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# THERMAL, SPECTRAL, MAGNETIC AND ELECTRICAL STUDIES OF COBALT(II) AND NICKEL(II) WITH 3-(3-PYRIDYL)ACRYLIC ACID

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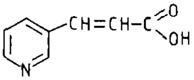
## ABSTRACT

The preparation and some properties of the complexes of 3-(3-pyridyl)acrylic acid with cobalt and nickel are described. Spectral, magnetic and solubility studies show that the complexes, which are hydrated, have polymeric octahedral structures. The thermal behaviour of these compounds has been studied by thermogravimetry (TG) and differential thermal analysis (DTA). Thermal decomposition studies show that the compounds lose water of crystallization followed by organic ligand to give the metal oxide. Electrical conductivity measurements at room temperature give results of $1.00 \times 10^{-6}$ $\Omega^{-1}$ $m^{-1}$ and $(1.6 \pm 0.4) \times 10^{-4}$ $\Omega^{-1}$ $m^{-1}$ for the cobalt and nickel complexes respectively. The current–voltage characteristics exhibit hysteresis, which is very marked for the nickel compound, and is attributed to current arising from dipolar orientation superimposed on a conduction current.

## INTRODUCTION

The molecule 3-(3-pyridyl)acrylic acid is interesting in having the following three potential sites for coordination to a metal ion: the nitrogen of the aromatic ring; the double bond between the carbon atoms and the oxygen atom(s) of the carboxylate ion.



3-(3-Pyridyl)acrylic acid (HPAA)

This paper reports thermal analysis studies of 3-(3-pyridyl)acrylic acid together with the complexes formed by the acid and the transition metals

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cobalt and nickel. Spectral and magnetic studies were used to characterize each metal complex and to interpret the type of coordination which takes place to the metal ion. Electrical conductivity measurements are also reported for the metal complexes.

## EXPERIMENTAL

### *Preparation of compounds*

The compounds were prepared by dissolving the metal carbonate in a hot aqueous solution of 3-(3-pyridyl)acrylic acid. The excess carbonate was removed by filtration. The compound was precipitated by concentrating the solution on a steam bath.

### *Measurements*

The concentration of the metal ion was obtained by a Perkin–Elmer 373 atomic absorption spectrophotometer and the carbon, hydrogen and nitrogen analyses were obtained using a Carlo Erba elemental analyser.

Electronic spectra were obtained on a Beckman Acta MIV spectrophotometer as solid diffuse reflectance spectra.

Infrared spectra were obtained using KBr discs, 4000–600 $cm^{-1}$, and polyethylene discs, 600–200 $cm^{-1}$, on a Perkin–Elmer infrared spectrophotometer model 598.

Magnetic measurements were performed by the Gouy method using $Hg[Co(SCN)_4]$ as calibrant. Each magnetic moment was corrected for diamagnetism using Pascal's constants [1].

Thermal analysis measurements were made using a Stanton Redcroft model STA 781 thermobalance. Thermogravimetry curves were obtained at a heating rate of 6 °C $min^{-1}$ in static air and over the temperature range 20–800 °C.

Electrical measurements were made on discs of the hydrous compounds and these discs were prepared by compressing powder material in a hydraulic press set to apply a force of 100 kN. The diameter of the discs was 13 mm and their approximate thickness was 1 mm. An electrode of diameter 4.9 mm, formed by applying a silver-based conductive paint through a mask, was provided on the flat sides of each disc. One electrode made contact with a copper heat sink and contact to the counter-electrode was by a spring-loaded pad. The current versus voltage characteristics at room temperature were obtained for d.c. conditions using a Keithley 610C electrometer to register current and a digital voltmeter for the voltage. The latter instrument was placed so that the current drawn by it did not pass through the electrometer. Readings were obtained for a series of increasing and decreasing voltages in both polarities. The thickness of each disc, which was needed for calculating the conductivity, was obtained using a micrometer.

