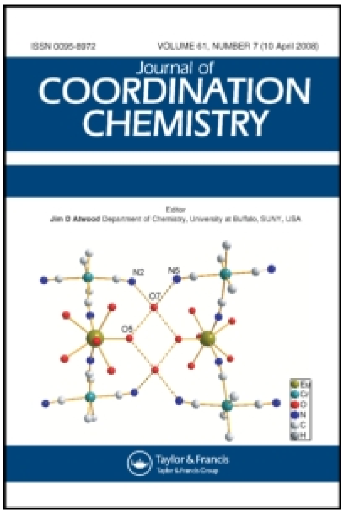

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# STRUCTURAL AND ELECTRICAL STUDIES OF SOME FIRST ROW COMPLEXES OF PYRAZINAMIDE

J. R. Allan[a]; A. D. Paton[a]; K. Turvey[b]; H. J. Bowley[c]; D. L. Gerrard[c]
[a] Department of Applied Chemical Scietices, Napier College, Edinburgh, Scotland, U.K. [b] Department of Physics, Napier College, Edinburgh, Scotland, U. K. [c] British Petroleum Research Centre, Sunbury, Middlesex, England, U. K.

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# STRUCTURAL AND ELECTRICAL STUDIES OF SOME FIRST ROW COMPLEXES OF PYRAZINAMIDE

J. R. ALLAN and A. D. PATON

*Department of Applied Chemical Sciences, Napier College, Edinburgh, Scotland, U.K.*

K. TURVEY

*Department of Physics, Napier College, Edinburgh, Scotland, U.K.*

H. J. BOWLEY and D. L. GERRARD

*British Petroleum Research Centre, Sunbury, Middlesex, England, U.K.*

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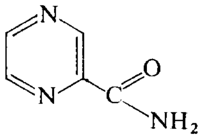
Complexes of pyrazinamide with the cobalt(II) chloride and bromide, nickel(II) thiocyanate and bromide and copper(II) chloride and bromide are described. Magnetic measurements and electronic and infrared spectroscopy have been used to investigate the stereochemistry of the complexes. Electrical measurements have shown the existence of two types of conduction in the compounds—ohmic and space charge effects with carrier trapping.

**Keywords:** Pyrazynamide, cobalt, nickel, copper, complexes, electrical conduction

## INTRODUCTION

The development of new semiconducting and conducting organometallic polymers is an important area of present day research because of their possible applications in solid state electro-optical systems. These materials can have prime roles in devices such as sensors and detectors where chemical and thermal stability are essential. A study of the complexes of pyrazine and substituted pyrazines has recently become of interest because of the possible formation of inorganic polymers. In this work we describe and discuss the structural properties, and the electrical measurements of complexes of pyrazinamide with cobalt(II) chloride and bromide, nickel(II) thiocyanate and bromide and copper(II) chloride and bromide. Pyrazinamide has four possible coordination sites—the two ring nitrogen atoms, the oxygen atom of the carbonyl group and the nitrogen atom of the amine group.



Pyrazinamide (pzA)

The complexes reported in the present investigation are all new compounds. Information concerning the stereochemistry of the complexes has been obtained from magnetic moments, and electronic and infrared spectra. Over the range of electrical fields applied in electrical measurements some of the compounds were found to exhibit purely ohmic behaviour and others showed space-charge-limited conduction.

## EXPERIMENTAL

### *Preparation of Complexes*

(*a*) A solution of 4 grams of metal halide in 40 $cm^3$ of ethanol was obtained by warming until the ethanol boiled. To this boiling solution was added 5 grams of pyrazinamide dissolved in ethanol. The precipitated complexes were filtered, washed with ethanol and dried at 50°C.

(*b*) KCNS (1.9 grams) dissolved in warm ethanol was added to 1.8 grams of $Ni(NO_3)_2$ dissolved in warm ethanol. The white precipitate was removed by filtration and the filtrate allowed to cool. A saturated solution of pyrazinamide was then added to the filtrate. The precipitated complex was filtered, washed with acetone and dried at 50°C.

The compounds prepared by these methods are listed in Table I. The metal ion was determined by AAS (Perkin-Elmer 373 atomic absorption spectrophotometer), and the carbon, hydrogen and nitrogen analyses by using a Carlo Erba elemental analyser.

