

Preparation, structural characterisation, and thermal and electrical studies of complexes of zinc, cadmium and mercury with 2-methylquinoxaline

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Abstract

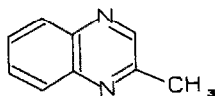
The chloro and bromo complexes of 2-methylquinoxaline (MeQ) with zinc(II), cadmium(II) and mercury(II) were prepared in ethanolic solution from which solid compounds were isolated of stoichiometry $Zn(MeQ)_2X_2$, $Cd(MeQ)X_2$ and $Hg(MeQ)X_2$ where X is chloride or bromide. Infrared spectral data suggest that the zinc compounds have a tetrahedral structure whilst an octahedral stereochemistry is proposed for the cadmium compounds. $Hg(MeQ)Br_2$ has an octahedral configuration similar to that of $Hg(MeQ)Cl_2$ whose structure has been previously determined by X-ray analysis. Thermogravimetry and differential thermal analysis techniques show that the zinc and cadmium compounds decompose with the loss of the organic ligand and the halogen to form the metal oxide. The mercury compounds decompose rapidly with complete evolution of the sample.

Electrical studies show that $Cd(MeQ)Br_2$ is the most conductive of the compounds and exhibits hysteresis and current saturation effects. All the other compounds show a slight departure from Ohm's law which is attributed to space charge effects. The temperature dependence of the conductivity is also reported.

INTRODUCTION

This work is an extension of studies previously reported by this laboratory on complexes of the first-row transition elements with quinoxaline and some of its substituted compounds [1–3]. In earlier studies of the first-row transition metal complexes of 2-methylquinoxaline [2], an anomalously highly coloured zinc complex, dichlorobis(2-methylquinoxaline)zinc(II), was reported. The colour of this complex was attributed to a metal–ligand charge transfer effect.

In this paper we report further studies on the metal complexes of 2-methylquinoxaline with zinc, cadmium and mercury. The compound 2-methylquinoxaline has two nitrogen atoms of the aromatic ring system which are capable of bonding to metal ions.



2-Methylquinoxaline

Spectral studies have been used to characterise each metal complex and to interpret the type of coordination which takes place between the metal atom and the ligand. The thermal decomposition of the complexes along with their electrical properties have also been studied.

EXPERIMENTAL

Preparation of the complexes

The complexes were prepared by dropwise addition of 2-methylquinoxaline (0.05 mol) to a boiling ethanol solution (70 cm³) of the metal chloride or bromide (0.025 mol). The resulting solution was heated for a further 15 minutes and then concentrated on a steam bath. The precipitated product was isolated by filtration, washed with a minimum of ethanol and air dried.

When a boiling ethanol solution of 2-methylquinoxaline and mercury(II) chloride was allowed to stand overnight, fine needle-like crystals were obtained which were suitable for X-ray crystallography.

Apparatus and measurements

The metal concentration in the complexes was determined using a Perkin-Elmer 373 atomic absorption spectrophotometer. The carbon, hydrogen and nitrogen analyses were made using a Carlo Erba model 1106 elemental analyser.

The infrared 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 Pye Unicam model SP3-300 infrared spectrophotometer. The electronic spectra were recorded as solid diffuse reflectance spectra using a Beckman Acta MIV spectrophotometer.

The thermal analysis measurements were made on a Stanton Redcroft model STA 1500 thermobalance. Thermogravimetry (TG) and differential thermal analysis (DTA) traces were obtained at a heating rate of 6°C min⁻¹ in static air. The 20–800°C temperature range was studied in all cases.