The temperature dependence of the conductivity was measured for each disc by placing it, still on its mount, in an electrically heated oven and monitoring the current under a constant applied voltage (6 V and 10 V for $Co(PAA)_2 \cdot 3H_2O$ and $Ni(PAA)_2 \cdot 3H_2O$ respectively). The disc temperatures during these measurements were obtained using a previously calibrated copper–constantan thermocouple (formed from S.W.G. 44 wires) mounted on the discs. The oven heater current was switched off temporarily each time that the disc current was measured.

## RESULTS AND DISCUSSION

In Table 1 the analytical results for the complexes are shown. They agree with the given formulae, and the stereochemistry of the compounds show that the maximum number of 3-(3-pyridyl)acrylic acid molecules present in any one compound is two. The compounds are hydrated.

The wavenumbers of the infrared absorption bands, as well as their descriptions and assignments, are given in Table 2. The infrared spectra of the metal complexes exhibit medium absorption bands in the region 3100–2800 $cm^{-1}$ assigned to the $\nu$(O–H) vibration of water [2]. The band in

TABLE 1

Analyses and magnetic moments of the compounds

| Compound | Theory (%) | | | | Experimental (%) | | | | $\mu$ (B.M.) |
|---|---|---|---|---|---|---|---|---|---|
| | M | C | N | H | M | C | N | H | |
| $Co(PAA)_2 \cdot 3H_2O$ | 14.41 | 46.95 | 6.84 | 4.39 | 13.82 | 46.66 | 6.73 | 4.42 | 5.27 |
| $Ni(PAA)_2 \cdot 3H_2O$ | 14.36 | 46.97 | 6.85 | 4.40 | 13.57 | 46.38 | 7.01 | 4.23 | 2.73 |

TABLE 2

Electronic spectral details of prepared compounds

| Compound | Peak position ($cm^{-1}$) | Dq ($cm^{-1}$) | $B$ ($cm^{-1}$) | $\beta$ |
|---|---|---|---|---|
| $Co(PAA)_2 \cdot 3H_2O$ | 8197<br>20833 | 937 | 920 | 0.95 |
| $Ni(PAA)_2 \cdot 3H_2O$ | 9524<br>16393<br>27027 | 952 | 989 | 0.95 |

TABLE 3

Infrared spectra (4000–200 $cm^{-1}$) for the isolated compounds

| Compound | $\nu$(O–H) ($H_2O$) | $\nu$(COOH) | $\nu$($COO^-$) | $\nu$(C=C) | $\nu$(C–O) | Ring vibrations | $\nu$(M–O) |
|---|---|---|---|---|---|---|---|
| HPAA | | 1697 (s) | | 1640 (m) | 1490 (m) | 1420 (m) 1030 (m) | |
| $Co(PAA)_2 \cdot 3\ H_2O$ | 3100–2842 (br, s) | | 1682 (s) | 1637 (m) | 1482 (m) | 1440 (m) 1038 (m) | 231 (w) 415 (w) |
| $Ni(PAA)_2 \cdot 3\ H_2O$ | 3100–2800 (br, s) | | 1684 (s) | 1638 (m) | 1481 (m) | 1438 (m) 1040 (m) | 253 (w) 410 (w) |

br, broad; s, strong; m, medium; w, weak.

the region 1640–1637 $cm^{-1}$ is assigned to the $\nu$(C=C) vibration. The $\nu$(C=C) vibration in the complexes shows little change to that of the free ligand, indicating that the ligand is not bonded to the metal ions. The spectra of the complexes in the region 2000–625 $cm^{-1}$ are also similar to those of the free ligand except for the bands due to the ring vibrations of the aromatic ring, which move to higher frequency, and the presence of a band around 1683 $cm^{-1}$, which corresponds to the $\nu(COO^-)$ vibration. These observations suggest that the nitrogen atom in the aromatic ring and the oxygen atoms of the carboxylate group are coordinated to a metal atom [3–6]. The $\nu$(M–O) vibrations that we identify are indicative of an octahedral environment for the metal ions [7].