The infrared spectra, Table II, were measured in KBr (4000–600 $cm^{-1}$) and polyethylene discs (600–200 $cm^{-1}$) on a Perkin-Elmer 598 infrared spectrophotometer. The electronic spectra, Table I, were measured on a Beckmann Acta MIV spectrophotometer as solid diffuse reflectance spectra. Magnetic measurements, Table I, were carried out by the Gouy method using $Hg[Co(SCN)_4]$ as calibrant. Diamagnetic corrections were applied using the atomic susceptibilities tabulated by Figgis and Lewis.[1]

For measurements of current—voltage (I–V) characteristics, discs of diameter 13 mm and of thickness in the range from 0.9 mm to 1.4 mm were prepared by compressing powders in a hydraulic press under a force of 100 kN. Circular electrodes of diameter 5.9 mm were formed on each side of the discs by applying a conducting silver paint through masks. The current for a series of applied steady voltages was measured using a Keithley 610C electrometer with the corresponding voltages measured by a digital voltmeter. The voltmeter was placed so that the current passing through it did not contribute to the electrometer current. The I–V characteristic for each disc was re-measured with reversed polarity and it was found that for any applied voltage in the two polarities the current agreed to within 10%. This is evidence that the contacts are non-blocking.

Where a linear I–V relationship was found the electrical conductivity, $\sigma$, was determined with the assumption that current flows perpendicular to the flat faces of the disc. The disc thickness was measured with a micrometer. With one exception, all the currents were measured only at room temperature; the exception was a sample of $Co(pzA)_2Cl_2$ which had been doped with iodine by exposing the powdered complex to iodine vapour. A disc of this doped compound, which had previously been shown to exhibit ohmic behaviour at room temperature, was heated by passing warm air over it whilst a constant voltage (within the ohmic range) was applied. The current was measured over a temperature range from 293 K to 353 K with the temperature determined from the e.m.f. of a calibrated copper–constantan thermocouple fixed onto the disc surface.

TABLE I
Analyses, magnetic moments and electronic spectral data for the compounds.

| | Calculated (%) | | | | Found (%) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Compound | Metal | Carbon | Nitrogen | Hydrogen | Metal | Carbon | Nitrogen | Hydrogen | μ(BM) | Peak Position ($cm^{-1}$) | Dq[a] | B[a] | β |
| $Co(pzA)_2Cl_2$ | 15.67 | 31.91 | 22.34 | 2.66 | 14.76 | 31.68 | 21.91 | 2.26 | 4.83 | 7812<br>17241 | 882 | 696 | 0.72 |
| $Co(pzA)_2Br_2$ | 12.67 | 25.81 | 18.06 | 2.15 | 11.86 | 25.44 | 17.79 | 2.11 | 4.39 | 7246<br>15030 | 392 | 701 | 0.72 |
| $Ni(pzA)_2(CNS)_2$ | 13.94 | 34.23 | 26.61 | 2.39 | 12.96 | 33.86 | 26.80 | 2.01 | 2.41 | 10101<br>16667<br>25324 | 1010 | 779 | 0.75 |
| $Ni(pzA)_2Br_2$ | 12.63 | 25.81 | 18.06 | 2.15 | 12.47 | 25.23 | 17.45 | 2.02 | 2.87 | 9091<br>14815<br>24390 | 909 | 795 | 0.76 |
| $Cu(pzA)_2Cl_2$ | 16.68 | 31.50 | 22.04 | 2.62 | 16.42 | 31.32 | 21.66 | 2.41 | 1.73 | 13699 | | | |
| $Cu(pzA)_2Br_2$ | 13.55 | 25.59 | 17.91 | 2.12 | 13.23 | 25.02 | 16.96 | 2.01 | 1.77 | 13330 | | | |

[a] Usual units.

TABLE II
Important infrared bands[a] for the compounds ($cm^{-1}$).

| Compound | ν(N–H) |  | ν(CNS) |  | Ring Vibrations |  | ν(C=O) | ν(M–O) | ν(M–X) | ν(M–N) |
|---|---|---|---|---|---|---|---|---|---|---|
| pzA | 3416(s) | 3156(s) |  |  | 1522(m) | 1438(m) | 1712(s) |  |  |  |
| $Co(pzA)_2Cl_2$ | 3442(s) | 3120(s) |  |  | 1521(m) | 1438(m) | 1708(s) | 288(w) | <200 |  |
| $Co(pzA)_2Br_2$ | 3360(s) | 3090(s) |  |  | 1530(m) | 1436(m) | 1688(s) |  | 309(m) |  |
| $Ni(pzA)_2(CNS)_2$ | 3430(s) | 3160(s) | 2080(s) | 2140(s) | 1524(m) | 1436(m) | 1687(s) | 290(w) |  | 225(w) |
| $Ni(pzA)_2Br_2$ | 3437(s) | 3080(s) |  |  | 1521(m) | 1436(m) | 1680(s) | 302(w) | <200 |  |
| $Cu(pzA)_2Cl_2$ | 3440(s) | 3130(s) |  |  | 1520(m) | 1435(m) | 1677(s) | 388(w) | 288(w) |  |
| $Cu(pzA)_2Br_2$ | 3430(s) | 3142(s) |  |  | 1520(m) | 1439(m) | 1708(s) | 385(w) | 268(w) |  |

[a] Intensities: s = strong; m = medium; w = weak.

