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THERMAL, STRUCTURAL AND ELECTRICAL STUDIES OF THE CHLORO COMPLEXES OF COBALT, NICKEL, COPPER AND ZINC WITH 2-METHYLQUINOXALINE

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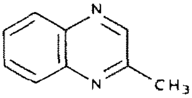
ABSTRACT

The chloro compounds of 2-methylquinoxaline (MeQ) with cobalt(II), nickel(II), copper(II) and zinc(II) were prepared in ethanolic solution from which the solid compounds were isolated. The suggested structure for the cobalt and zinc compounds is tetrahedral, while for the nickel and copper compounds it is octahedral. The techniques of thermogravimetry and differential thermal analysis show that the compounds $Co(MeQ)_2Cl_2$ and $Ni(MeQ)_2Cl_2$ form intermediate compounds before the metal halide is produced. The compound $Cu(MeQ)Cl_2$ undergoes decomposition with loss of the 2-methylquinoxaline and the formation of copper(II) chloride, while the compound $Zn(MeQ)_2Cl_2$ decomposes with loss of the 2-methylquinoxaline and chlorine and the formation of zinc oxide.

From the electrical measurements on the compounds isolated from ethanolic solution, it was found that two distinct groups exist: $Co(MeQ)_2Cl_2$ and $Ni(MeQ)_2Cl_2$ have nearly equal and relatively high conductivities, whilst $Cu(MeQ)Cl_2$ and $Zn(MeQ)_2Cl_2$ have nearly equal but relatively low conductivities. Within each group the temperature dependence of electrical conductivity is similar but it differs between the groups.

INTRODUCTION

This work is a continuation of previously reported studies on complexes of quinoxaline and the first-row transition elements [1]. The compound 2-methylquinoxaline has two possible donor sites: the nitrogen atoms of the aromatic ring system.



2-methylquinoxaline (MeQ)

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In this paper we report studies of the chloro complexes of cobalt, nickel, copper and zinc with 2-methylquinoxaline. Spectral and magnetic measurements have been used to characterise each metal complex and to interpret the type of coordination which takes place with the metal ion. The thermal decomposition of the complexes along with their electrical conductivity has been studied.

EXPERIMENTAL

Preparation of complexes

The metal(II) halide (0.05 mol) was dissolved in a minimum of boiling ethanol. To the boiling ethanol solution 0.10 mol of 2-methylquinoxaline was added dropwise with stirring. The resulting solution was heated for a further 15 min and then concentrated on a steam bath. The precipitated product was then isolated by filtration and washed with a minimum of ethanol and air dried.

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 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. Measurements of magnetic moments were made using the Gouy method with $Hg[Co(SCN)_4]$ as calibrant. Each magnetic moment was corrected for diamagnetism using Pascal's constants [2].

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 °C min^{-1} in static air. The 20–500 °C temperature range was studied in all cases. Intermediate compounds were isolated using $Co(MeQ)_2Cl_2$ and $Ni(MeQ)_2Cl_2$ as starting materials by heating them at a fixed temperature on the thermobalance until a constant weight was obtained.

Electrical conduction measurements were performed under d.c. conditions on discs of the compounds which were prepared by compressing the sample powder. The details of the method used have been described previously [1]. For each of the compounds isolated from solution, two discs were prepared (having thicknesses in the range 0.94–1.35 mm, diameters of 13 mm and electrodes of diameter 4.9 mm) and the room temperature current I versus voltage V characteristics were obtained over the range ±30 V. No significant assymmetry in the characteristics under the two polarities was observed for any disc. The electrical conductivities, as inferred from the two discs of the same compound, were in satisfactory agreement, especially for $Co(MeQ)_2Cl_2$ and $Ni(MeQ)_2Cl_2$. Since different disc thicknesses were used for the first and second set of characteristics of each compound, this reproducibility between the pairs of discs confirms that there was no potential drop at the electrode–compound contacts. The symmetry observed in the I versus V characteristics for positive and negative V applied to the same disc also supports this contention. The temperature dependence of the conductivity under an applied voltage of 10 V was also obtained for discs of the compounds using the previously described method [1].

