applied Chemical Sciences, Napier College, Edinburgh (Gt. Britain)

K. TURVEY

Department of Physics, Napier College, Edinburgh (Gt. Britain)

H.J. BOWLEY and D.L. GERRARD

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

(Received 21 April 1987)

ABSTRACT

The chloro and bromo compounds of quinoxaline with manganese(II), cobalt(II), nickel(II) and copper(II) have been prepared in ethanolic solution. The thermal behaviour of these compounds was studied by thermogravimetry (TG) and differential thermal analysis (DTA). The thermal decomposition studies show that the compounds dichlorobis(quinoxaline) cobalt(II), dibromobis(quinoxaline) cobalt(II) and dibromobis(quinoxaline) manganese(II) form intermediate compounds before the metal halide is produced. The other compounds undergo decomposition with loss of organic ligand and the formation of the metal halide. Electrical conductivities at room temperature range from 1.4×10^{-6} Ω^{-1} m^{-1} for $MnCl_2Q$ to 2.3×10^{-3} Ω^{-1} m^{-1} for both $CoCl_2Q_2$ and $CoBr_2Q_2$. There appears to be a correlation between electrical conductivity and coordination number of the metal atom. From the temperature dependence of conductivity, information has been obtained for donor or acceptor ionization energies. Decomposition temperature, as electrically determined, is in good agreement with the TG method.

INTRODUCTION

The development of new semiconducting and conducting organometallic polymers is an important area of current research because of the potential applications in solid state electro-optical systems. These materials can have prime roles in devices such as sensors, detectors and electrophotographic units where chemical, photo and thermal stability are essential. A study of the complexes of pyrazine and substituted pyrazines has recently become of interest because of the possible formation of inorganic polymers, their availability, and their thermal stabilities. Pyrazines have two possible donor nitrogen atoms in the ring system and are much weaker bases than pyridine

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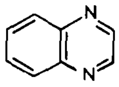

Quinoxaline

[1]. A few papers have been published describing some novel complexes of cobalt, nickel and copper with the benzopyrazine, quinoxaline [2–5].

The present work was undertaken to ascertain the thermal stability and to obtain information about the electrical conductivity of these compounds. The manganese compounds are novel.

EXPERIMENTAL

Preparation of complexes

The chloro and bromo complexes of manganese were prepared by dissolving 0.05 mol of either the manganese chloride or bromide in a minimum of boiling ethanol. To the boiling ethanol solution 0.10 mol of quinoxaline was added gradually with stirring. The resulting solution was heated for a further 15 min after which the product was isolated by filtration. The complex was washed with a minimum of ethanol followed by anhydrous diethyl ether and then air dried.

The cobalt, nickel and copper complexes were prepared as reported in the literature [2–5].

Analyses of complexes

The halide content of the complexes was determined by argentimetric titration.

Chloride

A solution containing a known weight of complex, acidified with acetic acid,, was titrated with standard silver nitrate solution using the adsorption indicator dichlorofluorescein [6].

Bromide

A solution containing a known weight of complex, acidified with acetic acid was titrated with standard silver nitrate solution using eosin as indicator [7].

The metal content of the complexes was carried out by complexometric titration except for copper where a gravimetric estimation was used.

Nickel

A solution of the complex, buffered to pH 10 was titrated with standard EDTA solution using bromopyrogallol red as indicator [8].

Cobalt

A solution of the complex was acidified with dilute sulphuric acid until the colour changed from red to yellow. The deep-red colour was restored by adding hexamine. The solution was warmed to 40 °C and titrated with EDTA solution using xylenol orange as indicator [9].

Manganese

A solution of the complex containing hydroxylammonium chloride was warmed. In order to keep the manganese in solution triethanolamine was added. The solution was made alkaline by the addition of a pH 10 buffer and titrated with EDTA solution using Eriochrome Black T as indicator [10].

Copper

Sodium hydroxide (2 M) was added to a solution of the complex until a slight permanent precipitate was obtained. This precipitate was dissolved by addition of dilute ethanoic acid. A slight excess of an ethanolic solution of salicylaldoxime was added at room temperature. The precipitate obtained was filtered and dried to constant weight [11].