The inter-electrode capacitance for $Ni(pzA)_2(CNS)_2$ was measured at a frequency of 10 kHz using a Wayne–Kerr B605 bridge. From the measured capacitance the relative permittivity was obtained by neglecting any effect of fringing fields at the edges of the electrodes.

The sign of the thermo–e.m.f. for $Ni(pzA)_2(CNS)_2$ and hence the type of the majority carriers was determined as follows. An unpainted portion of a disc of the complex was placed on a copper strip at room temperature. A bare copper wire wound around a heating element was heated till one of its ends was at a temperature of approximately 353 K. When this hot copper tip was touched onto the portion of disc the electrical circuit was completed and the direction of current flow through the Keithley 610C electrometer was noted. During this measurement the current for the heating element was switched off. This method of determining the polarity of the thermo–e.m.f. has been described by Seeger.[2]

## RESULTS AND DISCUSSION

In Table I the analytical results for the complexes isolated from solution are shown. They agree with the given formulae and the stoichiometry of the complexes. The visible reflectance spectrum of dibromobis(pyrazinamide)cobalt(II), Table I, resembles that normally found for the cobalt(II) ion in a tetrahedral environment.[3] The possibility of a tetrahedral structure is further supported by the Dq value,[4] Table I, and the magnetic moment which is found to be in the range 4.2–4.8 BM.[3] The far infrared spectrum of the compound, Table II, is also consistent with a tetrahedral configuration for the cobalt ion.[5]

The visible reflectance spectra of dichlorobis(pyrazinamide)cobalt(II), dithiocyanatobis(pyrazinamide) nickel(II) and dibromobis(pyrazinamide) nickel(II) are characteristic of cobalt and nickel ions in octahedral environments.[6] An octahedral structure is also consistent with the Dq values[4,7] and the magnetic moments,[6] both being listed in Table I. The far infrared spectra, Table II, also support the octahedral configuration for the metal ions in these compounds.[8]

The compounds dichlorobis(pyrazinamide)copper(II) and dibromobis(pyrazin amide)copper(II) show a broad band in their visible reflectance spectra at 13699 $cm^{-1}$ and 13330 $cm^{-1}$, respectively, indicating an octahedral environment for the copper atom since square planar copper(II) compounds show bands of near equal intensity at about 15000–18000 $cm^{-1}$ [9–11] and regular tetrahedral copper(II) compounds give no bands due to d–d transitions between 10000 and 20000 $cm^{-1}$.[12,13] The broadness of the band in each of the copper compounds is due to Jahn–Teller distortion.[14] The magnetic moment of each compound is similar to the spin only value. The far infrared spectrum (Table II) also is consistent with the copper ion being in an octahedral environment.[5]

The compounds isolated from solution were all obtained as powders and without X-ray analysis no definite structures can be deduced. However, spectroscopic and magnetic data along with the chemical composition of the compounds allow us to postulate probable structures. The infrared spectrum of pyrazinamide is similar to that of the compounds in the region 4000–650 $cm^{-1}$. However, differences in the spectra are observed between 3000 and 3600 $cm^{-1}$ for the ν(N–H) bands where a shift to higher frequency, Table II, is observed. It is suggested that this shift indicates that any hydrogen bonding in the pure amide breaks down on complex formation.[15] Attempts to identify the presence of hydrogen bonding were unsuccessful due to the insolubility of the pyrazinamide in tetrachloromethane.[6] The ν(C=O) band shifts to lower frequency on coordination indicating that the carbonyl group of each pyrazinamide molecule is acting as an electron donor to the metal atom.[15] Crystallographic studies,[16]nuclear magnetic resonance studies[17] and infrared spectra[18-20] have shown that amides do bond to metals through the carbonyl oxygen. The ring vibrations of the pyrazinamide show little change on coordination. The position of the bands for the thiocyanate group in dithiocyanatobis(pyrazinamide)nickel(II) would suggest that the thiocyanate is acting as a bridging ligand in this compound.[21]

The poor solubility of the compounds dichlorobis(pyrazinamide)cobalt(II), dibromobis(pyrazinamide)copper(II) and dichlorobis(pyrazinamide)copper(II) in most polar and non-polar solvents suggests that the compounds may have polymeric structures. Thus these compounds are considered to have a chain of metal atoms (M) bonded to thiocyanate or halogen atoms (X) with the pyrazinamide molecules above and below the plane of the M–X chain bonded to each metal through the oxygen of the amide group. Dibromobis(pyrazinamide)cobalt(II), which is soluble in polar and non-polar solvents has a tetrahedral structure. The cobalt atom is bonded to two halogen atoms and the oxygen of the amide group in each pyrazinamide molecule.