RESULTS AND DISCUSSION

The analytical results of the complexes are given in Table 1. These analyses agree with the given formulae proposed for the compounds.

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 compounds would suggest that the cobalt ion is in a tetrahedral environment while the nickel ion is in a octahedral environment [3,4]. The values obtained for the magnetic moments supports this suggestion [3,4]. In the copper complex, a broad charge-transfer band which extends from the ultraviolet into the visible region is observed. This band exhibits a shoulder at 14925 cm^{-1} which has been assigned to the d–d transition $^2E_g(D) \rightarrow {}^2T_{2g}(D)$ [3,4]. The magnetic moment for this compound is lower than the spin-only value indicating a strong copper–copper interaction. In the electronic spectrum of the zinc complex, bands which are considered to be due to charge transfer are observed.

The wavenumbers of the IR absorption bands for MeQ and for its chloro complexes isolated from ethanolic solution are given in Table 2 together with the descriptions and assignments. The IR spectrum of MeQ is very similar to that of its complexes in the region 4000–600 cm^{-1} except that the bands due to the aromatic-ring vibrations are shifted to higher frequencies on formation of the complexes. This would suggest that the nitrogen atoms of the aromatic ring are coordinated to a metal atom [3]. The ν(M–Cl) bands in the spectra of the nickel and copper complexes show that the metal ions are in a six-coordinate environment, while the corresponding bands for the cobalt and zinc complexes indicate that the metal ions are in four-coordinate environment [3–5].

No single crystals for any of the compounds were isolated from solution, thus without X-ray analysis no definite structures can be described. How-

TABLE 1

Analyses of the initial and intermediate compounds

Compound	Colour	Calculated (%)				Found (%)			
		M	C	H	N	M	C	H	N
$Co(MeQ)_2Cl_2$ [a]	Grey–blue	14.09	51.69	3.89	13.39	13.66	50.78	3.65	12.92
$Co(MeQ)Cl_2$ [b]	Purple–brown	21.50	39.44	2.94	10.22	21.12	39.24	2.74	10.02
$Co(MeQ)_{1/3}Cl_2$ [b]	Brown	33.12	20.25	1.51	5.24	33.02	18.66	1.33	4.44
$Ni(MeQ)_2Cl_2$ [a]	Red	14.04	51.72	3.85	13.40	13.96	51.24	3.71	12.93
$Ni(MeQ)Cl_2$ [b]	Pale brown	21.44	39.47	2.94	10.23	20.91	38.62	2.34	9.47
$Cu(MeQ)Cl_2$ [a]	Black	22.80	38.79	2.89	10.05	22.36	38.25	2.66	9.76
$Zn(MeQ)_2Cl_2$ [a]	Blue	15.39	50.86	3.76	13.18	15.16	50.89	3.82	12.96

[a] Initial compound isolated from ethanolic solution.

[b] Intermediate compound produced by heating the corresponding initial compound.

TABLE 2

Spectral data and molecular moments of compounds isolated from solution [a]

Compound	Electronic spectra		IR spectra (4000–200 cm^{-1})			μ (B.M.)
	Peak position (cm^{-1})	d–d Transition	Ring vibrations (cm^{-1})	ν(M–Cl) (cm^{-1})	ν(M–N) (cm^{-1})	
MeQ			1596(s),			
			1492(s)			
$Co(MeQ)_2Cl_2$	8 196	$^4A_2(F) \rightarrow {}^4T_1(F)$	1613(s),	327	290	4.72
	15 625	$^4A_2(F) \rightarrow {}^4T_1(P)$	1501(s)			
$Ni(MeQ)_2Cl_2$	11 764	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	1610(s),	207	292	3.16
	18 939	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	1497(s)			
	25 510	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$				
$Cu(MeQ)Cl_2$	22 222 (CT)	–	1618(s),	242	296	1.61
	14 925 (sh)	$^2E_g(D) \rightarrow {}^2T_{2g}(D)$	1498(s)			
$Zn(MeQ)_2Cl_2$	17 391 (CT)	–	1616(s),	330	286	–
	18 587 (CT)	–	1500(s)			
	28 169 (CT)	–				