The d–d bands from the electronic spectra of the complexes are shown in Table 3. The position of the bands confirms that the metal ion in each of the compounds is in an octahedral environment [2]. The Dq values are consistent with this stereochemistry [8].

The magnetic moments for the compounds agree with the suggestion of an octahedral environment for the metal ions [2].

The poor solubility of the compounds in both polar and non-polar solvents implies that the compounds have polymeric structures [2].

The fact that the compounds were isolated as powders and not as single crystals prevents a complete structure determination. However, spectroscopic and magnetic data enable us to predict that a planar metal–oxygen chain is formed between two molecules of the 3-(3-pyridyl)acrylate and a metal ion. Each metal ion is thus bonded to four oxygen atoms in a plane and a nitrogen atom of an aromatic ring in adjacent planes to give a layer structure with a coordination number of six for the metal ion. The water molecules are attached by hydrogen bonding in each complex.

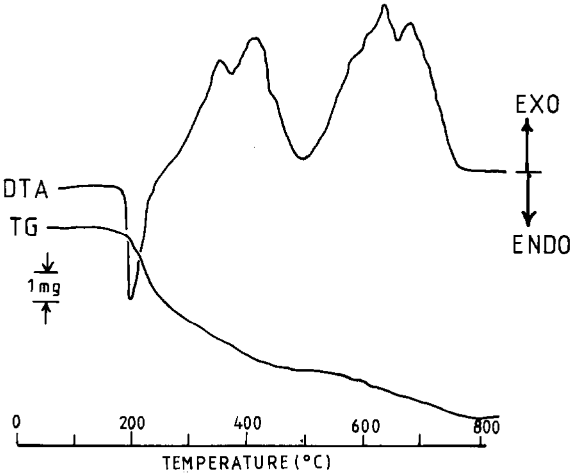

Fig. 1. TG and DTA traces of 3-(3-pyridyl)acrylic acid. Sample weight, 5.43 mg.

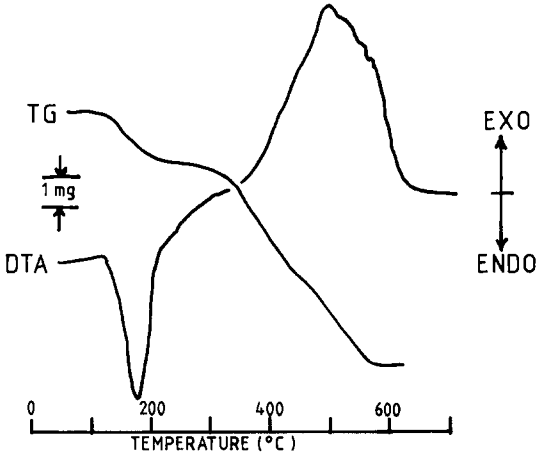

Fig. 2. TG and DTA traces of $Co(PAA)_2 \cdot 3H_2O$. Sample weight, 10.1 mg.

The thermogravimetry (TG) and differential thermal analysis (DTA) traces for 3-(3-pyridyl)acrylic acid and the complexes with cobalt(II) and nickel(II) are given in Figs. 1–3. The TG curve for 3-(3-pyridyl)acrylic acid shows that the acid is thermally stable in the temperature range 20–140 °C. Its pyrolytic decomposition begins at 140 °C and finishes at 740 °C with total elimination of the sample. The DTA curve of 3-(3-pyridyl)acrylic acid shows an endothermic peak at 253.9 °C owing to melting. The acid then decomposes immediately, producing two exothermic peaks.