TABLE III
Electrical properties of the compounds (room temperature).

| Compound | Fig. showing I *versus* V relationship | Value of m from the expression $I \propto V^m$ | $\sigma$ at low voltage ($\Omega^{-1}\,m^{-1}$) |
|---|---|---|---|
| $Co(pzA)_2Cl_2$ | | 1.00 | $1.8 \times 10^{-9}$ |
| $Co(pzA)_2Br_2$ | | 1.00 | $2.3 \times 10^{-11}$ |
| $Ni(pzA)_2(CNS)_2$ | 2 | $2.01 \pm 0.03$ | |
| $Ni(pzA)_2Br_2$ | 3 | 1.86 ($V < 50$ volt)<br>3.17 ($V > 50$ volt) | |
| $Cu(pzA)_2Cl_2$ | 2 | $1.80 \pm 0.01$ | |
| $Cu(pzA)_2Br_2$ | 3 | 1.06 ($V < 79$ volt)<br>12.1 ($V > 79$ volt) | $1.7 \times 10^{-10}$ |

The principal results of the electrical measurements at room temperature are summarised in Table III. The compounds $Co(pzA)_2Cl_2$ and $Co(pzA)_2Br_2$ exhibit ohmic behaviour throughout the voltage range investigated for these compounds (0–50 volts). The conductivities for these compounds are $1.8 \times 10^{-9}\,\Omega^{-1}\,m^{-1}$ and $2.3 \times 10^{-11}\,\Omega^{-1}\,m^{-1}$, respectively. The considerable difference between these conductivities almost certainly reflects differing levels of impurities rather than any effect attributable to the two halogens. For $Co(pzA)_2Cl_2$ the effect of iodine addition on the conductivity was studied. The iodine-doped compound, like the undoped form, showed ohmic behaviour at room temperature over the full voltage range investigated (0–40 volts). The conductivity for the iodised form is $1.4 \times 10^{-9}\,\Omega^{-1}\,m^{-1}$, which is close to the value of $1.8 \times 10^{-9}\,\Omega^{-1}\,m^{-1}$ for the uniodised form. This suggests that no donor or acceptor centres are introduced by iodine addition. The temperature dependence of conductivity for the iodised $Co(pzA)_2Cl_2$ is shown in Fig. 1 as a plot of ln $\sigma$ versus 1/T. It was noted that during cooling to room

