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Structural, thermal and electrical studies of some transition metal compounds of 2,3-cyclododecenopyridine

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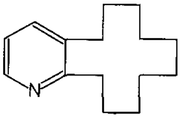
Abstract

The chloro complexes of manganese, cobalt, nickel, copper and zinc with 2,3-cyclododecenopyridine were prepared in ethanolic solution from which solid compounds were isolated. The suggested structure for the cobalt and zinc compounds is tetrahedral while for the manganese, nickel and copper compounds it is octahedral The techniques of thermogravimetry and differential thermal analysis show that 2,3-cyclododecenopyridine nickel(II) chloride and bis(2,3-cyclododecenopyridine) copper(II) chloride form intermediate compounds before their metal oxides are produced. The other compounds lose the organic ligand and the halogen to give the metal oxide.

A linear correlation, believed to be associated with tunnelling of electrons between intermolecular barriers, has been found between $\ln \sigma_0$ and ΔE where these quantities are defined by the equation $\sigma = \sigma_0 \exp(-\Delta E/2kT)$ for the temperature dependence of the conductivity.

INTRODUCTION

Thermal analyses, structural and electrical studies of some first row transition metal complexes with substituted pyridines have previously been reported [1–4]. In most of these cases the pyridine ring was either fused or linked to benzoid moieties. In the present investigation we consider a molecule where the pyridine ring is fused to an alicyclic system. The compound 2,3-cyclododecenopyridine has one donor site for forming bonds with metal ions: the nitrogen atom of the aromatic ring.



2,3-Cyclododecenopyridine ($C_{15}H_{23}N$)

We report studies of the chloro complexes of manganese, cobalt, nickel, copper and zinc with 2,3-cyclododecenopyridine. Spectral and magnetic measurements were 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 and their electrical conductivity have been investigated.

EXPERIMENTAL

Preparation of complexes

(A) The metal(II) halide (0.05 mol) was dissolved in the minimum volume of boiling ethanol. To the boiling ethanol solution, 0.10 mol of 2,3-cyclododecenopyridine 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 filtered, washed with the minimum volume of ethanol and air dried.

(B) Other complexes, with smaller amounts of the ligand, were obtained by heating the compounds prepared by method A. The heating was performed on a thermobalance at a fixed temperature until a constant weight remained.

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 Beckmann Acta MIV spectrophotometer. Measurements of magnetic moments were made using the Gouy method with $Hg[Co(SCN)_4]$ as calibrant. The thermal analysis measurements were made on a Stanton Redcroft Model 1500 thermobalance. Thermogravimetry (TG) and differential thermal analysis (DTA) curves were obtained at a heating rate of 6 °C min^{-1} in static air. The 20–800 °C temperature range was studied in all cases.

Electrical measurements, comprising (i) current as a function of voltage at room temperature and (ii) current as a function of temperature at fixed voltage, were obtained for the five initially prepared compounds only. For these measurements, discs of diameter 13 mm and thickness in the range 0.56–0.98 mm, were formed by compressing powder in a hydraulic press which was set to apply a force of 100 kN. An electrode 4.9 mm in diameter was placed concentrically on each of the two flat faces of every disc by applying conductive silver paint through masks. Contact to the electrodes on a given disc was made by placing the disc on a copper strip (which made contact to the lower electrode) whilst sprung steel wire held an aluminium pad on the upper electrode. The measurements of current involved in (i) and (ii) above were obtained using a Keithley 610C electrometer. For (i) the voltage was increased from zero to 30 V and then decreased back to zero, in both cases in 2 V increments; this was repeated for reversed polarity. For (ii), each disc in turn was placed in an electrically heated oven and heated over the approximate temperature range 293–350 K, with subsequent cooling back to the original temperature. During this thermal cycle, a constant potential of 10 V was applied across the disc whilst pairs of readings of current and temperature were obtained at frequent intervals. The latter readings used a calibrated copper–constantan thermocouple, formed from 44 SWG wires, having its hot and cold junctions respectively on the disc and in melting ice.