Electrical conduction measurements were performed under direct current conditions on discs of the compounds prepared by compressing a powdered sample of the complex. These discs were 13 mm in diameter and their thicknesses ranged from 0.52 to 1.66 mm. Electrodes of 4.9 mm diameter were formed on the flat surfaces of the discs by applying a

TABLE 1
Analyses of the compounds

Compound	Colour	Theory (%)				Found (%)			
		Metal	Carbon	Nitro- gen	Hydro- gen	Metal	Carbon	Nitro- gen	Hydro- gen
Zn(MeQ) ₂ Cl ₂	Purple	15.40	50.91	13.19	3.80	15.16	50.89	12.96	3.82
Zn(MeQ) ₂ Br ₂	Purple	12.73	42.10	10.90	3.14	12.89	42.08	10.83	3.08
Cd(MeQ)Cl ₂	Red	34.32	33.01	8.55	2.46	34.19	33.30	8.51	2.59
Cd(MeQ)Br ₂	Red	27.00	25.96	6.72	1.94	26.77	25.82	6.60	1.88
Hg(MeQ)Cl ₂	Purple	48.26	26.00	6.74	1.94	48.09	25.87	6.61	1.81
Hg(MeQ)Br ₂	Purple	39.75	21.42	5.55	1.60	39.98	21.44	5.67	1.57

silver-based conductive paint. Details of the methods used for electrical measurements have been previously described [1,3].

RESULTS AND DISCUSSION

The analytical results for the complexes isolated from solution are shown in Table 1. The experimental data agree with the given formulae and stoichiometry of the complexes.

All the complexes, except for Hg(MeQ)Cl₂, were isolated from solution as powders and, hence, no definite structures can be described for these complexes. In the case of dichloro(2-methylquinoxaline)mercury(II), suitable crystals for X-ray analysis were isolated from solution and its structure determination has been reported by this laboratory [4]. The structure of dichloro(2-methylquinoxaline)mercury(II) consists of dimeric units with chloride bridging between the mercury atoms. A polymer chain is produced by chloride bridging between each of the dimeric units. An octahedral environment for each of the mercury atoms is obtained by the bonding of a molecule of 2-methylquinoxaline to each of the mercury atoms as shown in Fig. 1.

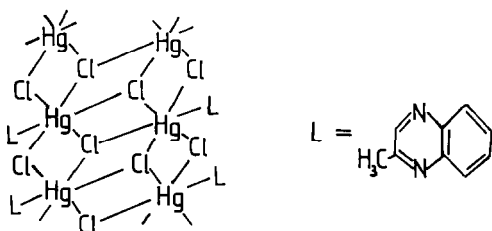


Fig. 1. Structure (not to scale) for dichloro(2-methylquinoxaline)mercury(II) as determined by X-ray analysis.

TABLE 2

Electronic and infrared spectra of the compounds (cm^{-1})

Compound	Electronic spectra peak position	Infrared spectra ($4000\text{--}200\text{ cm}^{-1}$)			
		Ring vibrations ^a		$\nu(\text{M-X})$	$\nu(\text{M-N})$
MeQ		1596 (s)	1492 (s)		
Zn(MeQ) ₂ Cl ₂	16529 17391 18587 28169	1616 (s)	1500 (s)	330	286
Zn(MeQ) ₂ Br ₂	16393 17331 18518 28169	1614 (s)	1501 (s)	246	< 200
Cd(MeQ)Cl ₂	15504 18349 20202	1617 (s)	1498 (s)	< 200	< 200
Cd(MeQ)Br ₂	15625 18349 20704	1616 (s)	1496 (s)	< 200	< 200
Hg(MeQ)Cl ₂	15873 19608 25000	1614 (s)	1494 (s)	335	< 200
Hg(MeQ)Br ₂	15505 19608 25316	1613 (s)	1493 (s)	236	< 200

^a s, sharp.

Thus for all the compounds studied, with the exception of $\text{Hg}(\text{MeQ})\text{Cl}_2$, it is only possible to suggest structures based on infrared spectral information as the d^{10} configuration of the metal ions obviates the use of magnetic and electronic spectral data in determining the stereochemistry of these complexes.

The wavenumbers of the IR absorption bands and their assignments are given in Table 2 for 2-methylquinoxaline and its complexes isolated from ethanolic solution. The IR spectrum of 2-methylquinoxaline is almost identical to that of its complexes in the $4000\text{--}600\text{ cm}^{-1}$ region, except for bands due to the vibrations of the aromatic ring system which are shifted to higher frequencies on complexation. This would suggest that bonding is taking place between the metal atom and the nitrogen atoms of the aromatic ring. Such a shift in ring vibration frequencies is observed in $\text{Hg}(\text{MeQ})\text{Cl}_2$ where, from its X-ray structure [4], bonding through the ring nitrogen atoms is known to occur.