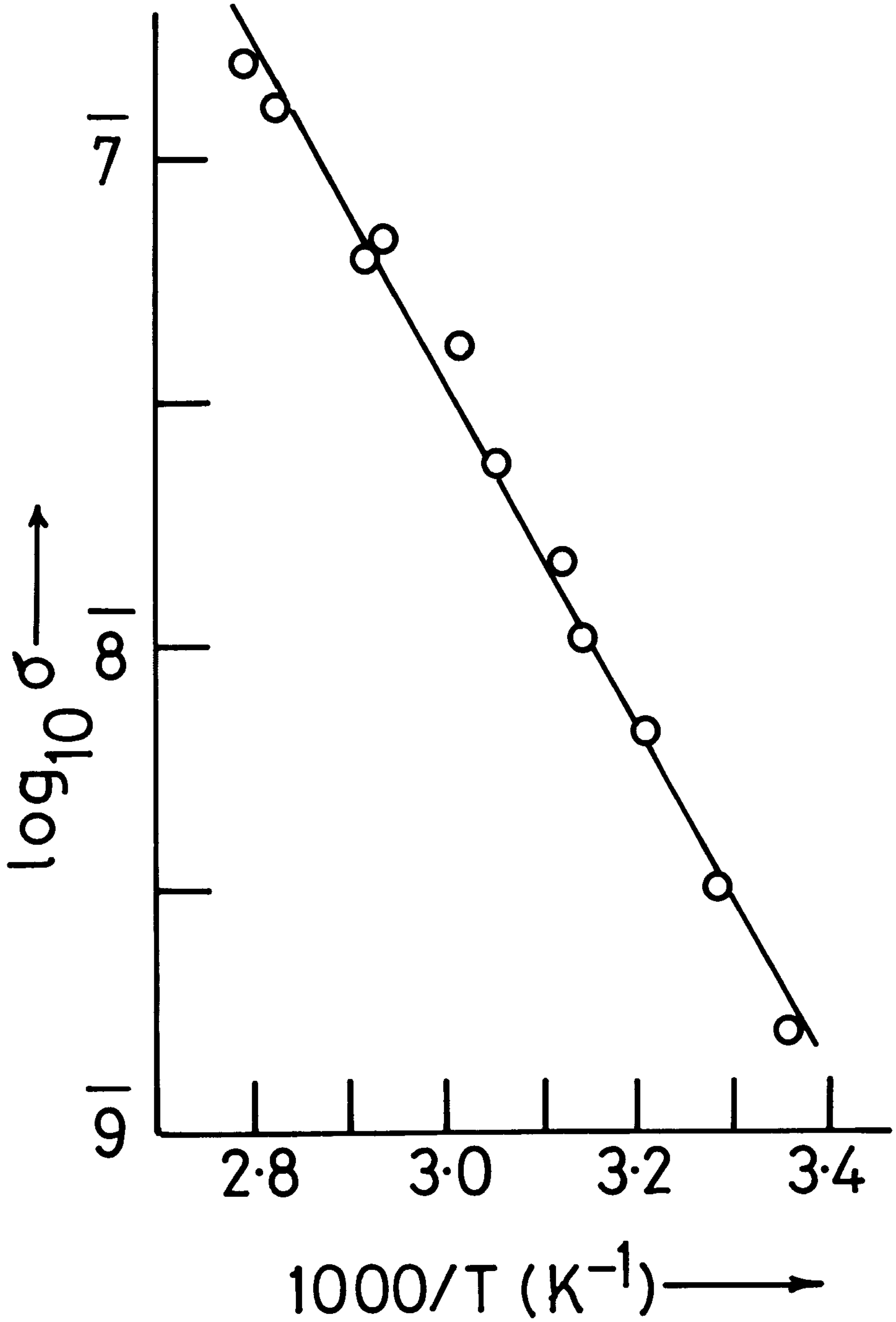


FIGURE 1 Plot of $\log_{10}\sigma$ versus 1/T for iodine-doped $Co(pzA)_2Cl_2$; $\sigma$ is in units of $\Omega^{-1}\,m^{-1}$.

temperature, and for a subsequent heating/cooling cycle, the data in the figure were closely reproduced indicating that the properties of the compound had not been permanently altered by heating. The gradient of the line in Fig. 1 leads to a value of 1.4 ± 0.1 eV for the parameter $\Delta E$ in the equation $\sigma = \sigma_0 \exp(-\Delta E/2kT)$. The quantity $\Delta E$ corresponds to an activation energy for the release of a free carrier either from the valence levels of the $Co(pzA)_2Cl_2$ molecules or from impurity centres. In terms of the band model it follows that for the former case the gap between valence and conduction bands is 1.4 eV and for the latter case this gap exceeds 1.4 eV. Based on an estimate of the density of $Co(pzA)_2Cl_2$ of $4 \times 10^3$ kgm$^{-3}$, the molecular concentration in the solid is approximately $6 \times 10^{27}$ m$^{-3}$. If, as a hypothesis, it is assumed that there is one free carrier per $Co(pzA)_2Cl_2$ molecule then using the above figure for the molecular concentration together with the measured room temperature conductivity, the drift mobility of the carriers is approximately $2 \times 10^{-18}$ m$^2$V$^{-1}$s$^{-1}$. This is many orders of magnitude smaller than typical microscopic mobilities indicating that in fact the free carrier concentration at room temperature is much less than the molecular concentration.

A log–log plot of the I–V characteristics for $Ni(pzA)_2(CNS)_2$ is shown in Fig. 2 and is linear for the full range of voltage investigated (30–350 volts). Using a least-squares linear regression program the gradient of this plot is 2.01 ± 0.03. This quadratic dependence of current with voltage can be explained as a space-charge-limited current (SCLC) and the theory for such currents in solids has been described by Mott and Gurney[22] for the case of a trap-free solid. Lampert[23] extended the model to include the case of shallow trapping and found the relationship