RESULTS AND DISCUSSION

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

The reaction of manganese(II) chloride with 2,3-cyclododecenopyridine in ethanolic solution resulted in the formation of a complex of stoichiometry $Mn(C_{15}H_{23}N)Cl_2$. The electronic reflectance spectrum (Table 2), of this compound suggests that the compound has an octahedral structure [5]. The weak bands observed have been assigned to the transitions $^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$ and $^6A_{1g}(S) \rightarrow {}^4E_g(G)$, $^4A_{1g}(G)$. The magnetic moment for the compound is 5.96 BM. This is similar to the spin-only value (high spin d^5 configuration, $S = 5/2$) which is normally observed for manganese(II) compounds. The compound $Co(C_{15}H_{23}N)Cl_2$ was formed between cobalt(II) chloride and 2,3-cyclododecenopyridine in ethanolic solution. The electronic reflectance spectrum (Table 2) of this compound is characteristic of cobalt(II) in a tetrahedral environment [6]. The observed transitions are $^4A_2(F) \rightarrow {}^4T_1(F)$ and $^4A_2(F) \rightarrow {}^4T_1(P)$. The magnetic moment for the compound agrees with the suggestion of a tetrahedral arrangement of ligands around the cobalt ion since it lies in the range 4.2–4.8 BM [6]. The nickel(II) ion forms a compound of stoichiometry $Ni(C_{15}H_{23}N)Cl_2$ in ethanolic solution with 2,3-cyclododecenopyridine. The electronic reflectance spectra (Table 2) of the compound resemble those normally found for nickel(II) in an octahedral environment [1]. The observed transitions are $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$. The suggestion of an octahedral structure for this compound is further supported by its magnetic moment which lies in the range 2.8–3.4 BM normally observed for compounds where the nickel ion is in an octahedral environment [5]. The copper compound isolated from

TABLE 1

Analyses of the compounds

Compound	Method of preparation	Theory (%)				Found (%)			
		Metal	Carbon	Nitrogen	Hydrogen	Metal	Carbon	Nitrogen	Hydrogen
$Mn(C_{15}H_{23}N)Cl_2$	A	16.00	52.49	4.08	6.75	15.96	52.28	4.21	6.58
$Co(C_{15}H_{23}N)Cl_2$	A	16.97	51.89	4.03	6.67	16.42	51.60	4.01	6.49
$Ni(C_{15}H_{23}N)Cl_2$	A	16.92	51.92	4.03	6.68	16.76	51.84	3.92	6.46
$Ni_3(C_{15}H_{23}N)_2Cl_6$	B	20.63	42.21	3.28	5.43	20.45	42.08	3.04	5.19
$Cu(C_{15}H_{23}N)_2Cl_2$	A	11.16	63.32	4.92	8.14	11.02	63.46	4.75	8.09
$Cu_3(C_{15}H_{23}N)_4Cl_6$	B	14.97	56.62	4.40	7.28	14.68	56.27	4.35	7.14
$Cu_3(C_{15}H_{23}N)_2Cl_6$	B	22.74	42.99	3.34	5.53	22.67	42.76	3.32	5.38
$Zn(C_{15}H_{23}N)_2Cl_2$	A	11.44	63.10	4.90	8.12	11.36	63.01	4.86	8.11

TABLE 2

Electronic spectra and magnetic measurements

Compound	Band position (cm^{-1})	d–d transition	μ (BM)
$Mn(C_{15}H_{23}N)Cl_2$	15625	${}^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$	5.96
	24096	${}^6A_{1g}(S) \rightarrow {}^4E_g(G)$, ${}^4A_{1g}(G)$	
$Co(C_{15}H_{23}N)Cl_2$	7352	${}^4A_2(F) \rightarrow {}^4T_1(F)$	4.23
	15503	${}^4A_2(F) \rightarrow {}^4T_1(P)$	
	19305		
$Ni(C_{15}H_{23}N)Cl_2$	8196	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	3.37
	13888	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	
	24271	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	
$Cu(C_{15}H_{23}N)_2Cl_2$	11904	${}^2E_g(D) \rightarrow {}^2T_{2g}(D)$	2.08

ethanolic solution has the stoichiometry $Cu(C_{15}H_{23}N)_2Cl_2$. A broad band is observed at 11 904 cm^{-1} in its reflectance spectrum, indicating that the copper ion is in an octahedral environment [5]. The compound has a magnetic moment of 2.08 BM, indicating no magnetic spin–spin interaction between copper atoms. The zinc compound isolated from ethanolic solution has the stoichiometry $Zn(C_{15}H_{23}N)_2Cl_2$. The compound is diamagnetic and no d–d bands are observed in its reflectance spectrum because the zinc ion has a d^{10} electronic configuration.