Metal-halogen and metal-nitrogen bands are assigned for the complexes and are reported in Table 2. For $\text{Hg}(\text{MeQ})\text{Cl}_2$, where chlorine bridging is present, the $\nu(\text{Hg-Cl})$ vibration reported is in good agreement

with literature values [5,6]. Similarly in $\text{Hg}(\text{MeQ})\text{Br}_2$, $\nu(\text{Hg}-\text{Br})$ at 236 cm^{-1} is consistent with the presence of bridging bromide species [5,6]. Hence it is proposed that the structure of $\text{Hg}(\text{MeQ})\text{Br}_2$ is identical to that of its analog $\text{Hg}(\text{MeQ})\text{Cl}_2$ whose structure has been described earlier [4].

The metal-halogen vibrations reported for the zinc compounds are consistent with the zinc ions having a tetrahedral environment [7-9]. Thus it is postulated that in the zinc compounds 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. For the cadmium complexes, the absence of metal-halogen bands above 200 cm^{-1} in the infrared spectra is strong evidence that the cadmium ion is present in an octahedral stereochemistry [7,8]. It is suggested that the structure is similar to the mercury compounds: dimeric units consisting of halide bridging between two cadmium atoms with further halide bridging between parallel dimeric units to form infinite, polymeric chains. The octahedral configuration of each cadmium ion is completed by the bonding of a molecule of 2-methylquinoxaline through one of its ring nitrogen atoms.

Although the metals in this study all have a d^{10} configuration, the electronic spectra of their complexes with 2-methylquinoxaline, Table 2, do, however, show several intense absorption bands which penetrate the visible region and hence account for the colours of the complexes. The absorption bands are considered to be a result of ligand charge transfer effects.

Thermal decomposition traces for the complexes are shown in Figs. 2-4. The zinc complexes of stoichiometry $\text{Zn}(\text{MeQ})_2\text{X}_2$, where X is either

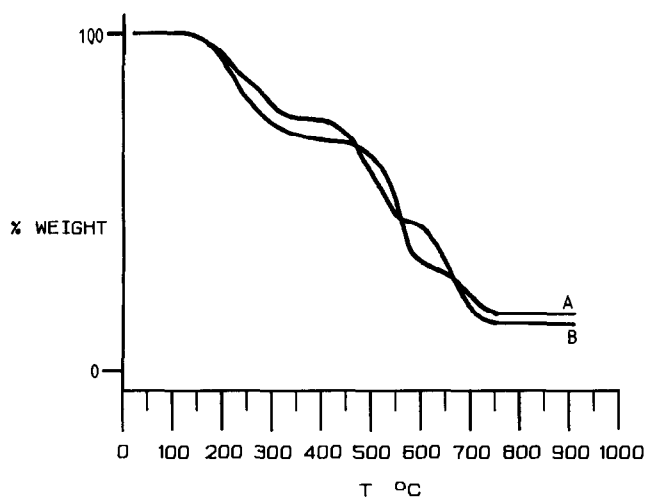


Fig. 2. Thermogravimetric (TG) curves for: curve A, $\text{Zn}(\text{MeQ})_2\text{Cl}_2$ (mass 11.93 mg); and curve B, $\text{Zn}(\text{MeQ})_2\text{Br}_2$ (mass 10.17 mg).

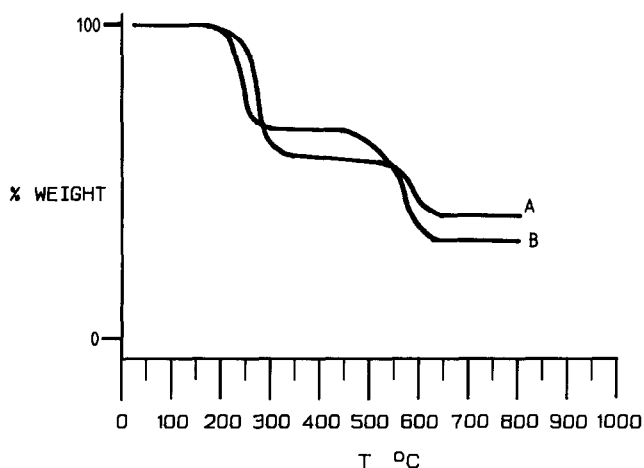


Fig. 3. Thermogravimetric (TG) curves for: curve A, Cd(MeQ)Cl₂ (mass 5.48 mg); and curve B, Cd(MeQ)Br₂ (mass 11.31 mg).