$$J = 9\varepsilon_0\varepsilon_r\mu\theta V^2/8L^3 \qquad (1)$$

where J is the current density for an applied voltage V between plane-parallel electrodes separated by the distance L, $\varepsilon_0\varepsilon_r$ is the permittivity of the material, $\mu$ is the microscopic carrier mobility and $\theta$ is the fraction of the carriers that are free, the fraction $1\text{-}\theta$ being in shallow traps. If $\theta$ is set to unity then the equation reduces to the Mott and Gurney formula. The I–V characteristics for $Ni(pzA)_2(CNS)_2$ indicates that the equation applies with fixed $\theta$. The relative permittivity, $\varepsilon_r$, of the compound was determined by measuring the capacitance between the electrodes using the same disc as for the current measurements. At a frequency of 10 kHz, with L = 1.33 mm and electrode diameter of 5.9 mm, the capacitance is 0.81 pF leading to a value of 4.8 for $\varepsilon_r$. Using the gradient obtained by re-plotting the I–V data as a graph of I versus $V^2$ together with the above result for $\varepsilon_r$, it is inferred that $\mu\theta = 3 \times 10^{-9}$ m$^2$V$^{-1}$s$^{-1}$. Since $\theta$ is necessarily less than unity it follows that the microscopic mobility ($\mu$) exceeds $3 \times 10^{-9}$ m$^2$V$^{-1}$s$^{-1}$. Meier[24] shows by simple reasoning based on the Heisenberg Uncertainty Principle that if $\mu < 10^{-5}$m$^2$V$^{-1}$s$^{-1}$ then conduction cannot be explained in terms of the band model and instead the mode of carrier transport is by hopping. Accordingly, if we assume $\theta > 3 \times 10^{-4}$, which is likely for the observation of SCLC,[25] then the hopping mechanism operates. The polarity of the thermo–e.m.f., which was measured as previously described on a piece of the $Ni(pzA)_2(CNS)_2$ disc used for obtaining the I–V data, was with the warmer contact positive. This indicates that free electrons rather than free holes are the carriers.

A log–log plot of the I–V characteristic for a disc of $Cu(pzA)_2Cl_2$ is shown in Fig. 2. This plot is linear throughout the investigated voltage range (20–350 volts) and the gradient (m) found by a least-squares analysis is 1.80 ± 0.01. Observations with m = 2 can readily be explained using Lampert's shallow trapping model as previously