The main bands in the IR spectra of 2,3-cyclododecenopyridine and its complexes isolated from the ethanolic solutions are listed in Table 3. The IR spectrum of 2,3-cyclododecenopyridine is almost identical with those of its complexes in the region 4000–600 cm^{-1} except for the bands due to the ring vibrations of the aromatic ring which move to higher wavenumbers in the complexes. This suggests that coordination occurs between the metal and the nitrogen atom in the ring [5]. Metal–chloride and metal–nitrogen bands are

TABLE 3

IR spectra (4000–200 cm^{-1}) [a]

Compound	Ring vibrations		ν(M–N)	ν(M–Cl)
$C_{15}H_{23}N$	1570(s)	1470(s)	–	–
$Mn(C_{15}H_{23}N)Cl_2$	1620(s)	1472(s)	252(m)	224(m)
$Co(C_{15}H_{23}N)Cl_2$	1592(s)	1479(s)	256(m)	308(s), 288(s)
$Ni(C_{15}H_{23}N)Cl_2$	1615(s)	1483(s)	266(m)	220(m)
$Cu(C_{15}H_{23}N)_2Cl_2$	1592(s)	1470(s)	268(m)	225(m)
$Zn(C_{15}H_{23}N)_2Cl_2$	1594(s)	1471(s)	250(m)	312(s), 298(s)

[a] s, strong; m, medium.

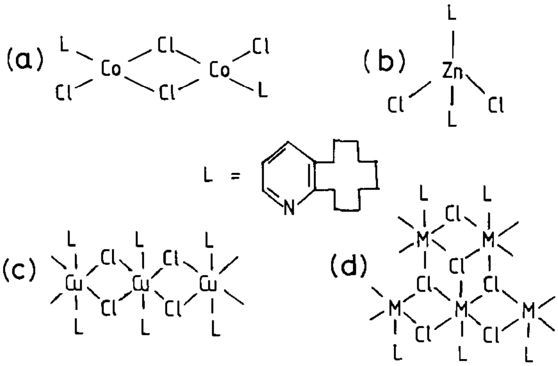


Fig. 1. Proposed stereochemistry of the metal complexes with cyclododecenopyridine (L): (a) $CoLCl_2$; (b) ZnL_2Cl_2; (c) CuL_2Cl_2; (d) $MLCl_2$ where M = Mn or Ni.

assigned for the complexes and are reported. The assignment of the ν(M–Cl) vibrations for the cobalt and zinc complexes shows that they have tetrahedral structures [6,7] while for the manganese, nickel and copper complexes the ν(M–Cl) vibrations are indicative of octahedral structures [5].

The fact that no single crystals were obtained on precipitation of the complexes from ethanolic solution means that no complete structure determination can be made. However, the spectroscopic and magnetic data enable us to infer that the metal atoms in the cobalt and zinc complexes are in a tetrahedral environment. It is suggested that the cobalt compound has a dimeric structure made up of bridging and terminal halogen atoms and the 2,3-cyclododecenopyridine molecules are present as terminal ligands (Fig. 1(a)). In the zinc compound, the zinc atom is bonded to two chlorine atoms and to two molecules of 2,3-cyclododecenopyridine through the nitrogen atom of the aromatic ring (Fig. 1(b)).

The poor solubility of the manganese, nickel and copper compounds in polar and non-polar solvents suggests that they have polymeric structures [5]. The copper compound, $Cu(C_{15}H_{23}N)_2Cl_2$, is considered to consist of a chain of copper atoms bonded to halogens with a 2,3-cyclododecenopyridine molecule on each side of the plane of the copper–halogen chain, bonded to the copper atom through the lone pair of electrons on the nitrogen atom of the aromatic ring (Fig. 1(c)). The manganese and nickel compounds, $Mn(C_{15}H_{23}N)Cl_2$ and $Ni(C_{15}H_{23}N)Cl_2$, are considered to consist of a double chain in which each halogen acts as a bridge between three metal atoms with the 2,3-cyclododecenopyridine molecules bonded through the nitrogen atoms of the aromatic ring on each side of the plane of the metal–halogen chains (Fig. 1(d)).

