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Spectral, Magnetic and Electrical Studies on Complexes of some First Row Transition Elements with Pyrazinecarboxylic Acid

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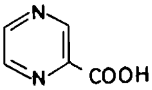
Abstract

The preparation and some properties of complexes of pyrazinecarboxylic acid with manganese, iron, cobalt, nickel and copper are described. Magnetic measurements, electronic and infrared spectra indicate that coordination takes place through the carboxyl group and a nitrogen atom of the aromatic ring. Electrical conductivity measurements made at room temperature yield conductivity values ranging from 1.7×10^{-13} Ω^{-1} m^{-1} to 1.9×10^{-8} Ω^{-1} m^{-1}. Iron and nickel complexes show transitions from ohmic to space charge limited conduction. The temperature dependences of conductivity are measured and discussed.

Introduction

In this work we describe and discuss the structural properties and some electrical measurements of the complexes of pyrazinecarboxylic acid with the first row transition metals manganese(II), iron(II), cobalt(II), nickel(II) and copper(II).

Pyrazinecarboxylic acid has four possible coordination sites: the two ring nitrogen atoms and the oxygen atoms of the carboxyl group.



Pyrazinecarboxylic acid (HPza)

No conductivity measurements have been previously reported on any of the complexes prepared in this investigation. The structure of the iron, cobalt and copper complexes have been previously reported [1–3].

Experimental

Two methods of preparation were used:

(a) 0.5 mol of pyrazinecarboxylic acid was dissolved in 120 cm^3 of warm water. The solution was boiled and the carbonate of the metal was added until no more carbon dioxide was evolved. The excess carbonate was removed by filtration and the compound was precipitated by concentrating the solution on a steam bath.

(b) 0.005 mol of pyrazinecarboxylic acid was dissolved in 150 cm^3 of water. 0.005 mol of hydrated copper(II) chloride was dissolved in 25 cm^3 of water. The solutions were mixed and dark blue crystals of $Cu(Pza)_2$ were deposited after standing overnight. Medium blue crystals of $Cu(Pza)_2(H_2O)_2$ were deposited a few days later.

The compounds prepared by these methods are listed in Table I. The magnetic moments (Table I) were made by the Gouy method using $Hg[Co(SCN)_4]$ as calibrant. Each magnetic moment has been corrected for diamagnetism using Pascal's constants [4]. The electronic spectra (Table II) were obtained on a Beckman ACTA MIV spectrometer as solid diffuse reflectance spectra. The infrared spectra (Table III) using KBr discs, 4000–600 cm^{-1}, and polyethylene discs, 600–200 cm^{-1} were obtained with a Perkin-Elmer infrared spectrophotometer model 598. The analysis of the metal ion was determined by a Perkin-Elmer 373 atomic absorption spectrophotometer; the carbon, hydrogen and nitrogen analyses using a Carlo Erba elemental analyser.

The conductivity of a sample was measured as a disc which was prepared by compressing powdered

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TABLE I. Analyses and Magnetic Moments of Complexes

Compound	Colour	Method of preparation	Theory (%)				Experimental (%)				μ (BM)
			Metal	C	N	Halogen	Metal	C	N	Halogen	
$Mn(Pza)_2 \cdot 2H_2O$	yellow	A	16.30	35.61	16.62	2.97	16.10	35.42	16.32	2.58	6.08
$Fe(Pza)_2(H_2O)_2$[a]	brown	A	16.53	35.52	16.57	2.96	16.34	35.10	16.28	2.66	5.38
$Co(Pza)_2(H_2O)_2$	orange	A	17.27	35.20	16.43	2.93	17.10	35.02	16.12	2.63	4.92
$Ni(Pza)_2(H_2O)_2$	green	A	17.23	35.22	16.44	2.93	17.08	35.14	16.22	2.74	2.42
$Cu(Pza)_2 \cdot 2H_2O$	dark blue	A	18.38	34.72	16.20	2.89	18.16	34.42	16.02	2.66	2.09
$Cu(Pza)_2(H_2O)_2$[b]	pale blue	B	18.38	34.72	16.20	2.89	18.30	34.32	15.98	2.59	1.78

