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Electrical and Structural Properties of Chloro Complexes of Cobalt, Nickel, Copper and Zinc with 3-(3-Pyridyl)acrylic Acid

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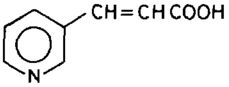
Abstract

The preparation and some properties of the chloro complexes of 3-(3-pyridyl)acrylic acid with cobalt, nickel, copper and zinc are described. Magnetic measurements, electronic and infrared spectra indicate that the compounds have octahedral structures with the 3-(3-pyridyl)acrylic acid bonded to the metal ions through the nitrogen atom in the aromatic ring system. Electrical conductivities for the compounds at room temperature lie in the narrow range from 1.8×10^{-6} Ω^{-1} m^{-1} (for the cobalt compound) to 3.7×10^{-5} Ω^{-1} m^{-1} (for the nickel compound). The current–voltage characteristics for all of the compounds are anomalous in exhibiting hysteresis which appears to be due to the presence of the olefinic bond. The activation energy for conduction in the cobalt compound has been obtained from the temperature dependence of the conductivity.

Introduction

In earlier work we have reported [1–5] electrical properties of metal complexes of mono and dicarboxylic acid. Amongst these, ohmic behaviour [3] and non-ohmic behaviour attributed to space charge conduction [1, 2, 4] and spatially asymmetric trap distributions [5] have been observed. As an extension to this work the effect of incorporating an olefinic bond into the complexes was considered desirable. To this end we have studied and now report some electrical and structural properties of the chloro complexes of 3-(3-pyridyl)acrylic acid with the first row transition metals cobalt, nickel, copper and zinc.

The compound 3-(3-pyridyl)acrylic acid has four possible coordination sites: the ring nitrogen atom, the double bond and the oxygen atoms of the carboxyl group.



3-(3-pyridyl)acrylic acid (HPAA)

Experimental

The compounds were prepared by adding a saturated solution of 3-(3-pyridyl)acrylic acid in boiling ethanol to 0.5 mol of the metal halide in 100 cm^3 of warm ethanol. The precipitated complexes were washed with a warm ethanolic solution and dried at 60 °C in an oven.

The compounds prepared are listed in Table I. The magnetic measurements (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 [6]. The electronic spectra (Table II) were obtained on a Beckmann ACTA MIV spectrophotometer 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.

Electrical conduction measurements under d.c. conditions were made on compressed powder discs of the compounds. The preparation of the discs and the method of obtaining the electrical data was as previously described [1–5].

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TABLE I. Analyses and Magnetic Moments of the Compounds[a]

Compound	Colour	Theory (%)				Experimental (%)				μ (BM)
		M	C	N	H	M	C	N	H	
$Co(HPAA)_2Cl_2$	violet	13.82	45.04	6.56	2.81	12.91	44.73	5.81	2.03	5.43
$Ni(HPAA)_2Cl_2$	green	13.78	45.06	6.57	2.81	13.44	44.86	6.11	2.96	3.25
$Cu(HPAA)_2Cl_2$	blue	15.02	45.40	6.62	2.83	14.37	45.10	6.04	2.37	2.01
$Zn(HPAA)_2Cl_2$	white	15.39	45.20	6.59	2.82	15.22	44.82	6.38	2.39	

[a] HPAA =

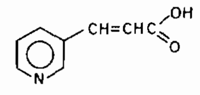

TABLE II. Important Infrared Bands of the Compounds (cm^{-1})[a]

Compound	ν(O–H)	ν(C=O)	ν(C=C)	ν(C–O)	δ (O–H)	Ring vibrations	ν(M–Cl)
HPAA	2450(m)	1697(s)	1640(m)	1230(m)	1320(m)	1586(m) 1420(m)	
$Co(HPAA)_2Cl_2$	2710(m) 2602(m)	1693(s)	1636(m)	1236(m)	1338(m)	1604(m) 1433(m)	252(w)
$Ni(HPAA)_2Cl_2$	2705(m) 2601(m)	1695(s)	1634(m)	1234(m)	1337(m)	1604(m) 1434(m)	245(w)
$Cu(HPAA)_2Cl_2$	2702(m) 2605(m)	1694(s)	1638(m)	1230(m)	1332(m)	1608(m) 1435(m)	236(w)
$Zn(HPAA)_2Cl_2$	2700(m) 2610(m)	1696(s)	1640(m)	1230(m)	1331(m)	1590(m) 1434(m)	<200

[a] s, strong; m, medium; w, weak.