chloride or bromide, undergo an endothermic reaction followed by an exothermic reaction with the loss of the organic ligand and the halogen, respectively, to produce zinc oxide. From the TG curve, Fig. 2, there is evidence of a possible intermediate formed following the loss of the first organic ligand but no stable compound could be isolated. For the compounds of stoichiometry Cd(MeQ)₂X₂, thermal decomposition, Fig. 3, occurs with an endothermic loss of the molecule of 2-methylquinoxaline to yield cadmium(II) halide. Confirmation of the presence of the cadmium halide was derived from their DTA traces which showed sharp endother-

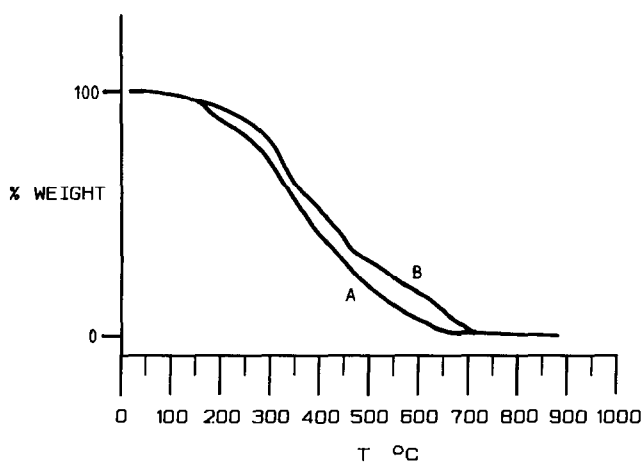


Fig. 4. Thermogravimetric (TG) curves for: curve A, Hg(MeQ)Cl₂ (mass 11.23 mg); and curve B, Hg(MeQ)Br₂ (mass 13.87 mg).

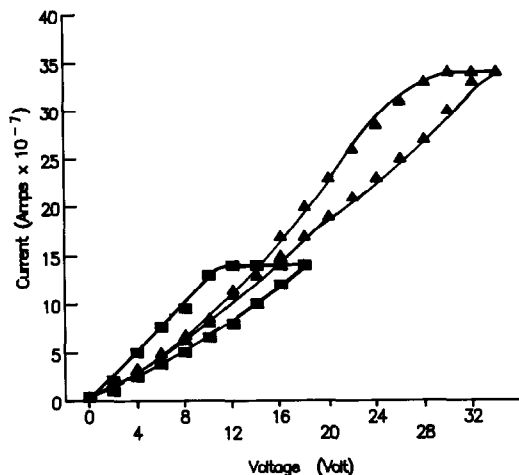


Fig. 5. Current (I) as a function of voltage (V) for a disc of $\text{Cd}(\text{MeQ})\text{Br}_2$ at room temperature: ■, data obtained under initial polarity; and ▲, data obtained under reversed polarity.

mic peaks at 570 and 575°C which correspond to the melting points of cadmium chloride and bromide respectively. The cadmium halides undergo an endothermic loss of the halogen to form the oxide. The TG traces of the mercury compounds $\text{Hg}(\text{MeQ})_2\text{X}_2$ (Fig. 4) are essentially featureless as both compounds undergo rapid decomposition with no stable intermediates evident. The mercury compounds $\text{Hg}(\text{MeQ})\text{Cl}_2$ and $\text{Hg}(\text{MeQ})\text{Br}_2$ begin to decompose at 110°C and 100°C, respectively, by an endothermic reaction. The thermal degradation of the mercury compounds is completed exothermically with complete evolution of the sample as observed from the TG curves.