The TG and DTA curves for the complexes formed between 3-(3-pyridyl)acrylic acid and cobalt(II) and nickel(II) are given in Figs. 2 and 3. The dehydration of the complexes starts below 150 °C and takes place in

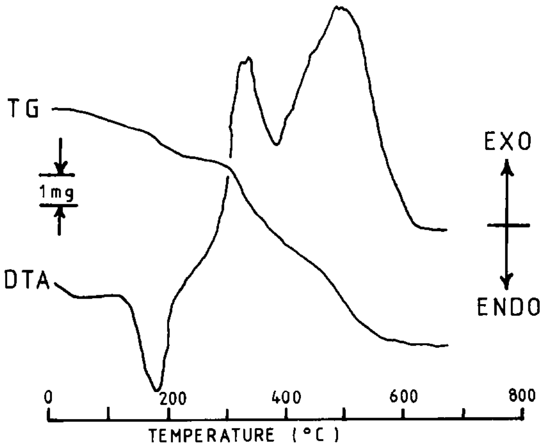

Fig. 3. TG and DTA traces of $Ni(PAA)_2 \cdot 3H_2O$. Sample weight, 9.9 mg.

TABLE 4

Dehydration processes of 3-(3-pyridyl)acrylic acid metal complexes

| Process | Peak temperature (° C) | Thermal nature of transformation | Weight loss (%) | | Enthalpy (kJ $mol^{-1}$) |
|---|---|---|---|---|---|
| | | | Calc. | Found | |
| $Co(PAA)_2 \cdot 3\,H_2O \rightarrow Co(PAA)_2$ | 174.9 | ENDO | 13.19 | 15.84 | 284.3 |
| $Ni(PAA)_2 \cdot 3\,H_2O \rightarrow Ni(PAA)_2$ | 192.7 | ENDO | 13.20 | 14.14 | 108.7 |

one step. The observed weight losses for these processes compare favourably with the theoretical values (Table 4). The expected endothermic peak for the dehydration processes associated with these compounds is observed in their DTA curves. The dehydration enthalpies were calculated and are given in Table 4. The decomposition of the anhydrous complexes follows immediately after the dehydration processes and the residual weights are in good agreement with the values required for the metal oxides. In the DTA curves, the decomposition processes correspond to exothermic effects as shown in Table 5.

Plots of the room temperature current ($I$) versus voltage ($V$) characteristics for discs of $Co(PAA)_2 \cdot 3H_2O$ and $Ni(PAA)_2 \cdot 3H_2O$ are shown in Fig. 4 and Fig. 5 respectively. For both compounds the magnitude $|I|$ of the current for a given magnitude $|V|$ of the voltage is greater as $|V|$ is increased than when it is decreased. This is valid irrespective of the polarity. For the nickel compound the effect is very pronounced, and it occurs to a much lesser extent for the cobalt compound. After completing the point-by-point measurements to obtain the data in the figures, each disc was re-cycled through the applied voltages corresponding to the first quadrant, and the new currents agreed to within a few per cent of those obtained originally. For the $Ni(PAA)_2 \cdot 3H_2O$ disc, with $|V| > 10$ V, the current drifted in the direction indicated by the vertical arrows in Fig. 5, suggesting a tendency of the characteristic to shift towards ohmic behaviour.

TABLE 5

Decomposition processes of 3-(3-pyridyl)acrylic acid metal complexes

| Process | Temperature range (° C) | Thermal nature of transformation | Residue weight loss (%) | |
|---|---|---|---|---|
| | | | Calc. | Found |
| HPAA → pyrolytic process | 178–740 | EXO | – | – |
| $Co(PAA)_2 \rightarrow Co_3O_4$ | 194–570 | EXO | 19.61 | 19.80 |
| $Ni(PAA)_2 \rightarrow NiO$ | 212–597 | EXO | 18.26 | 20.20 |