[a] Ref. 1. [b] Ref. 2. Pza =

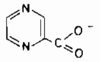

TABLE II. Electronic Spectra of the Complexes (cm^{-1})

Compound	Peak position (cm^{-1})	Dq	B	β
$Co(Pza)_2(H_2O)_2$	$\nu_1 = 9173$ $\nu_2 = 15380$ $\nu_3 = 26310$	621	945	0.97
$Ni(Pza)_2(H_2O)_2$	$\nu_1 = 8130$ $\nu_2 = 16840$ $\nu_3 = 21740$	813	946	0.90
$Cu(Pza)_2(H_2O)_2$	$\nu_1 = 16660$			
$Cu(Pza)_2 \cdot 2H_2O$	$\nu_1 = 15040$			

material in a hydraulic press under a force of 10^5 N. The diameter of each disc was 13 mm and the thickness was approximately 1.2 mm. Thicknesses were accurately determined using a micrometer. Circular electrodes of 5.9 mm diameter were formed on the flat surfaces of each disc using a mask and silver-based conductive paint. Use of compressed powder discs for conductivity measurements has been reviewed by Meier [5] and he concludes that for materials of such low conductivity as those reported here errors due to resistance at inter-granular contacts are not significant.

Pressure contacts were made onto the painted electrodes and the dark current was measured for a series of applied voltages using a Keithley 610C electrometer in a d.c. circuit. The applied voltages were measured with a digital voltmeter placed directly across the power supply terminals so that only the current through the sample disc was registered on the electrometer. Readings of current for a series of voltages with reversed polarity were also obtained to test for asymmetry which, if found, would indicate the presence of a potential barrier close to the metal–semiconductor contact. The observed degree of asymmetry in current for the same voltage in both polarities was less than 10% which was regarded as confirmation that the electrodes were not significantly rectifying. Conductivity was obtained from the gradient of the current *versus* voltage graph in cases where the graph was linear by assuming that charge flows between the electrodes along flow lines perpendicular to each electrode.

To test for photoconductivity, a white light source was shone onto each disc whilst a voltage was applied across the electrodes but no change of current from the dark value was observed.

The temperature dependence of conductivity was obtained by monitoring the current flowing between the electrodes under a fixed potential difference with temperature adjusted by a stream of warm air. The

TABLE III. Important Infrared Bands of the Complexes (cm^{-1})[a]

Compound	ν(C–O)	Ring vibrations		ν(C=O)	ν(M–O)		ν(M–N)
Pza	1470(m)	1515(m)	1418(m)	1695(s)			
$Mn(Pza)_2 \cdot 2H_2O$	1466(m)	1525(m)	1421(m)	1660(s)	294(s), 230(s)		460(m)
$Fe(Pza)_2(H_2O)_2$	1462(m)	1517(m)	1418(m)	1662(s)	276(s)	Fe–OH 370(m)	480(m)
$Co(Pza)_2(H_2O)_2$	1460(m)	1522(m)	1418(m)	1636(s)	272(s)	Co–OH 310(m)	460(m)
$Ni(Pza)_2(H_2O)_2$	1464(m)	1523(m)	1419(m)	1622(s)	280(s)	Ni–OH 309(m)	464(m)
$Cu(Pza)_2 \cdot 2H_2O$	1465(m)	1523(m)	1416(m)	1631(s)	256(s), 340(s)		468(m)
$Cu(Pza)_2(H_2O)_2$	1461(m)	1529(m)	1415(m)	1644(s)	248(s), 326(s)	Cu–OH 450(m)	464(m)

[a] m = medium, s = strong.

sample disc temperature was measured using a calibrated copper–constantan thermocouple (both wires of 44 S.W.G.) fixed to the disc surface. With this arrangement the temperature range from room temperature to a maximum of 353 K was covered.

Results and Discussion

Analytical

In Table I the analytical results for the complexes are shown. They agree with the given formulae and the stoichiometry of the compounds show that the maximum number of pyrazinecarboxylic acid molecules present in any one compound is two. All of the compounds have water molecules present.