Apparatus

The infrared spectra were obtained using KBr discs (4000–600 cm^{-1}), and polyethylene discs (600–200 cm^{-1}), on a Perkin–Elmer infrared spectrophotometer model 598.

The electronic spectra were obtained on a Beckmann ACTA M IV spectrophotometer as solid diffuse reflectance spectra.

Magnetic measurements were carried out by the Gouy method using $\text{Hg[Co(SCN)}_4]$ as calibrant and have been corrected for diamagnetism using Pascal's constants [12].

The thermal analysis studies were done using a Stanton Redcroft model STA 781 thermobalance. Thermogravimetry and differential thermal analysis curves were obtained at a heating rate of 6 °C min^{-1} in static air. In all cases the 20–500 °C temperature range was studied. The intermediate compounds isolated for dibromobis(quinoxaline) manganese(II), dichlorobis (quinoxaline) cobalt(II) and dibromobis(quinoxaline) cobalt(II) were obtained by heating these compounds on the thermobalance at a fixed temperature until a constant weight was obtained.

Electrical conductivity measurements were made on discs of the compounds. These discs were 13 mm in diameter and approximately 1 mm in thickness and were prepared by compressing powdered complex in a hydraulic press set to apply a force of 100 kN. Electrical contacts of diameter 5.9 mm were made concentrically on each flat face of a disc by applying a conducting paint containing silver. D.C. measurements of current (I) for a series of applied voltages (V) were obtained for $0 < V < 120$ V using a Keithley 610C electrometer to register current. The voltmeter was placed so that the current drawn by it did not pass through the electrometer. To test the contacts were not blocking, the polarity was reversed and in all cases this led to less than 4% change in the magnitude of the current. In determining the conductivity it was assumed that charge flow was perpendicular to the electrodes and the disc thicknesses were measured using a micrometer.

Further conductivity measurements were obtained for temperatures above room temperature. A calibrated copper–constantan thermocouple, prepared from S.W.G. 44 wires, was mounted on a disc placed in an electrically heated oven. With a potential of 40 V applied, the disc current was monitored during slow heating. To avoid the problem of electrical pick-up into the disc circuit from the oven heating circuit, the heater current was temporarily switched off for each measurement of disc current.

RESULTS AND DISCUSSION

The manganese compounds show no bands due to *d–d* transitions in the visible region of their electronic spectra. The magnetic moments of the chloro and bromo compounds, which are 5.75 BM and 5.71 BM respectively, correspond to five unpaired electrons suggesting either a tetrahedral or octahedral structure. The absence of a band in the infrared spectra of the chloro compound corresponding to the ν(Mn–Cl) vibration and in the bromo compound corresponding to the ν(Mn–Br) vibration at < 200 cm^{-1} would suggest a six-coordinate environment for the manganese atom [13]. The cobalt compounds have tetrahedral structures [2] while the nickel and copper compounds have octahedral structures [3–5].

The compound analyses are given in Table 1 and the thermal decomposition products are listed in Table 2. The compounds of stoichiometry MX_2Q_2 decompose via intermediate compounds to give the metal halide. The decomposition scheme is

$$MnBr_2Q_2 \rightarrow MnBr_2Q \rightarrow MnBr_2Q_{1/2} \rightarrow MnBr_2$$

$$CoCl_2Q_2 \rightarrow CoCl_2Q_{3/2} \rightarrow CoCl_2Q_{1/2} \rightarrow CoCl_2$$

$$CoBr_2Q_2 \rightarrow CoBr_2Q \rightarrow CoBr_2$$

The compounds of stoichiometry MX_2Q decompose with loss of the one molecule of quinoxaline to give the metal halide.