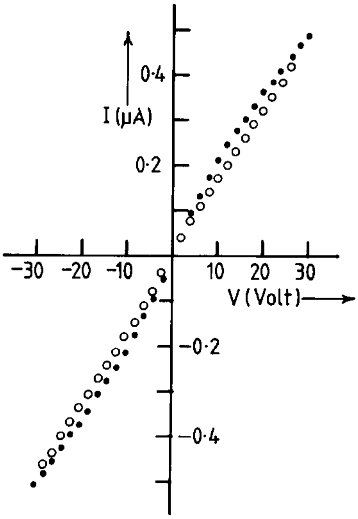

Fig. 4. Room temperature plot of current $I$ versus voltage $V$ for a disc of Co(PAA)$_2$·3H$_2$O having a thickness of 1.12 mm. ●, $|V|$ increasing; ○, $|V|$ decreasing.

There can be little doubt that the hysteresis observed in the $I$ versus $V$ curves is due to alignment of polar molecules in the field, giving a displacement current superimposed on a conduction current. It is to be expected that the degree of hysteresis would be influenced by the time taken to take the measurements, but we have not investigated this. It is estimated that the data in Figs. 4 and 5 were each collected in about 10 min.

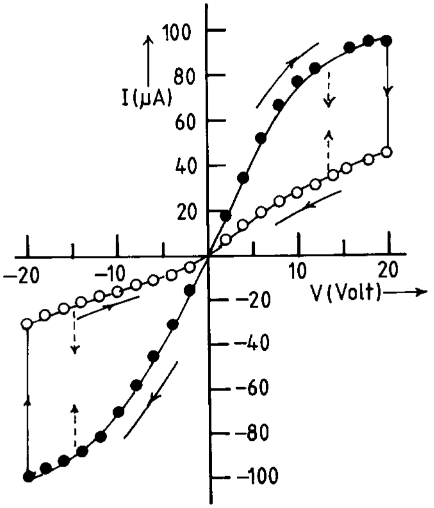

Fig. 5. Room temperature plot of current $I$ versus voltage $V$ for a disc of Ni(PAA)$_2$·3H$_2$O having a thickness of 0.89 mm. ●, $|V|$ increasing; ○, $|V|$ decreasing; ⇢, direction in which curve drifts for $|V| > 10$ V.

TABLE 6

Electric properties of the prepared compounds

| Compound | $\sigma$ [a] <br> ($\Omega^{-1}$ m$^{-1}$) | $\dfrac{\oint_{QI} I \, dV}{I_m V_m}$ [b] | $\Delta E$ [c] <br> (eV) |
|---|---|---|---|
| $Co(PAA)_2 \cdot 3H_2O$ | $1.00 \times 10^{-6}$ | 0.054 | 0.36 |
| $Ni(PAA)_2 \cdot 3H_2O$ | $(1.6 \pm 0.4) \times 10^{-4}$ | 0.415 | 9.2 |

[a] Values listed are electrical conductivities ($\sigma$) at room temperature.

[b] $\oint_{QI}$ denotes a clockwise path of integration around the loop in the first quadrant of the $I$ versus $V$ characteristic for room temperature ($V_m$ is the maximum applied voltage and $I_m$ is the corresponding current).

[c] $\Delta E$ is the parameter appearing in the equation $\sigma = \sigma_0 \exp(-\Delta E/2kT)$ and values are obtained from the linear sections AB and CD of Fig. 6 and Fig. 7 respectively. The applicability of the above equation for range CD is doubtful.

Consideration was given to the possibility that Joule heating caused decomposition, but this was rejected for the following reasons. (i) The data on re-cycling around the first quadrant would not be reproduced if the material had been altered. (ii) The maximum temperature rise $\Delta T_m$ in the disc as calculated from $\Delta T_m = \sigma V_m^2/2K$ for a disc with one side in contact with a large capacity heat sink (where $\sigma$ and $K$ are the electrical and thermal conductivities respectively with $V_m$ the maximum applied voltage) is less than 0.7 °C for the nickel compound. This is based on taking $K = 0.05$ W m$^{-1}$ °C$^{-1}$, the value appropriate to cork, and is expected to yield an over-estimate for $\Delta T_m$.

