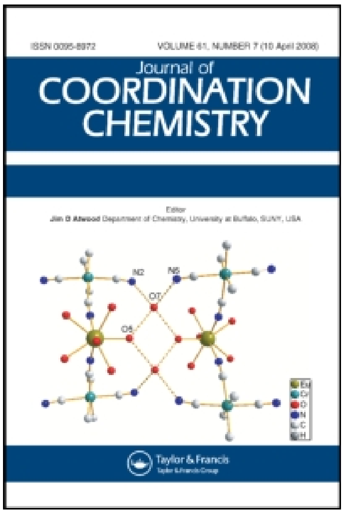

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Spectral, Magnetic and Electrical Studies on Complexes of some First Row Transition Elements with 2,9-Dimethyl-4,7-Diphenyl-1,10-Phenanthroline

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SPECTRAL, MAGNETIC AND ELECTRICAL STUDIES ON COMPLEXES OF SOME FIRST ROW TRANSITION ELEMENTS WITH 2,9-DIMETHYL-4,7-DIPHENYL-1,10-PHENANTHROLINE

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Some new compounds of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline with cobalt(II), nickel(II), copper(II) and zinc(II), have been prepared in ethanolic solution. The cobalt, nickel and zinc compounds have tetrahedral structures while the copper compound has an octahedral structure. All of the compounds, including 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline itself, exhibit a superlinear I *versus* V relationship. It is concluded that the metal ion in the complexes does not play an important role in electrical conduction.

Keywords: 1,10-phenanthrolines, complexes, conduction, solid state, properties

INTRODUCTION

This work is a continuation of previously reported studies on the electrical, spectral and magnetic properties of complexes of some transition metals with heterocyclic ligands.[1-5] Spectral and magnetic studies have shown that most of these previously investigated compounds have polymeric structures with the metal ion in an octahedral environment. The electrical measurements indicate that some compounds exhibit ohmic behaviour while others show the presence of space charge limited current. In the compounds formed between pyrazine-2,3-dicarboxylic acid and manganese, cobalt, nickel and zinc a current component opposing the applied voltage was observed.[3] The high conductivity observed for the two-ring quinoxaline complexes compared with the single ring pyrazine complexes has encouraged us to investigate a set of compounds containing a multi-ring system because of the potential for application in solid state devices such as electro-optical systems.

This paper reports some electrical, spectral and magnetic studies of the dichloro

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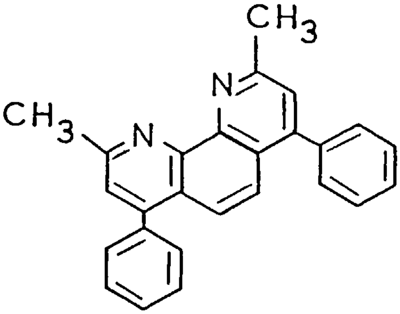
* Author for correspondence

complexes of 2,9-dimethyl-4,7-diphenyl-1,10 phenanthroline with cobalt, nickel, copper and zinc.



2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (phen).

EXPERIMENTAL

Preparation of Compounds

1.5 g of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline dissolved in 40 cm^3 of warm ethanol was added to 1 g of the metal halide dissolved in 25 cm^3 of warm ethanol. The mixture was boiled and as the volume of ethanol decreased, the complex precipitated. The complexes were recrystallized from ethanol and dried at 50°C in an oven. The compounds prepared by the above method are listed in Table I.

TABLE I
Analytical and magnetic data for the complexes.

	Calc(%)				Found(%)				
Compound	M	C	H	N	M	C	H	N	μ(B.M.)
Co(phen)Cl_2	12.01	63.69	4.52	5.71	11.44	62.91	4.44	5.12	4.42
Ni(phen)Cl_2	11.97	63.72	4.52	5.71	11.22	63.41	4.21	5.10	3.44
Cu(phen)Cl_2	12.83	63.10	4.48	5.66	12.66	63.02	4.12	5.45	1.76
Zn(phen)Cl_2	13.16	62.86	4.46	5.63	12.42	62.66	4.08	5.45	dia.

Apparatus and Measurements

The analysis of the metal ion was determined by using a Perkin-Elmer 373 atomic absorption spectrophotometer and carbon, hydrogen and nitrogen analyses using a Carlo Erba elemental analyser. The magnetic moments, Table I, were measured by the Gouy method using Hg[Co(SCN)$_4$] as calibrant. Each magnetic moment has been corrected for diamagnetism using Pascal's constants.[6] The infrared spectra, Table II, using KBr (4000–600 cm^{-1}) and polyethylene discs (600–200 cm^{-1}) were obtained with a Perkin-Elmer 598 infrared spectrophotometer. The electronic spectra, Table III, were obtained with the compounds in chloroform solution using a Beckman Acta MIV spectrophotometer.