Infrared Spectra

The wavenumbers of the infrared absorption bands as well as their descriptions and assignments are given in Table III. The infrared spectra of the compounds $Mn(Pza)_2 \cdot 2H_2O$ and $Cu(Pza)_2 \cdot 2H_2O$ show medium absorption bands present in the region 3510–3200 cm^{-1}, $\nu(OH)$ and 1630–1580 cm^{-1}, $\delta(HOH)$ confirming the presence of water of crystallization [6]. The presence of bands in the infrared spectra for the compounds $Fe(Pza)_2(H_2O)_2$, $Co(Pza)_2(H_2O)_2$, $Ni(Pza)_2(H_2O)_2$ and $Cu(Pza)_2(H_2O)_2$ at 370, 310, 308 and 450 cm^{-1} would suggest that the water is coordinated to each of the metal ions on these compounds [6]. The infrared spectrum of the pyrazinecarboxylic acid is almost identical to that of its complexes in the region 2000–625 cm^{-1} except for the bands due to ring vibrations of the aromatic ring which move to a higher frequency and the band due to the carboxyl group which moves to a lower frequency. This would suggest that the nitrogen atoms in the aromatic ring and the oxygen of the carboxyl group are coordinated to a metal atom [7–9]. Metal–oxygen and metal–nitrogen bands are observed for the complexes and are reported in Table III.

Electronic Spectra

The d–d bands from the electronic spectra of the complexes are shown in Table II. The position of the bands indicates that the metal ion in each of the compounds is in an octahedral environment [7]. The *Dq* values in Table II for the cobalt and nickel compounds are consistent with this stereochemistry [10]. The manganese compound shows no d–d transition bands in the visible region. The band at 20620 cm^{-1}, observed in the electronic spectra of the iron compound, is typical of a charge transfer band found in six coordinate iron(II) compounds [11].

Magnetic Moments

The magnetic moments for the cobalt and nickel compounds would suggest that the cobalt and nickel atoms are in an octahedral environment [7, 12]. The magnetic moments for the manganese, iron and copper compounds are higher than the spin-only values suggesting some orbital contribution to the magnetic moments in these compounds.

Solubility

The poor solubility of the compounds in both polar and non-polar solvents implies that the compounds have polymeric structures [7].

In the compounds $Co(Pza)_2(H_2O)_2$, $Cu(Pza)_2(H_2O)_2$ and $Fe(Pza)_2(H_2O)_2$ it is considered that a planar arrangement is formed between two molecules of the pyrazinecarboxylic acid and a metal atom. A ring nitrogen atom and an oxygen atom of the carboxyl group for each pyrazinecarboxylic acid molecule are involved in coordination to the metal atom. The coordination of the two water molecules to a single metal atom above and below the plane results in the formation of a distorted octahedral structure. Hydrogen bonding is observed between the hydrogen atoms of the water molecules and the uncoordinated oxygen atoms of the carboxyl groups in a neighbouring unit giving a polymeric structure [1–3]. It is suggested by analogy that the compound $Ni(Pza)_2(H_2O)_2$ has a similar structure.

In the compound $Cu(Pza)_2 \cdot 2H_2O$, for each molecule of pyrazinecarboxylic acid, one ring nitrogen atom and two oxygen atoms of the carboxyl group are used in forming coordinate bonds with a copper atom. A ring nitrogen atom and one of the oxygen atoms of the carboxyl group is coordinated to a copper atom to give a planar arrangement similar to that discussed for the previous compounds in this paper while the remaining oxygen atom of the carboxyl group is coordinated to an equivalent nearby copper atom in a neighbouring unit to give a polymeric structure. This means that each copper atom has a coordination number of six and is thus in an octahedral environment [2]. It is suggested that the compound $Mn(Pza)_2 \cdot 2H_2O$ has a similar structure. The water molecules in these compounds are attached by hydrogen bonding.