To specify the hysteresis, the dimensionless ratio $\oint_{QI} I \, dV/I_m V_m$ (in which the symbol $\oint_{QI}$ denotes clockwise integration around the loop in the first quadrant and $I_m$ is the current corresponding to the voltage $V_m$) was evaluated and is listed in Table 6. The integration was performed numerically using Simpson's rule.

We have previously observed [9] a similar hysteresis effect in the $I$ versus $V$ characteristics for the chloro complexes of cobalt, nickel and zinc with 3-(3-pyridyl)acrylic acid except that the enclosed area in the third quadrant of the plots for these compounds is much less than in the first quadrant. As in the present paper, the hysteresis is most prominent for the nickel compound.

The electrical conductivities ($\sigma$) at room temperature are listed in Table 6 for the two compounds. In each case the value of $\sigma$ is calculated from the mean gradient of the $I$ versus $V$ plot assuming that the current flow is perpendicular to the electrodes. The large range of uncertainty in the quoted conductivity for the nickel compound is a reflection of the highly non-linear nature of the $I$ versus $V$ plot.

The parameter $\Delta E$ in the equation $\sigma = \sigma_0 \exp(-\Delta E/2kT)$ [10,11] is given in Table 6 for each compound and is found from the linear regions AB

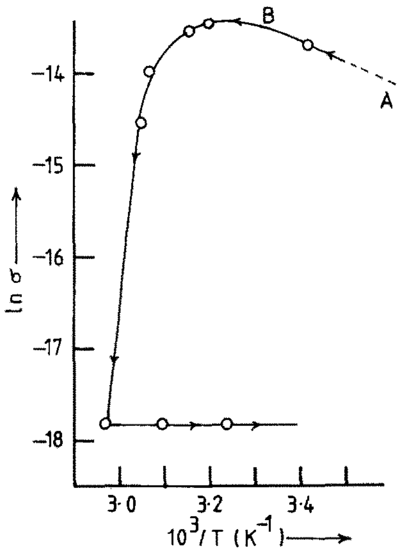

Fig. 6. Plot of ln $\sigma$ versus $10^3/T$ for the same Co(PAA)$_2\cdot$3H$_2$O disc as for Fig. 4 ($\sigma$ is in units of $\Omega^{-1}$ m$^{-1}$).

and CD of Fig. 6 and Fig. 7 respectively. Both compounds evidently decomposed during heating as is shown by the fact that on cooling back to room temperature the conductivity had changed markedly. For the cobalt compound $\Delta E$ is 0.35 eV, which is a plausible energy for ionization of a free carrier either by the intrinsic process or by release from impurity centres. In

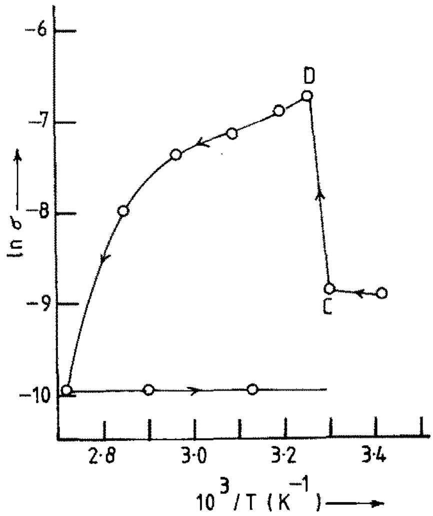

Fig. 7. Plot of ln $\sigma$ versus $10^3/T$ for the same Ni(PAA)$_2\cdot$3H$_2$O disc as for Fig. 5 ($\sigma$ is in units of $\Omega^{-1}$ m$^{-1}$).

the case of the nickel compound the very sharp rise in conductivity with increase in temperature over the range CD (Fig. 7) yields $\Delta E = 9.2$ eV and, with this anomalously high indicated activation energy, doubt must arise concerning its significance.

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