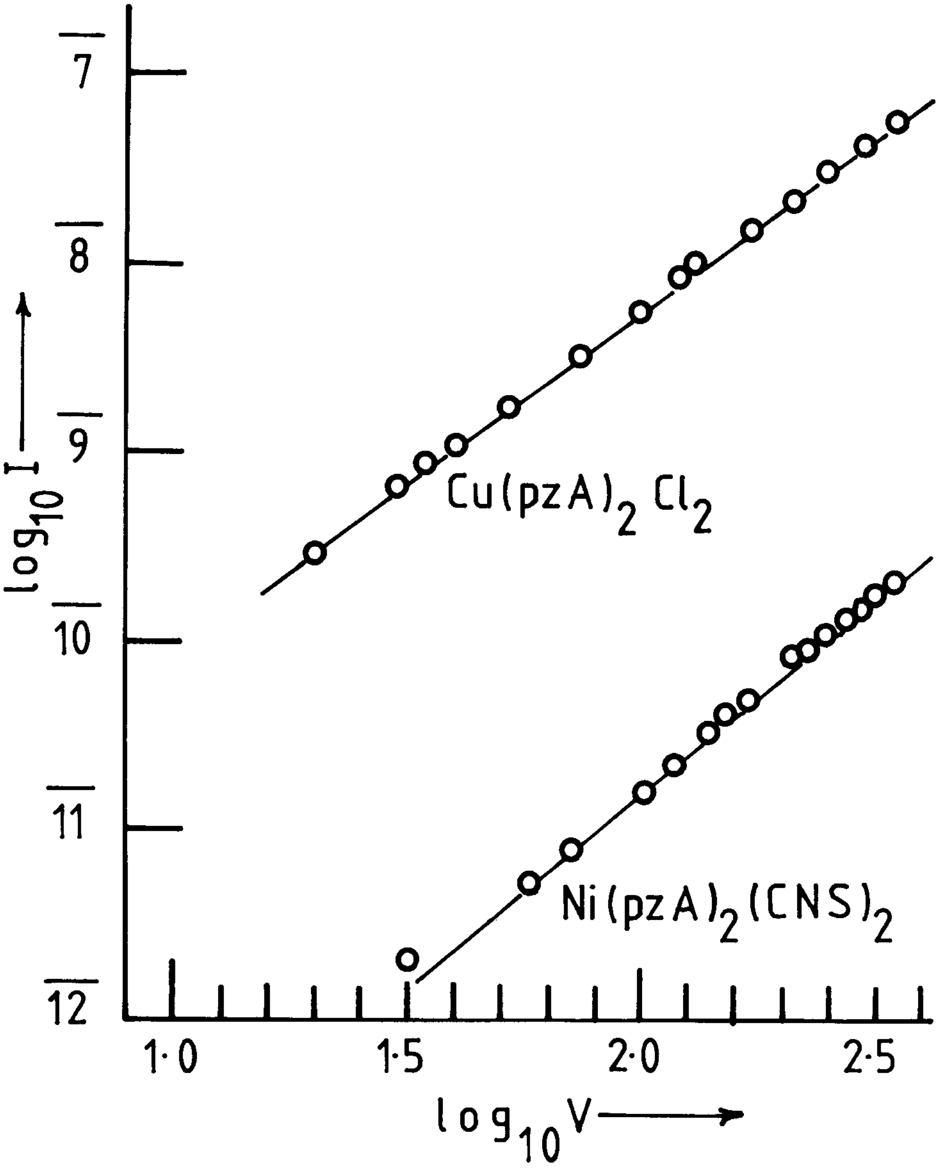


FIGURE 2 Log–log plots of room temperature I–V characteristics for the compounds $Cu(pzA)_2Cl_2$ and $Ni(pzA)_2(CNS)_2$. I and V are respectively in units of amps and volts.

noted and Rose[26] explains a constant value of m > 2 in terms of a model involving a trap distribution which is exponential in energy. Attempts have been made[27,28] to explain values of m in the range $1 < m < 2$, as found here for $Cu(pzA)_2Cl_2$, but these models fail to explain why m is constant over more than a decade of voltage change. If it is assumed that the carrier microscopic mobility decreases with the applied field E, according to $\mu \alpha E^{-\alpha}$ and with $\alpha > 0.2$, then the observations of $m = 1.80$ could be explained. However, although a decrease of mobility with increase of field is known to occur[29] it would not be expected at the relatively low fields (23 $kVm^{-1}$ to 400 $kVm^{-1}$) encountered during the measurements of current. For contacts which are rectifying and inject both electrons and holes, Sze[30] shows that it is possible to produce a current which is sum of an ohmic term and a term proportional to the square of the applied voltage. A suitable combination of these terms could produce a nearly constant value of m for a wide voltage range and with $1 < m < 2$. Some support that this is valid for the $Cu(pzA)_2Cl_2$ disc is obtained by noting that the I–V data fit closely to a linear plot when I/V is plotted against V.

The I–V measurements for the compound $Ni(pzA)_2Br_2$, plotted logarithmically in Fig. 3, exhibit a gradient of $m = 1.86$ for $V < 50$ volts and $m = 3.2$ for $V > 50$ volts. The remarks made for $Cu(pzA)_2Cl_2$ concerning the appearance of $m < 2$ are applicable also to the lower voltage range for $Ni(pzA)_2Br_2$ but, because m is closer to 2.0, the difficulty is less acute. The I–V characteristics for $Ni(pzA)_2Br_2$ are in approximate accord with the Lampert model which predicts $I \propto V^2$ until the voltage reaches the value $V_{TFL}$ at which the traps are filled and the current then rises more rapidly with an increase of voltage. In this model $V_{TFL}$ is given by[23] (*2*)

$$V_{TFL} = \frac{e L^2 N_{to}}{2\varepsilon_o \varepsilon_r} \qquad (2)$$

where e is the electronic charge and $N_{to}$ is the trap concentration. Using $L = 0.90$ mm and taking $V_{TFL} = 50$ volts, together with $\varepsilon_r \sim 5$, equation (*2*) gives $N_{to} = 3 \times 10^{16}\ m^{-3}$. This concentration is lower than the molecular concentration of the compound by a factor of about $10^{11}$, suggesting a very high purity.

The log–log plot of I versus V for the compound $Cu(pzA)_2Br_2$, Fig. 3, exhibits nearly ohmic behaviour (with $m = 1.06$) at low voltage followed by a much more rapid rise of current with voltage. The field corresponding to the onset of this sharp rise is only 85 $kVm^{-1}$ so it is improbable that breakdown occurs at this point. It is suggested that the rapid increase of current with voltage is at a trap-filled limit although in the Lampert model[23] there is a considerable transition voltage range between ohmic behaviour and trap filling.

All of the compounds prepared in these laboratories, with the exceptions of $Co(pzA)_2Cl_2$ and $Co(pzA)_2Br_2$, exhibit electrical characteristics indicative of SCLC. As pointed out by Rose and Smith[25] the observation of SCLC is only possible if trap concentrations and hence impurity concentrations are very low. Measurements of SCLC can therefore form an important tool in assessing the purity of a semiconducting material. If it is assumed that all of the compounds studied have a microscopic carrier mobility of similar order, then it follows that amongst our preparations $Co(pzA)_2Cl_2$ and $Co(pzA)_2Br_2$ have the highest trap concentrations.