Electrical Measurements

The results of the observed electrical properties are summarized in Table IV. The dark conductivity at room temperature ranged from 1.7×10^{-13} Ω^{-1} m^{-1} for $Cu(Pza)_2(H_2O)_2$ to 1.9×10^{-8} Ω^{-1} m^{-1} for $Co(Pza)_2(H_2O)_2$. Since no trend of conductivity with composition is evident it is probable that the measured conductivities are strongly influenced by impurities. The compound $Mn(Pza)_2 \cdot 2H_2O$ exhibits ohmic behaviour over the studied range (Fig. 1). The current *versus* voltage relationship for $Co(Pza)_2$-

TABLE IV. Summary of Electrical Properties of the Complexes

Compound	Nature of *I* *vs.* *V* (room temperature)	σ At low voltage (room temperature) (Ω^{-1} m^{-1})	Temperature dependence of σ	Δ*E* from eqn. (3)[a] (eV)
$Mn(Pza)_2 \cdot 2H_2O$	ohmic	2.9×10^{-9}	ln σ *vs.* 1/*T* is linear	0.74
$Fe(Pza)_2(H_2O)_2$	ohmic for $V < 200$ V. SCLC contribution for $V > 200$ V	1.6×10^{-12}	ln σ *vs.* 1/*T* is linear	0.99
$Co(Pza)_2(H_2O)_2$	ohmic	1.9×10^{-8}	σ decreased as *T* increased. Permanent change at $T \leqslant 330$ K	
$Ni(Pza)_2(H_2O)_2$	ohmic for $V < 200$ V. SCLC contribution for $V > 200$ V	1.4×10^{-12}	ln σ *vs.* 1/*T* is linear	0.49
$Cu(Pza)_2 \cdot 2H_2O$	$I \propto V^{0.44}$		not investigated	
$Cu(Pza)_2(H_2O)_2$	ohmic	1.7×10^{-13}	possible indication of impurity ionisation and exhaustion	1.60

[a] Δ*E* calculated from linear section of ln σ *vs.* 1/*T* graph.

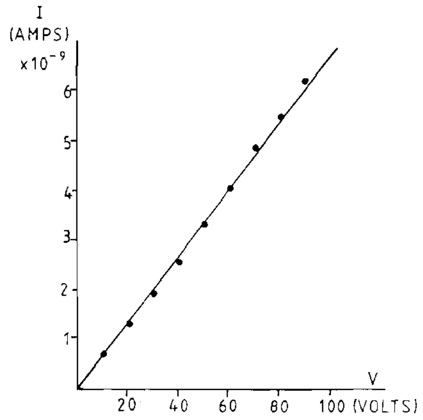

Fig. 1. Room temperature *I* *vs.* *V* characteristic for $Mn(Pza)_2 \cdot 2H_2O$.

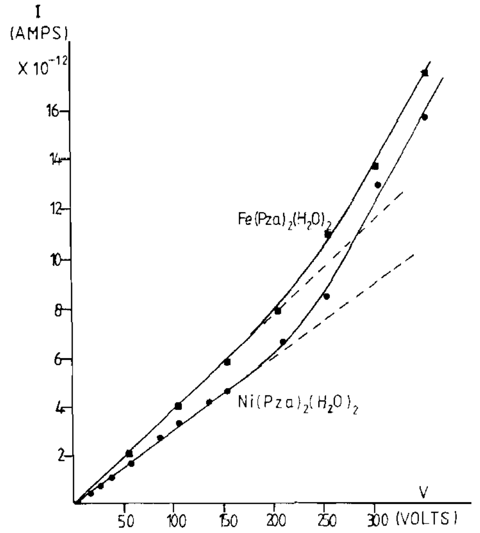

Fig. 2. Room temperature *I* *vs.* *V* characteristic for $Ni(Pza)_2(H_2O)_2$ and $Fe(Pza)_2(H_2O)_2$. Extrapolation of the linear dependences to higher voltages are shown.

$(H_2O)_2$ was also found to be linear throughout the investigated range which was up to 5×10^{-8} A. The compounds $Ni(Pza)_2(H_2O)_2$ and $Fe(Pza)_2(H_2O)_2$ (Fig. 2) exhibit very closely ohmic behaviour up to 200 volts but at higher voltages the current grows more rapidly with the voltage. As the departure from linearity occurs for both of these compounds when the Joule heating rate is only about 1.4×10^{-9} W, any suggestion that the enhanced current for $V > 200$ V is due to heating can be ruled out. It is confidently claimed that non-ohmic behaviour at $V > 200$ V is due to the onset of a space charge limited current (SCLC). The description and theory for this type of current in solids was given by Mott and Gurney [13] who showed that the current density was proportional to the square of the voltage between the electrodes and inversely proportional to the cube of the electrode separation for the case of plane parallel electrodes. Mott and Gurney's model assumed that the charge density within the solid is due to mobile charge. Lampert [14] has extended the model to cover cases where mono-energetic trapping is important and showed that in the voltage range dominated by SCLC, with traps not all filled, the current density *J* is given by the equation:

$$J = \frac{9\epsilon_0 \epsilon_r \mu \theta V^2}{8L^3} \qquad (1)$$

where ϵ_0 is the permittivity of free space, ϵ_r is the relative permittivity, μ is the carrier mobility (only one sign of carrier is considered), *V* is the potential difference across electrodes separated by the distance L and θ is the ratio of mobile carrier concentration to the sum of mobile plus trapped carrier concentrations. If the trapped carrier concentration is zero then $\theta = 1$ and eqn. (1) reduces to the original Mott and Gurney formula. Observation of current density proportional to V^2 has been reported in many compounds, both inorganic and organic. Experimental evidence for $J \propto L^{-3}$ has been much less frequently observed although it has been reported by Barbe and Westgate [15]. It is shown in Lampert's paper that a cross-over voltage V_{oc} exists such that for $V < V_{oc}$ the current is ohmic and for $V > V_{oc}$ eqn. (1) applies. V_{oc} is expressed by the equation:

$$V_{oc} = \frac{en_0L^2}{\epsilon_0\epsilon_r\theta} \qquad (2)$$

where e is the magnitude of the electronic charge and n_0 is the equilibrium concentration of the mobile carriers. Abrupt change in the voltage dependence of the current does not occur at V_{oc} but instead the change occurs over a small voltage range in the vicinity of V_{oc}. For approximate work V_{oc} can be taken as the voltage for which the current density is about 30% higher than would be predicted by an extrapolation of the ohmic region. From Fig. 2 it follows that for both $Fe(Pza)_2(H_2O)_2$ and $Ni(Pza)_2(H_2O)_2$ the value of V_{oc} is near 400 V. Taking $\epsilon_r = 5$ as an estimate for both compounds and using the above value for V_{oc} combined with the measured values for L, it is found from eqn. (2) that $n_0/\theta \simeq 8 \times 10^{16}$ m^{-3}. Substituting this value for n_0 along with the measured low field conductivity σ into the equation $\sigma = n_0e\mu$ information about the carrier mobility is obtained. In this way it is found that for both the compounds $Fe(Pza)_2(H_2O)_2$ and $Ni(Pza)_2(H_2O)_2$ $\mu\theta$ is approximately 1×10^{-10} m^2 V^{-1} s^{-1}. The product $\mu\theta$ is the mean drift velocity per unit field in the presence of traps and these reduce the drift velocity. The microscopic mobility μ, which is the drift velocity per unit field for motion between traps, is rarely less than 10^{-8} m^2 V^{-1} s^{-1} in solids [16] suggesting that θ is much less than 1, hence trapping is a major effect. Although the microscopic mobility is very unlikely to be as small as 10^{-10} m^2 V^{-1} s^{-1}, nonetheless it is probable that it is sufficiently small to indicate hopping conduction [17]. Other compounds with values of $\mu\theta$ even lower than that reported here for $Fe(Pza)_2(H_2O)_2$ and $Ni(Pza)_2(H_2O)_2$ have been observed. The $\mu\theta$ for polythene has been reported as 10^{-15} m^2 V^{-1} s^{-1} [18].

The current *versus* voltage characteristic observed at room temperature for $Cu(Pza)_2 \cdot 2H_2O$ is anomalous (Fig. 3a). The current initially increased rapidly with voltage and at higher voltages increased at progressively lesser rates. When the same data is replotted on log–log scales (Fig. 3b) it fits closely to a straight line, showing that a law of the form $I \propto V^n$ describes the characteristic, with $n = 0.44$. We are unable to offer any explanation for this form of I *versus* V characteristic which empirically fits remarkably well to a simple equation. As the voltage was increased in 50 volt increments the current initially overshot its final value by a factor of about three before settling down in a time of a few seconds. This behaviour suggests there is a very high trap concentration. In Table IV no entry has been made for the room temperature conductivity at small voltage since if indeed the expression $I \propto V^{0.44}$ is maintained down to infinitesimally small voltages, it would yield infinite conductivity.