TABLE II
Characteristic infrared spectral data for the compounds (4000–200 cm^{-1}).

Compound	Ring Vibrations		$\nu_{M\text{-}X}$		$\nu_{M\text{-}N}$
phen	1599(s)	1489(s)			
Co(phen)Cl_2	1608(s)	1492(s)	348(s),	320(s)[a]	270(m)[b]
Ni(phen)Cl_2	1603(s)	1491(s)	321(s).	354(s)[c]	276(m)[b]
Cu(phen)Cl_2	1602(s)	1493(s)	310(s)[d]		270(m)[b]
Zn(phen)Cl_2	1603(s)	1494(s)	324(s)[e]		273(m)[b]

[a] Ref. 13. [b] Ref. 16. [c] Ref. 14. [d] Ref. 12. [e] Ref. 15.

TABLE III
Electronic spectral data for the complexes.[a]

Compound	Peak Position (cm^{-1})	d–d Transition
Co(phen)Cl_2	7575 $(\varepsilon = 12)$	${}^4A_2(F) \rightarrow {}^4T_1(F)$
	17483 $(\varepsilon = 24)$	${}^4A_2(F) \rightarrow {}^4T_1(P)$
Ni(phen)Cl_2	10362 $(\varepsilon = 15)$	${}^3T_1(F) \rightarrow {}^3T_2(F)$
	16140 $(\varepsilon = 2.5)$	${}^3T_1(F) \rightarrow {}^3A_2(F)$
	20576 $(\varepsilon = 13)$	${}^3T_1(F) \rightarrow {}^3T_1(P)$
Cu(phen)Cl_2	12048 $(\varepsilon = 11)$	${}^2E_g(D) \rightarrow {}^2T_{2g}(D)$

[a] The extinction coefficients (mol^{-1} m^2) are given in parentheses.

Electrical measurements were made under d.c. conditions on discs of the compounds, including the free ligand, formed by compressing a powder. These discs were of 13 mm diameter and thicknesses ranged from 0.66 mm to 1.59 mm. Electrodes of 4.9 mm diameter were formed on the flat faces of the discs by applying a silver-based conductive paint. Details of the method have been previously described.[1–5] For each compound the current was measured at room temperature as a function of applied voltage with voltage increasing and decreasing in both polarities. The current was also measured under a fixed applied voltage of 10 V as the disc temperature was changed over the typical range 290 K to 360 K. These readings were obtained during heating and cooling.

RESULTS AND DISCUSSION

The compounds listed in Table I, all of which were isolated from ethanolic solution, have stoichiometry M(phen)Cl_2 where M = Co, Ni, Cu, Zn.

The wavenumbers of the infrared absorption bands as well as their descriptions and assignments are given in Table II. The infrared spectra of the complexes are almost identical to that of the 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline in the region 4000–600 cm^{-1} except for the bands due to the ring vibrations of the aromatic ring which move to higher frequency on forming complexes. This would suggest that the nitrogen atom in the aromatic ring is coordinated to a metal atom.[7] Metal–nitrogen and metal–halogen bands observed for each complex in the region 600–200 cm^{-1} are also reported in Table II.

The d–d bands from the electronic absorption spectra of the compounds are shown in Table III. The position of the bands and the values of the extinction coefficients indicate that the nickel and cobalt ions are in a tetrahedral environment,[8] while the copper ions are in an octahedral environment.[7,8]

From the measured magnetic moments, Table I, there also is evidence[9–11] that the metal ions in the cobalt and nickel compounds are in a tetrahedral environment. This is consistent with the structure deduced from the electronic spectra. The magnetic moment for the copper compound is similar to the spin-only value.

The far infrared spectra, Table II, would support an octahedral structure for the copper compound[12] and a tetrahedral structure for the cobalt and nickel compounds.[13–15] The band at 324 cm^{-1} in the zinc compound is indicative of a tetrahedral structure.

The fact that no suitable single crystals could be obtained for each of the compounds means that no complete structure determination can be made. In the cobalt and nickel compounds the metal atom is bonded to two chlorine atoms and to the two nitrogen atoms of the 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline molecule. In the copper compounds it is suggested that there is a planar arrangement of ligands about the copper atom with the apical positions free to coordinate to halogens in neighbouring Cu(phen)Cl_2 groups.[12]