Electrical measurements were made for the manganese, nickel and copper compounds in which the coordination number of the metal atom is six and

TABLE 1

Analysis of compounds

Compound [a]	Colour	% Metal		% Halide	
		Calc.	Found	Calc.	Found
$MnCl_2Q$	Yellow	21.5	21.0	27.7	26.9
$MnBr_2Q_2$	Yellow	11.6	11.5	33.6	33.6
$MnBr_2Q$	Yellow	15.9	14.7	46.3	45.5
$MnBr_2Q_{1/2}$	Yellow	19.6	18.7	57.1	56.7
$CoCl_2Q_2$ [b]	Blue	15.1	15.0	18.2	18.0
$CoCl_2Q_{3/2}$	Blue	18.1	17.8	21.8	21.0
$CoCl_2Q_{1/2}$	Blue	30.2	29.6	36.4	35.4
$CoBr_2Q_2$ [b]	Blue	12.3	12.1	33.4	33.1
$CoBr_2Q$	Blue	16.9	15.8	45.8	44.9
$NiCl_2Q$ [c]	Yellow	22.6	22.3	27.3	26.9
$NiBr_2Q$ [c]	Yellow	16.8	16.5	45.8	45.7
$CuCl_2Q$ [d]	Green	24.0	23.4	26.8	25.9
$CuBr_2Q$ [d]	Brown	18.0	17.5	45.2	44.8

[a] Q, Quinoxaline. [b] ref. 2. [c] ref. 3. [d] ref. 5.

for the cobalt compounds in which the coordination number of the metal atom is four. The measured electrical conductivities at room temperature, derived from gradients of linear regions of corresponding I vs. V plots, are listed in Table 3. Figure 1 shows plots of room temperature conductivity (on a logarithmic scale) against atomic number z of the transition metal for each halogen, although points are absent for $z = 26$ since the iron(II) compounds

TABLE 2

Thermal decomposition products

Starting material	Decomposition temperature (K)	Resulting compound	% Weight loss	
			Calc.	Found
$MnCl_2Q$	353 (Endo) [a]	$MnCl_2$	50.8	50.9
$MnBr_2Q_2$	353 (Endo)	$MnBr_2Q$	27.4	29.0
	439 (Endo)	$MnBr_2Q_{1/2}$	13.7	13.4
	521 (Endo)	$MnBr_2$	13.7	13.4
$CoCl_2Q_2$	324 (Endo)	$CoCl_2Q_{3/2}$	16.7	16.5
	448 (Endo)	$CoCl_2Q_{1/2}$	33.4	33.2
	552 (Endo)	$CoCl_2$	16.7	16.8
$CoBr_2Q_2$	448 (Endo)	$CoBr_2Q$	27.2	26.6
	521 (Endo)	$CoBr_2$	26.5	26.5
$NiCl_2Q$	510 (Endo)	$NiCl_2$	50.1	50.7
$NiBr_2Q$	326 (Endo)	$NiBr_2$	37.3	37.0
$CuCl_2Q$	430 (Endo)	$CuCl_2$	49.2	50.8
$CuBr_2Q$	404 (Endo)	$CuBr_2$	36.8	35.9

[a] Endo, endothermic reaction.

TABLE 3

Electrical properties

Compound	Room temperature conductivity (Ω^{-1} m^{-1})	ΔE in the equation $\sigma = \sigma_0 \exp(-\Delta E/2kT)$ (eV)
$MnCl_2Q$	1.40×10^{-6}	0.82
$MnBr_2Q_2$	1.02×10^{-3}	1.32
$CoCl_2Q_2$	2.31×10^{-3}	
$CoBr_2Q_2$	2.30×10^{-3}	
$NiCl_2Q$	1.99×10^{-4}	0.64
$NiBr_2Q$	1.37×10^{-3}	
$CuCl_2Q$	5.14×10^{-6}	
$CuBr_2Q$	6.92×10^{-5}	

were not prepared. In the series studied, there is a peak conductivity corresponding to the cobalt compounds for both halogens and this peak is more pronounced for the chloride series. To the accuracy attainable in the measurements, the conductivities of $CoCl_2Q_2$ and $CoBr_2Q_2$ are identical. As previously noted, for all of the compounds except those containing cobalt, the structure is octahedral. For the cobalt compounds the structure is tetrahedral and it may be significant that peak conductivity is associated with this different structure.