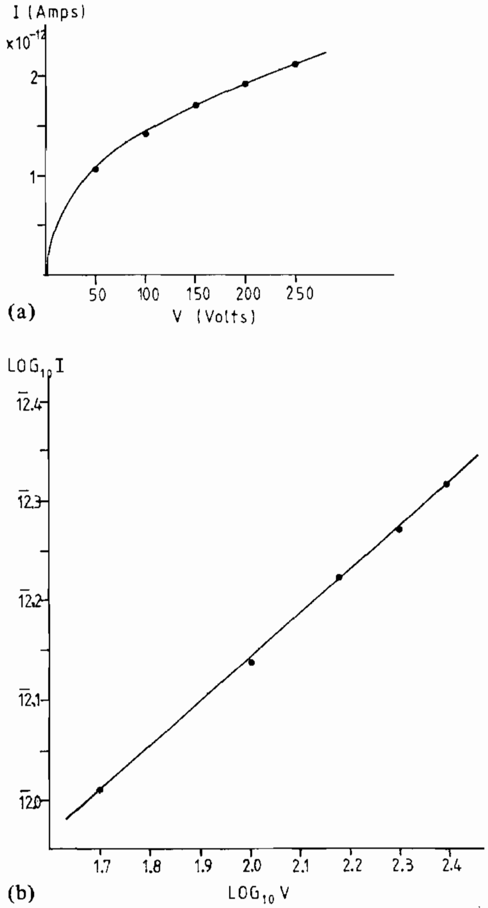

Fig. 3. (a) Room temperature I *vs.* V characteristic for $Cu(Pza)_2 \cdot 2H_2O$. (b) $\log_{10} I$ *vs.* $\log_{10} V$ for $Cu(Pza)_2 \cdot 2H_2O$. I and V are respectively in units of amps and volts.

The results for the temperature dependence of σ are analysed in Figs. 4 and 5. For a semiconductor at sufficiently high temperature that the free electron and hole concentrations greatly exceed the concentrations of donors and acceptors, *i.e.* the material is intrinsic, then it is approximately true to write:

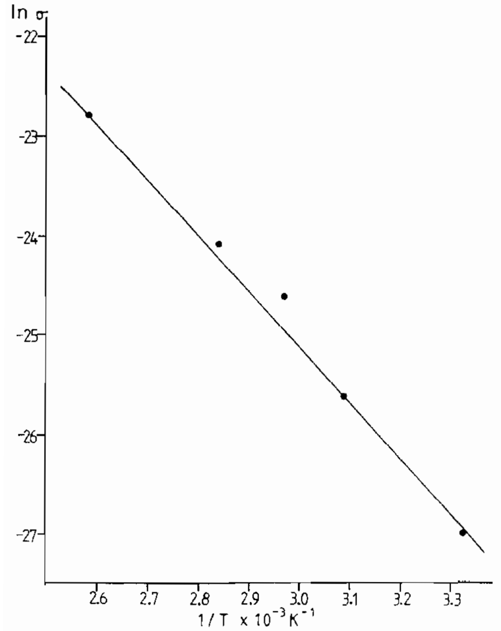

Fig. 4. Plot of ln σ *vs.* $1/T$ for $Fe(Pza)_2(H_2O)_2$. σ is in units of $\Omega^{-1}\,m^{-1}$.