The results of the thermogravimetric studies are given in Figs. 2–6 and Table 4. The TG traces show that the manganese, cobalt and zinc compounds begin to decompose at 135 °C, 156 °C and 175 °C, respectively, with loss of organic ligand and chloride to give the metal oxide. The DTA trace

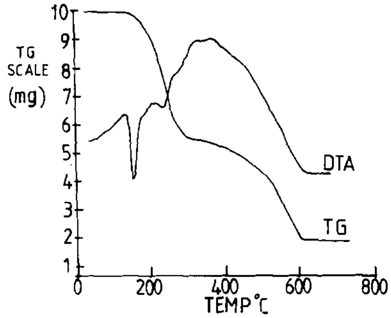


Fig. 2. TG and DTA traces for $Mn(C_{15}H_{23}N)Cl_2$. Sample weight, 9.99 mg.

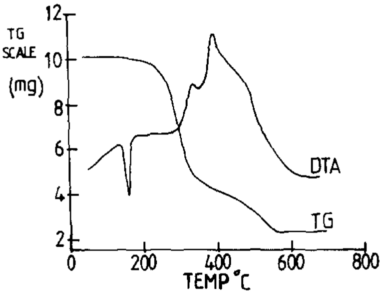


Fig. 3. TG and DTA traces for $Co(C_{15}H_{23}N)Cl_2$. Sample weight, 10.24 mg.

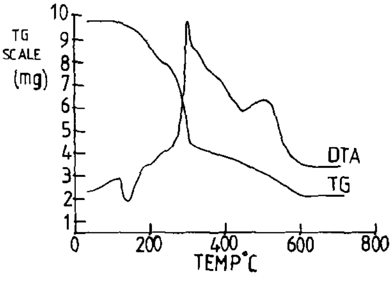


Fig. 4. TG and DTA traces for $Ni(C_{15}H_{23}N)Cl_2$. Sample weight, 9.98 mg.

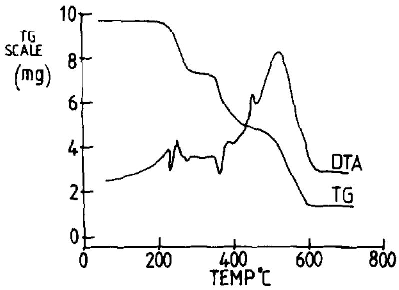


Fig. 5. TG and DTA traces for $Cu(C_{15}H_{23}N)_2Cl_2$. Sample weight, 9.67 mg.

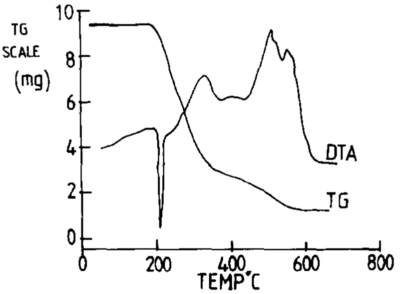


Fig. 6. TG and DTA traces for $Zn(C_{15}H_{23}N)_2Cl_2$. Sample weight, 9.68 mg.

for each of the compounds indicates that the weight loss is accomplished by endothermic and exothermic reactions (Figs. 2–6). The nickel compound undergoes an endothermic reaction at 118°C with loss of one-third of a molecule of 2,3-cyclododecenopyridine, followed by an exothermic reaction at 253°C and loss of the remaining two-thirds of a molecule of 2,3-cyclododecenopyridine and chlorine to give NiO.

The originally prepared copper compound, $Cu(C_{15}H_{23}N)_2Cl_2$, undergoes endothermic reactions at 176 and 345°C, followed by an exothermic reaction at 456°C. At each of these three temperatures there is, per molecule of the original compound, loss of two-thirds of a molecule of 2,3-cyclododecenopyridine, thus accounting for all the ligand initially present. In addition, in the exothermic process at 456°C, the chlorine atoms are expelled and the final residue is CuO.