Since the current through a disc of the compound was measured with voltage increasing and decreasing in both polarities, it follows that for any given voltage magnitude four readings of current were obtained. These four currents agreed in absolute value always within 10% and usually much closer than this, indicating that the silver paint contacts are not rectifying. Graphs of mean current magnitude (I) against mean applied voltage magnitude (V) were drawn from the data obtained at room temperature and in all cases slight departure from ohmic behaviour was displayed; the curves bent upwards with increasing V. Log–log plots of I *versus* V were linear for all of the compounds showing that $I \propto V^m$ with m constant for any given compound. Values of m as found from the gradients of these lines, based on least-squares linear regression, are listed in Table IV. It is seen that over the range of electric fields covered, which was up to 3×10^4 Vm^{-1}, the range of values of m is from 1.06 to 1.31. A model has been described elsewhere[17,18] which leads to a relationship of the form $I = AV + BV^2$ where A and B are constants for a given device and it is reasonable to suggest that with a suitable combination of the linear and quadratic terms this equation could also describe the observed results. Accordingly, for each compound I/V was plotted against V since such a graph would be linear if $I = AV + BV^2$ is a valid relationship. Figures 1 and 2 show plots of $\log_{10}I$ *versus* $\log_{10}V$ and I/V *versus* V based on the same data for the phen. The description of the results by $I \propto V^m$ is seen to be much superior to $I = AV + BV^2$ and the same conclusion was reached also for the complexes. Values of m greater than $m = 2$ can readily be explained[19–21] on the basis of space charge limited current (SCLC) in the presence of a trap distribution which is exponentially distributed in energy, and values of m slightly less than two, say $1.80 < m < 2.00$, have been explained by the present authors[4] by incorporating partial saturation of drift velocity into the model.

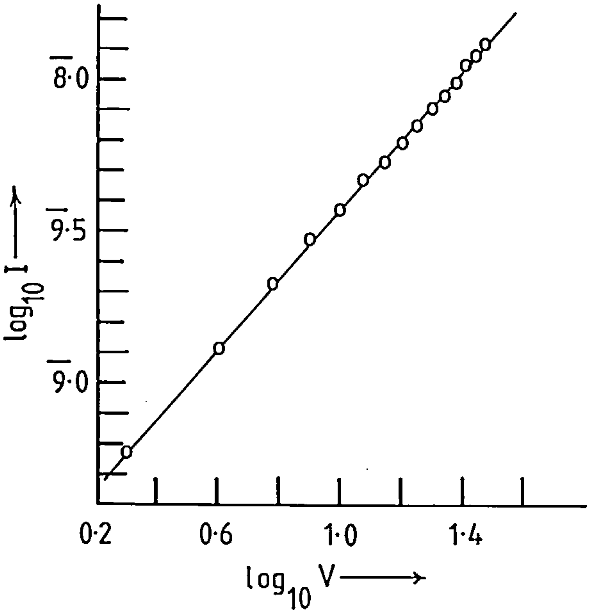


FIGURE 1 Plot of $\log_{10}$ I *versus* $\log_{10}$ V for a disc of phen of thickness 1.59 mm at room temperature.

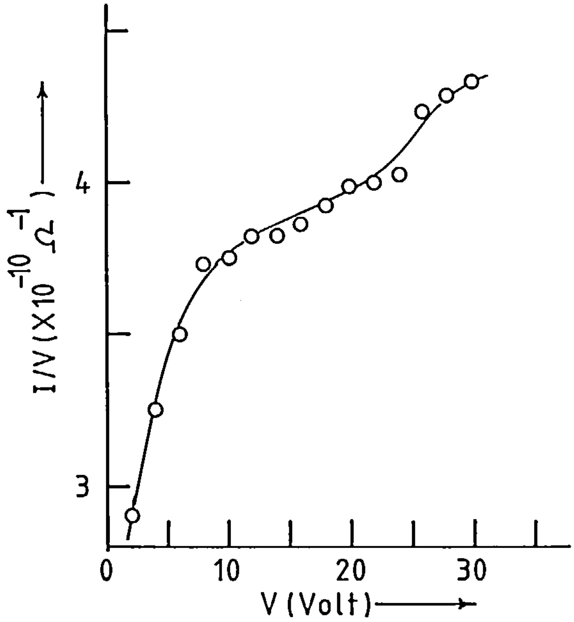


FIGURE 2 Plot of I/V *versus* V for a disc of phen at room temperature. The same experimental data is used as for Figure 1.

It is more problematical to explain values of m which significantly exceed unity and yet are much less than 1.5, as found here for phen and its chloro complexes. SCLC through a suitable non-exponential trap distribution could explain the behaviour, although no definitive model appears to be available in the literature. Over a similar range of electric fields to those used here, values of m in the range $0.80 < m < 1.25$ have been reported[22] for poly(phenyleneaminochloranils).

TABLE IV
Electrical properties of the compounds.