A device in which $I \propto V^2$, as found for the $Ni(pzA)_2(CNS)_2$ disc, could have application in electrical power measurement and would be suited to conditions where voltage fluctuations are involved, *e.g.*, in electrical noise determinations. For such a device, connected in series with a diode, the mean current passed would be directly proportional to the mean noise power.

The highest conductivity observed for the compounds at room temperature ($1.8 \times 10^{-9}\ \Omega^{-1}\ m^{-1}$) is much too low to be useful for most semiconductor devices although it is anticipated that with suitable doping the conductivities may be raised by many orders of magnitude.

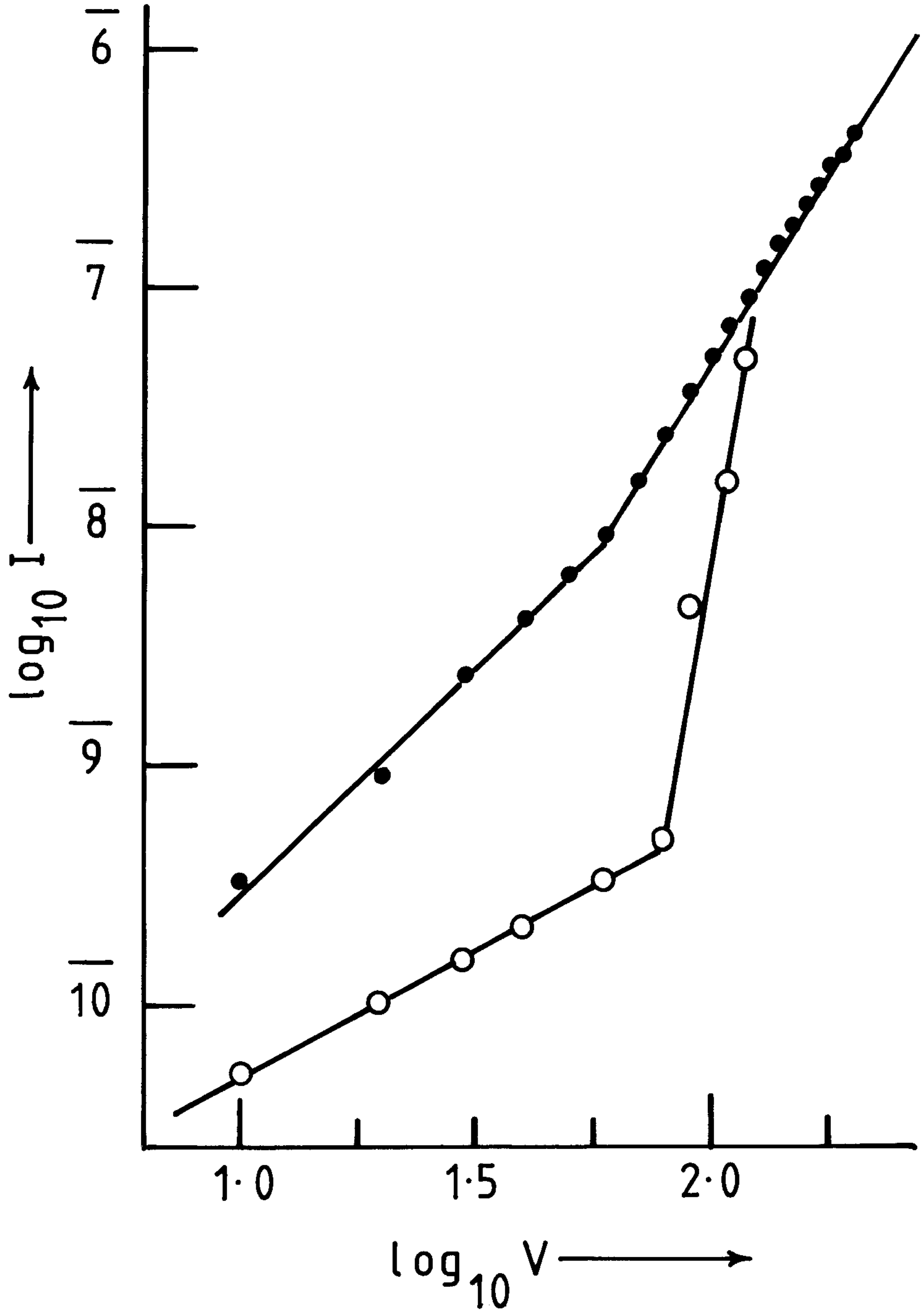


FIGURE 3 Log–log plots of room temperature I–V characteristics for the compounds $Ni(pzA)_2Br_2$ (upper plot) and $Cu(pzA)_2Br_2$ (lower plot). I and V are respectively in units of amps and volts.

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