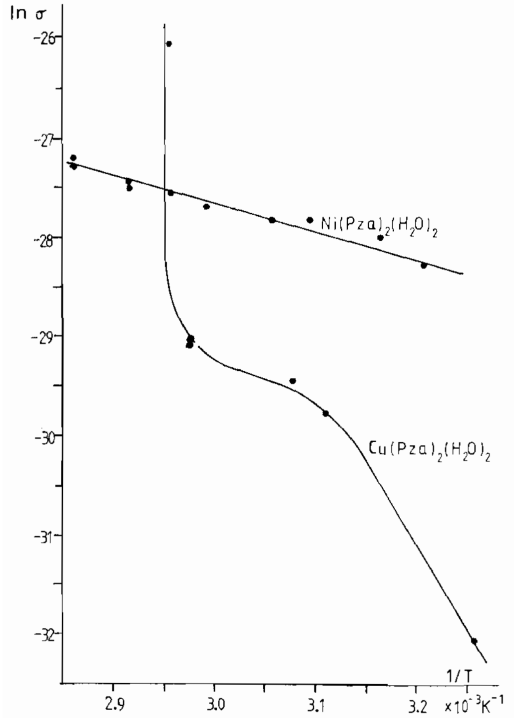

Fig. 5. Plots of ln σ *vs.* $1/T$ for $Ni(Pza)_2(H_2O)_2$ and $Cu(Pza)_2(H_2O)_2$. σ is in units of $\Omega^{-1}\,m^{-1}$.

$$\sigma = \sigma_0 \exp\left(\frac{-\Delta E}{2kT}\right) \qquad (3)$$

with ΔE equal to the band-gap energy [19]. For an n-type semiconductor in which the temperature is low enough that many donors are not ionised an equation similar to eqn. (3) still applies but with ΔE now equal to the donor ionisation energy [19]. It has been assumed that the temperature dependence of mobility is very weak compared to that for the free carrier concentration in obtaining eqn. (3). In both of the above temperature ranges a graph of ln σ *versus* $1/T$ would be linear with different gradients and between these two temperature ranges a flat region is predicted to exist where the donors are exhausted. Similar remarks can be made for a material containing acceptor centres instead of donors. More complicated conclusions apply for a semiconductor in which donors and acceptors are present in nearly equal concentrations [19, 20]. Yet a further complication arises in analysing the temperature dependence of σ since for hopping conduction an equation like eqn. (3) also holds but with ΔE twice the activation energy for hopping.

Values obtained for the parameter ΔE of eqn. (3) are given in Table IV. Without more information about the variation of σ over a wider temperature range it is not possible to be conclusive about the physical significance of the measured value of ΔE. For the compound $Cu(Pza)_2(H_2O)_2$, the shape of ln σ *versus* $1/T$ (Fig. 5) is qualitatively similar to that for a semiconductor which exhibits impurity ionisation at the lower temperatures and valence band to conduction band transitions at high temperatures. The value of 1.6 eV obtained for the impurity ionisation energy on the basis of this view seems surprisingly large. The very sharp rise in σ near $1/T = 2.95 \times 10^{-3}\ K^{-1}$ may in fact be due to a chemical decomposition rather than to a transition between valence and conduction bands.

The temperature dependence of current at fixed voltage for the compound $Co(Paz)_2(H_2O)_2$ is shown in Fig. 6. This dependence is highly anomalous in that the conductivity decreases with increase of

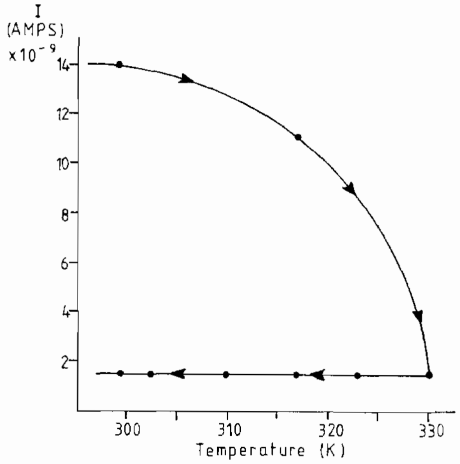

Fig. 6. Current *vs.* temperature dependence for $Co(Pza)_2(H_2O)_2$ at a constant voltage of 40 volts.

temperature. After the temperature of 330 K had been reached, further measurements of current were obtained as the disc cooled. The graph shows that the current remains constant during the cooling phase. Clearly some chemical change has occurred in the disc.

The electrical properties which have been reported here exhibit a wide diversity amongst the different complexes. It is very probable that this diversity is associated more with the presence of accidentally introduced impurities than to the different transition metals in the complexes. An obvious omission is that no investigation has been made of whether the conductivities are n or p type. Further work on electrical properties of related compounds is in progress with some emphasis on the observation of space charge effects and we plan to report this in a future paper.

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