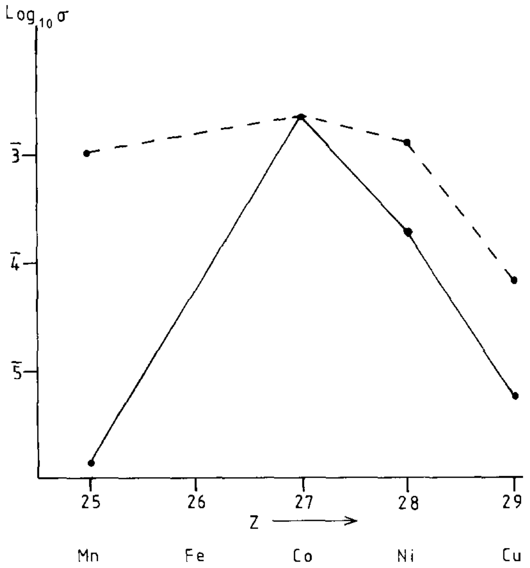

Fig. 1. Semi-logarithmic plot of conductivity (σ) at room temperature vs. atomic number (z) of transition metal M in the chloro (———) and bromo (— — —) compounds. The units of σ are Ω^{-1} m^{-1}.

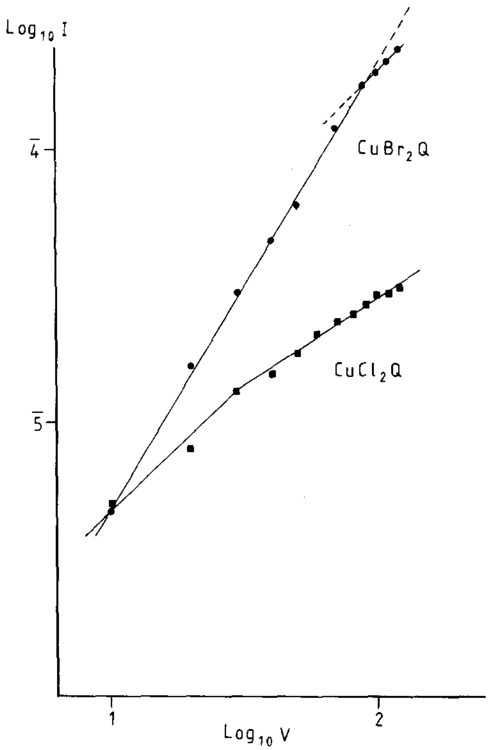

Fig. 2. Log–log plots of current (*I*) vs. voltage (*V*) for $CuCl_2Q$ and $CuBr_2Q$ at room temperature. *I* and *V* are in units of A and V, respectively.

The *I* vs. *V* plot for $MnCl_2Q$ is linear throughout the studied range ($0 < V < 120$) and for $NiCl_2Q$ the plot is linear at low voltage. The compounds $MnBr_2Q_2$, $CoBr_2Q_2$, $NiBr_2Q$ and $CoCl_2Q_2$ each exhibit *I* vs. *V* plots having an extensive linear region for $V > 15$ V and extrapolation of this line to the voltage axis gives an intercept in the range 10–15 V. This behaviour suggests an electrode-limited injection in the range $0 < V < 15$ V [14]. For $CuBr_2Q$ the *I* vs. *V* plot is curved upwards for $0 < V < 70$ V and becomes linear at higher voltages. When the same data are plotted on a log–log scale, Fig. 2, it can be seen that for $0 < V < 70$ V the points fit closely to $I \propto V^{1.64}$ and the points for higher voltages correspond to ohmic behaviour. Again, this suggests electrode-limited injection. Figure 2 also shows that for $CuCl_2Q$ the behaviour is nearly ohmic at low voltage ($V < 25$ V) and at higher voltages $I \propto V^{0.6}$ indicating polarization effects [15].

The *I* vs. *V* plots for $NiCl_2Q$ and $CoCl_2Q_2$, Figs. 3 and 4, respectively, are each anomalous in exhibiting a maximum followed at higher voltage by saturation. These plots were obtained with increasing voltage but when the voltage was again reduced to zero the data followed a different curve. It is apparent that decomposition has occurred although the discs were mounted