The room temperature current (I) versus voltage (V) characteristics were obtained for each compound under conditions of rising and falling voltage in both polarities. These characteristics indicate that $\text{Cd}(\text{MeQ})\text{Br}_2$ is the most conductive of the group of compounds. However, this compound also exhibits hysteresis and current saturation as shown in Fig. 5. For the polarity of the voltage initially applied, the current during growth of the voltage reaches a plateau where further increases in voltage have no effect on the flow of current. Reduction of the applied voltage produces a current at a level lower than the original current. When the polarity is reversed the hysteresis and saturation effect is evident although saturation then occurs at a higher voltage. These effects are found to be reproducible not only with the same disc but on another disc of the same compound, suggesting that the cause is in the properties of the compound itself rather than being due to the contacts because neither effect was observed for the other compounds and these were contacted by the same method. For crystalline inorganic solids, a saturation current density is known [10,11] to

TABLE 3

Electrical properties of the compounds

Compound	$\sigma \times 10^8$ ^a ($\Omega^{-1} \text{ m}^{-1}$)	m ^b	ρ^2 ^c	ΔE ^d (eV)	
				Heating	Cooling
Zn(MeQ) ₂ Cl ₂	3.10	1.25 ± 0.02	0.991	1.12	1.51
Zn(MeQ) ₂ Br ₂	8.10	1.14 ± 0.02	0.998	1.50	2.41
Cd(MeQ)Cl ₂	3.08	1.13 ± 0.03	0.997	1.18	1.48
Cd(MeQ)Br ₂ ^e	351	—	—	—	1.41
Hg(MeQ)Cl ₂	3.27	1.14 ± 0.01	0.998	1.39	1.22
Hg(MeQ)Br ₂	2.48	1.07 ± 0.01	0.998	1.26	1.62

^a Room temperature (21°C) conductivity for a mean field of $1 \times 10^4 \text{ V m}^{-1}$. (Mean field \equiv applied voltage/disc thickness.)

^b m is the exponent in the expression $|I| \propto |V|^m$ for the room temperature (21°C) characteristics of current (I) as a function of voltage (V). Least-squares fitting of a line to a plot of $\ln |I|$ against $\ln |V|$ was used to determine m .

^c Coefficient of determination in fitting m .

^d ΔE is the activation energy in the equation $\sigma = \sigma_0 \exp(-\Delta E/2kT)$. Least-squares fitting of a line to a plot of $\ln \sigma$ against T^{-1} was used to determine ΔE . Separate results are given for heating and cooling cycles.

^e Owing to the saturation effect exhibited by this compound, σ at room temperature is estimated from the linear portion of the I versus V characteristic.

exist due to scattering of hot electrons by acoustic and, more especially, optical phonons. It is possible that a similar mechanism operates for Cd(MeQ)Br₂ although the electric field for the onset of saturation is about an order of magnitude less than would be expected. The hysteresis effect has been observed in other compounds [12,13] which have been investigated using the same electrical method and was attributed to a combination of conduction and polarisation currents. Because Cd(MeQ)Br₂ does not obey Ohm's law, a true value of the conductivity cannot be defined. However, for the purpose of comparison with other materials, a conductivity has been determined from the linear portions of the I versus V data and is listed in Table 3.

As previously mentioned, no hysteresis or saturation effects were observed for the other compounds. All of these compounds exhibited slight upward curvature in the graphs of I versus V and, hence, exhibited slight departures from Ohm's law. When the data for the compounds are plotted logarithmically, the resulting graphs are linear, showing that I is proportional to V^m . The gradient, m , of each logarithmic plot was determined using least-squares regression. The values of m are in the range 1.07–1.25 and are listed in Table 3 along with the corresponding coefficient of determination (ρ^2) for the least-squares regression. The closeness to unity of all the ρ^2 values demonstrates the validity of the $I \propto V^m$ law. The fact that m exceeds unity is evidence for space charge conduction although the