All the initially prepared compounds were found to increase in electrical conductivity (by about 15%) on reversal of the applied voltage polarity after an initial voltage application. The compounds all exhibit a small departure from Ohm's law as may be seen from the non-unity values of the exponent m listed in Table 5 for the room temperature current (I) against voltage (V)

TABLE 4

Thermal decomposition products

Starting material	Decomposition temperature (°C)	Product	Weight loss (% of initial weight)	
			Calc.	Found
$Mn(C_{15}H_{23}N)Cl_2$	135	Mn_2O_3	79.33	79.87
$Co(C_{15}H_{23}N)Cl_2$	156	Co_3O_4	78.42	79.14
$Ni(C_{15}H_{23}N)Cl_2$	118	$Ni_3(C_{15}H_{23}N)_2Cl_6$	20.87	20.84
	253	NiO	78.47	78.95
$Cu(C_{15}H_{23}N)_2Cl_2$	176	$Cu_3(C_{15}H_{23}N)_4Cl_6$	25.44	25.54
	345	$Cu_3(C_{15}H_{23}N)_2Cl_6$	50.88	50.35
	456	CuO	86.02	86.40
$Zn(C_{15}H_{23}N)_2Cl_2$	175	ZnO	85.74	86.58

TABLE 5

Electrical properties of the initially prepared compounds

Compound	m [a]	$\sigma \times 10^7$ [b] (Ω^{-1} m^{-1})	ΔE [c] (eV) Heating	Cooling	Combined heating and cooling
$Mn(C_{15}H_{23}N)Cl_2$	1.17 ± 0.02	1.55 ± 0.17	1.09 ± 0.06	1.35 ± 0.04	1.26 ± 0.05
$Co(C_{15}H_{23}N)Cl_2$	1.31 ± 0.02	1.55 ± 0.15	0.96 ± 0.07	1.48 ± 0.06	1.25 ± 0.14
$Ni(C_{15}H_{23}N)Cl_2$	1.20 ± 0.02	0.50 ± 0.04	1.37 ± 0.22	1.93 ± 0.11	1.65 ± 0.13
$Cu(C_{15}H_{23}N)_2Cl_2$	1.55 ± 0.02	15.2 ± 1.1	0.39 ± 0.09	0.93 ± 0.04	0.69 ± 0.09
$Zn(C_{15}H_{23}N)_2Cl_2$	1.23 ± 0.01	0.37 ± 0.02	1.18 ± 0.04	1.72 ± 0.07	1.49 ± 0.10

[a] 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.

[b] Room temperature (21°C) conductivity for a mean field of 1×10^4 V m^{-1} (mean field ≡ applied voltage/disc thickness).

[c] 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, cooling and the combined heating/cooling cycle.

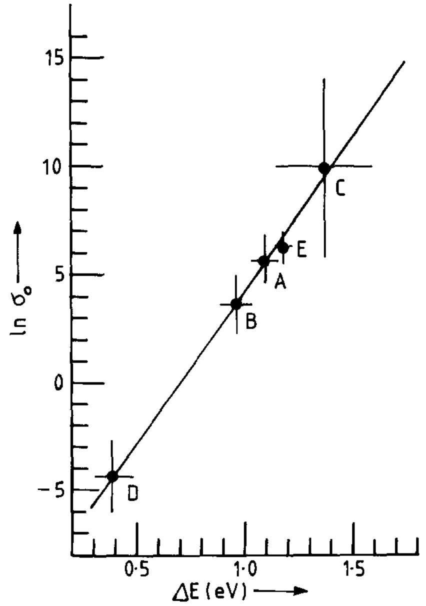


Fig. 7. Plot of $\ln \sigma_0$ against ΔE (with σ_0 and ΔE defined by the equation $\sigma = \sigma_0 \exp(-\Delta E/2kT)$ for the temperature dependence of conductivity σ) for the complexes, based on values of σ_0 and ΔE for heating: A, $Mn(C_{15}H_{23}N)Cl_2$; B, $Co(C_{15}H_{23}N)Cl_2$; C, $Ni(C_{15}H_{23}N)Cl_2$; D, $Cu(C_{15}H_{23}N)_2Cl_2$; E, $Zn(C_{15}H_{23}N)_2Cl_2$. The line is fitted by least squares and has the equation $\ln \sigma_0 = (14.3 \pm 0.6)\,\Delta E - (10.1 \pm 0.6)$ with σ_0 and ΔE respectively in units of Ω^{-1} m^{-1} and eV.

characteristics (m is the exponent in the empirical expression $|I| \propto |V|^m$). The small excess of each value of m over unity is attributed to partial space-charge limitation of current. The room temperature conductivities given in Table 5 refer to an arbitrarily chosen mean field of 1×10^4 V m^{-1} although, because departure from Ohm's law is small, similar conductivities would be obtained for other fields within the measurement range. The conductivity for the copper compound is higher by almost one order of magnitude than for the next most conductive compound. No explanation is offered for this behaviour—it is not because two molecules of the ligand are associated with one metal atom because this is also the case for the zinc complex and this is the least conductive. There is no apparent correlation between measured conductivities and the nature of the metal atom environment.