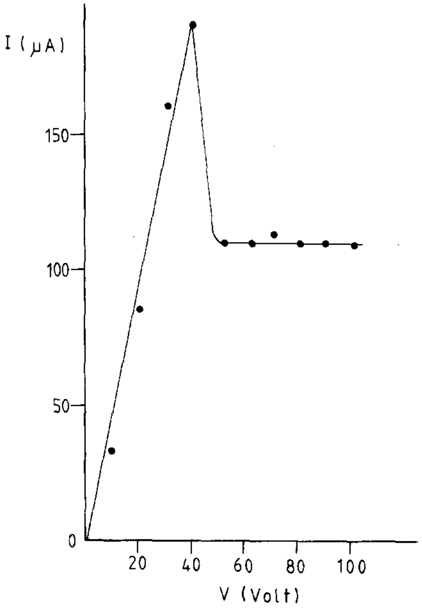

Fig. 3. I vs. V plot for $NiCl_2Q$ nominally at room temperature.

on a heat sink and the dissipation rate corresponding to the maximum current for $NiCl_2Q$ was only 76 mW.

The temperature dependence of conductivity for the compounds $MnBr_2Q_2$, $NiBr_2Q$ and $CoCl_2Q_2$ are analyzed in Fig. 5 by plotting ln σ against T^{-1} (σ = conductivity, T = absolute temperature). A linear region in these plots corresponds to relationship of the form $\sigma = \sigma_0 \exp(-\Delta E/2kT)$ with constant σ_0 and ΔE. Values obtained for ΔE using the gradients of these

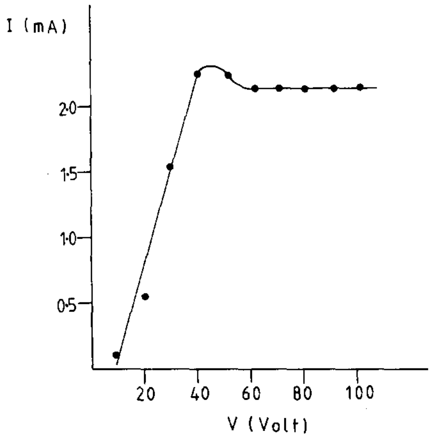

Fig. 4. I vs. V plot for $CoCl_2Q_2$ nominally at room temperature.

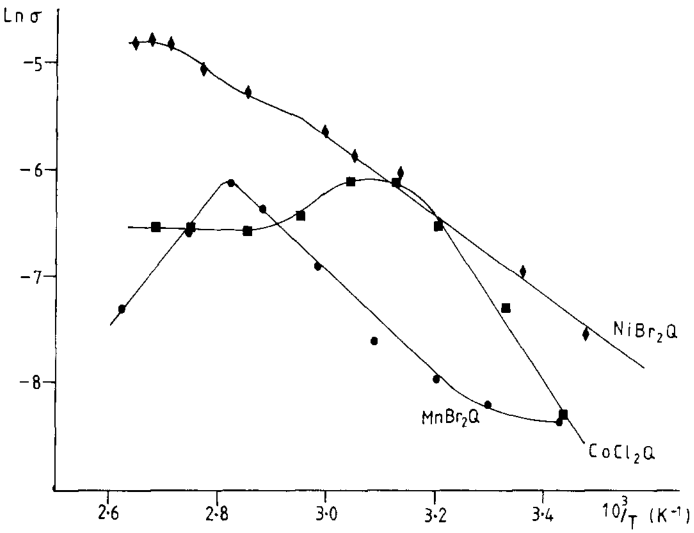

Fig. 5. Plots of ln σ vs. $10^3/T$ for $NiBr_2Q$, $CoCl_2Q_2$ and $MnBr_2Q_2$ (σ = conductivity in units of Ω^{-1} m^{-1} and T = absolute temperature in units of Kelvin).

linear regions are listed in Table 3. Assuming that enhanced conductivity at elevated temperature is due to thermal activation of electrons from donor centres or holes from acceptor centres, both for uncompensated material, then ΔE represents the respective donor or acceptor ionization energies [16]. The maxima in the plots in Fig. 5 are due to thermal degradation. This is confirmed by the observation that when the discs were heated beyond the maxima and then allowed to cool the data for cooling followed different curves from those for heating. The temperature for maximum conductivity, taken from Fig. 5, for $CoCl_2Q_2$ and $MnBr_2Q_2$ (which are the compounds showing well defined peaks in the figure) are 323 K and 353 K respectively. Comparing these temperatures with the corresponding endothermic decomposition temperatures of 324 K and 353 K respectively (Table 2), the agreement is seen to be excellent.

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