[a] CT, charge transfer; sh, shoulder; s, strong.

ever, the spectroscopic and magnetic data allow possible structures to be postulated. The poor solubility of the copper and nickel complexes in polar and non-polar solvents indicates that they have polymeric structures [3]. It is thus suggested that the structure of the nickel complex is a chain of nickel atoms bonded to halogens with the 2-methylquinoxaline molecules above and below the plane of the metal–halogen chain. The copper compound consists of parallel chains of copper atoms bonded to halogens with the 2-methylquinoxaline molecules as bridging units between adjacent chains, forming a sheet structure. The cobalt and zinc compounds each have tetrahedral structures in which the metal ion is bonded to two chloride ions and to two nitrogen atoms. One of these nitrogen atoms is present in the aromatic ring for each of the pair of 2-methylquinoxaline molecules.

The thermal decomposition data are given in Table 3. The cobalt and nickel compounds (which have the stoichiometry $M(MeQ)_2Cl_2$) decompose via intermediate compounds to give the metal halide. The decomposition scheme is

$$Co(MeQ)_2Cl_2 \xrightarrow{\text{endo}} Co(MeQ)Cl_2 \xrightarrow{\text{exo}} Co(MeQ)_{1/3}Cl_2 \xrightarrow{\text{exo}} CoCl_2$$

$$Ni(MeQ)_2Cl_2 \xrightarrow{\text{endo}} Ni(MeQ)Cl_2 \xrightarrow{\text{exo}} NiCl_2$$

The copper compound has the stoichiometry $Cu(MeQ)Cl_2$ and decomposes exothermically with the loss of the molecule of 2-methylquinoxaline to yield copper(II) chloride. The zinc compound, having the stoichiometry $Zn(MeQ)_2Cl_2$, undergoes an endothermic reaction immediately followed by

TABLE 3

Thermal-decomposition products

Starting material	Decomposition temperature (K)	Product	Weight loss [a] (%)	
			Calc.	Found
$Co(MeQ)_2Cl_2$	418 (endo)	$Co(MeQ)Cl_2$	34.47	32.52
	488 (exo)	$Co(MeQ)_{1/3}Cl_2$	22.98	22.66
	628 (exo)	$CoCl_2$	11.49	10.68
$Ni(MeQ)_2Cl_2$	454 (endo)	$Ni(MeQ)Cl_2$	34.49	34.33
	567 (exo)	$NiCl_2$	34.49	34.16
$Cu(MeQ)Cl_2$	413 (exo)	$CuCl_2$	51.74	50.96
$Zn(MeQ)_2Cl_2$	426 (endo/exo)	ZnO	19.16	20.84

[a] The weight loss in each process is expressed as a percentage of the weight of the initial compound.

an exothermic reaction with loss of the organic ligand and chlorine, respectively, to produce zinc oxide.

The I versus V graphs, which are not reproduced here, are slightly curved upwards for all compounds. When the same data are plotted on double logarithmic scales, the resulting graphs are linear showing that $I \propto V^m$. The gradient, m, of each logarithmic plot was determined using a least-squares program. The values of m are in the range $1.12 < m < 1.50$ and are listed in Table 4, together with the corresponding coefficient of determination (ρ^2) for the least-squares fitting. The closeness of all the ρ^2 values to unity demonstrates the validity of the $I \propto V^m$ law and the fact that m exceeds unity is evidence for space charge conduction. A plausible alternative expression relating I and V is $I = AV + BV^2$ in which A and B are constant for a given disc and this equation, which has a theoretical basis [6,7], would be verified for the discs if linear plots of I/V versus V are obtained. However, the fit of a linear relationship to I/V versus V is poor for all the discs, as examplified by $Co(MeQ)_2Cl_2$ for which the resulting coefficient of determination is only 0.61 (to be contrasted with 0.996 for the $I \propto V^m$ law). Values of m in a similar range to those reported here have been observed for other organometallic compounds [8,9] as has the superiority of the $I \propto V^m$ law over $I = AV + BV^2$ [8,9]. Since $m \neq 1$, it is not possible to specify a unique conductivity; instead the conductivities (defined as current density per unit field) were determined for a field of 1×10^4 V m^{-1} and are listed in Table 4. This field is chosen as being representative of the middle of the range of applied fields.