From the temperature dependence of the electrical conductivity, values of the activation energy ΔE in the equation $\sigma = \sigma_0 \exp(-\Delta E/2kT)$ (where σ is the conductivity at absolute temperature T) were determined and are listed in Table 5. Although the maximum temperature (350 K) to which the compounds were heated in investigating the temperature dependence of the conductivity is well below that found from thermogravimetry for the onset

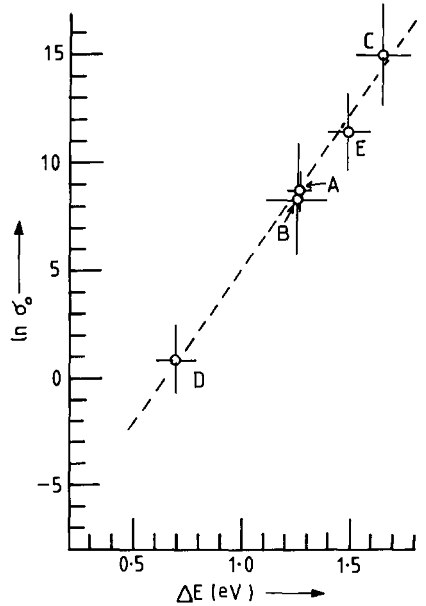


Fig. 8. Plot of $\ln \sigma_0$ against ΔE (with (σ_0 and ΔE defined by the equation $\sigma = \sigma_0 \exp(-\Delta E/2kT)$ for the temperature dependence of conductivity σ) for the complexes, based on values of σ_0 and ΔE from the combined heating and cooling cycle: A, $Mn(C_{15}H_{23}N)Cl_2$; B, $Co(C_{15}H_{23}N)Cl_2$; C, $Ni(C_{15}H_{23}N)Cl_2$; D, $Cu(C_{15}H_{23}N)_2Cl_2$; E, $Zn(C_{15}H_{23}N)_2Cl_2$. The line is fitted by least squares and has the equation $\ln \sigma_0 = (14.3 \pm 0.7)\,\Delta E - (9.3 \pm 0.9)$ with σ_0 and ΔE respectively in units of Ω^{-1} m^{-1} and eV.

of decomposition, there is poor agreement between ΔE values from the heating and cooling phases. Despite this poor reproducibility, there is clear evidence from Figs. 7 and 8 of a correlation between the activation energy ΔE and the pre-exponential factor σ_0 in the conductivity equation $\sigma = \sigma_0 \exp(-\Delta E/2kT)$. The linearity of the plots in these two figures shows that the correlation is of the form $\ln \sigma_0 = \alpha \, \Delta E + \beta$ in which α and β are constants for the series of complexes investigated. Moreover, the lines in the plots have essentially the same equation because from Fig. 7, $\alpha = 14.3 \pm 0.6$ $(\text{eV})^{-1}$ and $\beta = -10.1 \pm 0.6$, whilst from Fig. 8, $\alpha = 14.3 \pm 0.7$ $(\text{eV})^{-1}$ and $\beta = -9.3 \pm 0.9$ (quoted values of α and β correspond to σ_0 expressed in units of Ω^{-1} m^{-1}). A correlation between $\ln \sigma_0$ and ΔE of the form described, also with $\alpha > 0$, has been observed [8,9] for other series of compounds and a plausible theoretical explanation [10,11] has been given in terms of electron tunnelling through successive intermolecular barriers in the bulk material. A different and equally plausible model has been offered [12] to explain the correlation, based on carrier tunnelling injection from the electrodes through a surface barrier. Our electrical data therefore suggest that one of these models is applicable for the complexes studied. The closeness of the fit of our data to the equation $\ln \sigma_0 = \alpha \, \Delta E + \beta$ is perhaps surprising because, amongst the complexes, there are two types of metal environment and two ratios of numbers of ligand molecules to metal atoms.

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