Compound	m^a	Conductivity^b ($\Omega^{-1} m^{-1}$)	ΔE^c (eV)
phen	1.13 ± 0.01	3.3×10^{-8}	1.61
$Co(phen)Cl_2$	1.06 ± 0.01	1.3×10^{-8}	1.40
$Ni(phen)Cl_2$	1.14 ± 0.04	2.9×10^{-6}	
$Cu(phen)Cl_2$	1.31 ± 0.03	2.2×10^{-8}	1.65
$Zn(phen)Cl_2$	1.22 ± 0.02	6.7×10^{-7}	0.39

[a] The number m is the exponent in the expression $I \propto V^m$ and has been determined from least-squares fitting of a line in a log I *versus* log V plot to room temperature data. [b] Conductivity listed is the ratio current density/mean field for a mean field of $1 \times 10^4\ Vm^{-1}$ at room temperature [c] ΔE is the activation energy in the equation $\sigma = \sigma_0 \exp(-\Delta E/2kT)$ and is determined from the gradients of $\ln \sigma$ *versus* 1/T graphs.

Since the electrical behaviour of the compounds is not ohmic it is not possible to assign a unique conductivity to each, but Table IV includes the conductivity (calculated from current density/mean field) corresponding to a mean of $1 \times 10^4\ Vm^{-1}$.

Figure 3 shows plots of $\ln \sigma$ *versus* $10^3/T$ for all of the compounds, except $Ni(phen)Cl_2$, where σ is the conductivity for an applied potential of 10V and T is the absolute temperature. For $Ni(phen)Cl_2$ the data obtained during heating was not reproduced during subsequent cooling but for the other compounds there was good reproducibility. From the gradient of the steep linear region of each curve in Figure 3 the activation energy ΔE in the equation $\sigma = \sigma_0 \exp(-\Delta E/2kT)$ has been determined and is listed in Table IV. For $Zn(phen)Cl_2$ the value of ΔE as found in this way is much lower than for phen, $Cu(phen)Cl_2$ or $Co(phen)Cl_2$. This suggests that the measured ΔE for the zinc compound corresponds to the ionization energy of a donor or acceptor impurity, but for the other compounds the measured ΔE corresponds to an intrinsic activation. It is consistent with this suggestion that for the compounds represented in Figure 3, the zinc compound has by far the highest room temperature conductivity.

The evidence from Figure 3 indicates that the metal ion in the $M(phen)Cl_2$ complexes does not play a major role in the electrical conductivity of the complexes since ΔE differs little amongst the compounds phen, $Cu(phen)Cl_2$ and $Co(phen)Cl_2$ and there is only a small difference between the room temperature conductivities for these three compounds. The relatively high room temperature conductivity for $Ni(phen)Cl_2$ is considered to be due to donor or acceptor impurities of small ionization energy.

In conclusion the conductivity of the phen complexes is much lower than those of the corresponding quinoxaline compounds.[2] This would indicate, contrary to scientific expectation, that the presence of a multi-ringed π electron system does not automatically lead to enhanced conductivity.

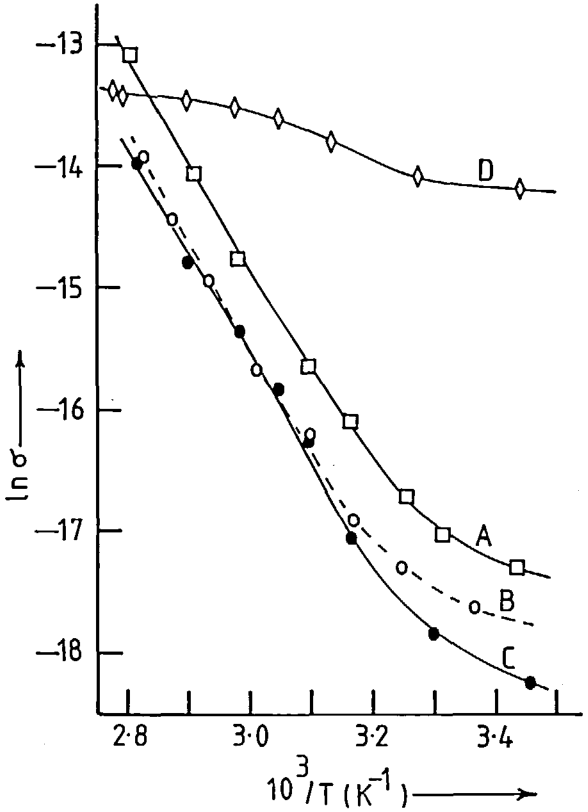


FIGURE 3 Plots of ln σ *versus* $10^3/T$ for A: (—□—) phen; B: (--O--) $Cu(phen)Cl_2$; C: (—●—) $Co(phen)Cl_2$; D: (—◇—) $Zn(phen)Cl_2$. The parameter σ is in units of $\Omega^{-1}\,m^{-1}$ and is determined with a constant 10V applied across the disc.

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