The temperature dependence of the conductivity is displayed in Figs. 1 and 2 as semi-logarithmic plots of the conductivity σ (as measured under an applied voltage of 10 V) against reciprocal absolute temperature T. Linearity of such plots would show the validity of the equation $\sigma = \sigma_0 \exp(-\Delta E/2kT)$

TABLE 4

Electrical properties of the 2-methylquinoxaline chloro complexes and comparison with quinoxaline chloro complexes

Compound	Z [a]	σ [b,c] (Ω^{-1} m^{-1})	ΔE [d] (eV)	m [a]	ρ^2 [f]	Compound	Z [a]	σ [b] (Ω^{-1} m^{-1})	ΔE [d] (eV)
						$MnCl_2Q$	6	1.40×10^{-6}	0.82
$Co(MeQ)_2Cl_2$	4	2.35×10^{-4} (±0.11)	–	1.14 ± 0.02	0.996	$CoCl_2Q_2$	4	2.31×10^{-3}	–
$Ni(MeQ)_2Cl_2$	6	1.90×10^{-4} (±0.03)	–	1.35 ± 0.15	0.984	$NiCl_2Q$	6	1.99×10^{-4}	0.64
$Cu(MeQ)Cl_2$	6	2.50×10^{-8} (±0.9)	1.2	1.18 ± 0.04	0.997	$CuCl_2Q$	6	5.14×10^{-6}	–
$Zn(MeQ)_2Cl_2$	4	3.10×10^{-8} (±0.7)	1.3	1.21 ± 0.02	0.995				

[a] Z, Coordination number.

[b] σ, Conductivity at room temperature.

[c] Conductivity corresponding to a field of 1×10^4 V m^{-1}; the error range indicates the spread for two discs.

[d] ΔE is the activation energy in the equation $\sigma = \sigma_0 \exp(-\Delta E/2kT)$.

[e] m is defined by $I \propto V^m$: the tabulated m is the mean from two discs at room temperature and the error range indicates the spread observed for these discs.

[f] ρ^2, Coefficient of determination in fitting m, averaged for the two discs.

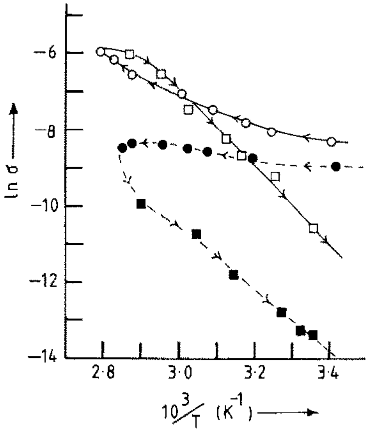

Fig. 1. Plots of ln σ versus $10^3/T$ (where σ is the conductivity for an applied voltage of 10 V, in units of Ω^{-1} m^{-1}, and T is the absolute temperature). ○———○, $Co(MeQ)_2Cl_2$, increasing T; □———□, $Co(MeQ)_2Cl_2$, decreasing T; ●– –●, $Ni(MeQ)_2Cl_2$, increasing T; ■– –■, $Ni(MeQ)_2Cl_2$, decreasing T.