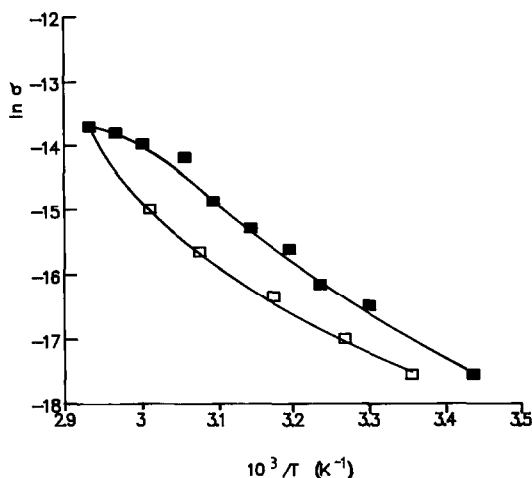


Fig. 6. Arrhenius plot (in the form of $\ln \sigma$ versus $10^3/T$ where σ = conductivity in units of $\Omega^{-1} \text{ m}^{-1}$ and T is the absolute temperature) for a disc of $\text{Hg}(\text{MeQ})\text{Br}_2$: ■, points obtained during heating; and □, points obtained during cooling.

model for this type of current limitation is more clearly formulated [14,15] to explain cases of $m > 2$ than it is for m only slightly larger than unity. Values of m in a similar range to those reported here have been observed for other organometallic compounds [2,16–18]. 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 $1 \times 10^4 \text{ V m}^{-1}$ and are listed in Table 3. This field is chosen as being representative of the mid-range of the applied fields covered in the electrical measurements.

The temperature dependence of the conductivity (σ) for $\text{Hg}(\text{MeQ})\text{Br}_2$ is shown in Fig. 6 as a plot of $\ln \sigma$ versus T^{-1} , where T is the absolute temperature. Linearity of such plots would show the validity of the equation $\sigma = \sigma_0 \exp(-\Delta E/2kT)$ where ΔE has the possible interpretation of being the activation energy for releasing free carriers. However, the data collected during cooling does not reproduce that during heating, even though the highest temperature reached was only 341 K which is below the temperature for onset of decomposition as found from the TG/DTA traces. The compounds $\text{Zn}(\text{MeQ})_2\text{Cl}_2$, $\text{Zn}(\text{MeQ})_2\text{Br}_2$, $\text{Cd}(\text{MeQ})\text{Cl}_2$ and $\text{Hg}(\text{MeQ})\text{Cl}_2$ exhibit a similar temperature dependence of conductivity to that described for $\text{Hg}(\text{MeQ})\text{Br}_2$. Values of ΔE calculated from the gradients of the best fitting lines for both the heating and cooling cycles, are listed in Table 3 for each compound. Evidently, as a result of the limited linearity of the plots and their non-reproduction for heating and cooling, caution must be exercised in the interpretation of the tabulated ΔE values.

From the plot of the temperature dependence of conductivity of $\text{Cd}(\text{MeQ})\text{Br}_2$ shown in Fig. 7, it can be seen that an increase in tempera-

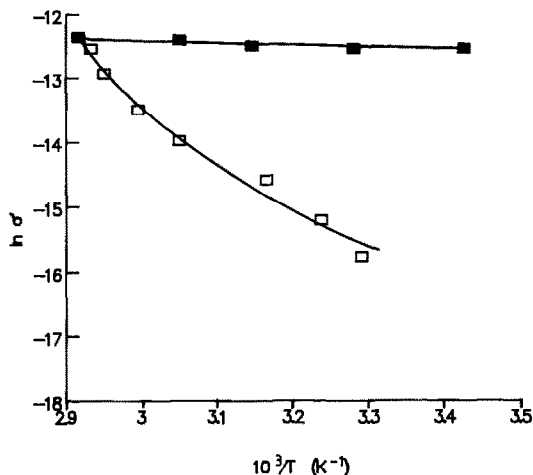


Fig. 7. Arrhenius plot (in the form of $\ln \sigma$ versus $10^3/T$ where σ = conductivity in units of $\Omega^{-1} m^{-1}$ and T is the absolute temperature) for a disc of $Cd(MeQ)Br_2$: ■, points obtained during heating; and □, points obtained during cooling.

ture has negligible effect on the conductivity. As this compound was the most conductive of the complexes prepared and exhibited current saturation at room temperature, a possible explanation is that the conductivity arises from activation of carriers from donor or acceptor levels which become fully ionised at room temperature.

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