where ΔE is the activation energy for releasing free carriers. However, as shown in Fig. 1 for $Co(MeQ)_2Cl_2$ and $Ni(MeQ)_2Cl_2$, the data collected during cooling does not reproduce that during heating even though the highest temperature reached was only 359 K. The cause of the discrepancy is not due to water being driven off during heating because the prepared discs were kept in a dessicator prior to taking the measurements. For $Cu(MeQ)Cl_2$ and $Zn(MeQ)_2Cl_2$ (Fig. 2), there is also poor reproducibility of the conductivity data during heating and cooling, although the disparity is not as

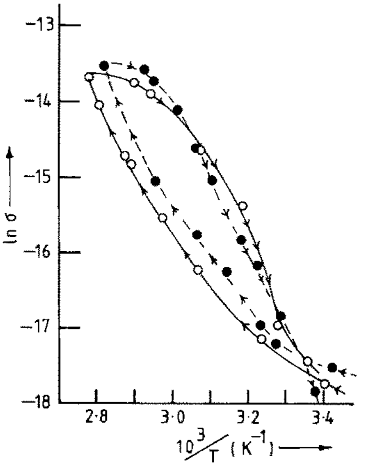

Fig. 2. Plots of ln σ versus $10^3/T$ (where σ is the conductivity for an applied voltage of 10 V, in units of Ω^{-1} m^{-1}, and T is the absolute temperature). ○———○, $Cu(MeQ)Cl_2$; ●– –●, $Zn(MeQ)_2Cl_2$.

marked as in Fig. 1. It follows that no meaningful values of ΔE can be assigned to $Co(MeQ)_2Cl_2$ or $Ni(MeQ)_2Cl_2$ and only rough values can be given to $Cu(MeQ)Cl_2$ and $Zn(MeQ)_2Cl_2$; these rough values, which are listed in Table 4, are based on the gradients of the best-fitting lines that can be drawn through the points in Fig. 2 for each compound.

Electrically, the compounds isolated from ethanolic solution fall into two distinct groups. The first group, consisting of $Co(MeQ)_2Cl_2$ and $Ni(MeQ)_2Cl_2$, have very similar and relatively high conductivities with similar shaped curves (Fig. 1) for their temperature dependencies of conductivity. The second group consists of $Cu(MeQ)Cl_2$ and $Zn(MeQ)_2Cl_2$ which, likewise, have closely similar but relatively low conductivities with nearly coincident curves (Fig. 2) for their temperature dependencies of conductivity. The coordination number of the metal ion in the 2-methylquinoxaline dichloro complexes apparently does not influence the conductivity to any great extent, because, of the four compounds investigated, each group contains one compound having a metal ion with coordination number four (viz. Co and Zn) and one compound having a metal ion with coordination number six (viz. Ni and Cu). In contrast to this, in our earlier work on chloro complexes of quinoxaline complexes with metal ions [1], the main results of which are reproduced in Table 4, we made the suggestion that the coordination number of the metal was an important factor in influencing the conductivity and this was supported also for the bromo complexes. If the number of MeQ molecules associated with each metal atom is of paramount importance in the electrical behaviour of the 2-methylquinoxaline compounds, then $Co(MeQ)_2Cl_2$, $Ni(MeQ)_2Cl_2$ and $Zn(MeQ)_2Cl_2$ would be expected to be electrically similar, with $Cu(MeQ)Cl_2$ in a class of its own, but this is contrary to the observations.

The tentative suggestion is made, although no explanation is offered, that the spin state of the metal is important in controlling the conductivity of the 2-methylquinoxaline chloro complexes. However, in the much more highly conjugated electron system for metalloporphyrin complexes studied recently [8], the spin state of the metal had little effect on the conductivity.

As earlier work [1] has investigated the conductivity of quinoxaline chloro complexes and the present report involves 2-methyl substituted quinoxaline chloro complexes, we consider it to be a natural extension to study the effect of substituting a single methyl group in other positions of the quinoxaline molecule. Work along these lines is planned.

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