TABLE III. Electronic Spectra of the Compounds

Compound	Peak position (cm^{-1})	Dq	B	β
$Co(HPAA)_2Cl_2$	6757 16393 18181	962	953	0.98
$Ni(HPAA)_2Cl_2$	8475 14184	847	983	0.94
$Cu(HPAA)_2Cl_2$	14084			

Results and Discussion

Analytical

In Table I the analytical results for the complexes are reported. They agree with the given formulae and the stoichiometry of the compounds shows that there are two molecules of 3-(3-pyridyl)acrylic acid present in each compound. All of the compounds are anhydrous.

Infrared Spectra

The wavenumbers of the infrared absorption bands, as well as their descriptions and assignments, are given in Table III. The infrared spectrum of 3-(3-pyridyl)acrylic acid is similar to that of its complexes in the region 2000–600 cm^{-1} except for the bands due to the ring vibrations of the aromatic ring which are at higher frequencies in the complexes than in the free acid. This suggests that in each complex the nitrogen atom in the aromatic ring is coordinated to a metal ion [7, 8]. The band at 1640 cm^{-1} has been assigned to the ν(C=C) vibration. The ν(C=C) vibration is little altered from the value of the free ligand showing that no bonding occurs between the π electron system and the metal ions. The slight lowering of the frequency of this signal in the spectra of the complexes is attributed to the effect of d_π–p_π overlap. The free acid shows a band between 2700–2300 cm^{-1} typical of ν(O–H) hydrogen bonded carboxylic acid groups [9]. In the spectra of complexes the ν(O–H) band is split into two moderately intense bands near 2702 and 2605 cm^{-1} suggesting that the oxygen atoms of the carboxylate group are not bonded to the metal [7, 8, 10, 11]. Furthermore, the ν(C=O) vibration frequencies as observed for the complexes are shifted only slightly towards lower values than for the free ligand. Metal–halogen vibrations are observed for the complexes and are reported in Table II. The assignments made for the ν(M–X) vibrations are consistent with those made for the ν(M–X) vibrations in octahedral cobalt, nickel and copper complexes with bridging halogen atoms [7, 8]. In the zinc complex no bands are observed above 200 cm^{-1} which could be assigned to the ν(Zn–Cl) vibration. This would suggest that the zinc ion is in an octahedral environment since tetrahedral compounds show strong absorption bands in the region 330–290 cm^{-1} [12].

Electronic Spectra

The d–d bands from the electronic spectra of the complexes are shown in Table III. The positions of the bands indicate that the metal ion in the cobalt, nickel and copper compounds is in an octahedral environment [7, 8]. The *Dq* values in Table III for the cobalt and nickel compounds are consistent with this stereochemistry [13].

Magnetic Moments

The magnetic moments for the cobalt and nickel compounds indicate that the metal atom is in an octahedral environment [7, 8]. The magnetic moment for the copper compounds is higher than the spin only value, suggesting some orbital contribution to the magnetic moment in this compound.

Proposed Stereochemistry

No single crystals of the compounds could be isolated from solution, thus without X-ray analysis, no definite structures can be described. However, the spectroscopic and magnetic data enable us to predict possible structures. It is thus postulated that the structure of the complexes is a chain of metal atoms bonded to halogens with 3-(3-pyridyl)acrylic acid molecules above and below the plane of the metal–halogen chain. The 3-(3-pyridyl)acrylic acid molecules are bonded to the metal atom through the lone pair of electrons on the nitrogen atom of the pyridine ring. It is further suggested that hydrogen bonding exists between adjacent 3-(3-pyridyl)acrylic acid molecules in the solid complexes.

The values of β, Table III, suggest only slight electron delocalisation between the metal and ligands [14].

Complexes of nicotinic acid and isonicotinic acid have been shown [7, 8] to have a similar structure to that proposed here for $M(HPAA)_2Cl_2$ compounds, but complexes of 2-pyrazine carboxylic acid and 2,3 pyrazine dicarboxylic acid have a different structure. For these complexes the oxygen atoms of the carboxylate group and the nitrogen atom of the aromatic ring are bound to the metal atom in each molecule [1, 5].

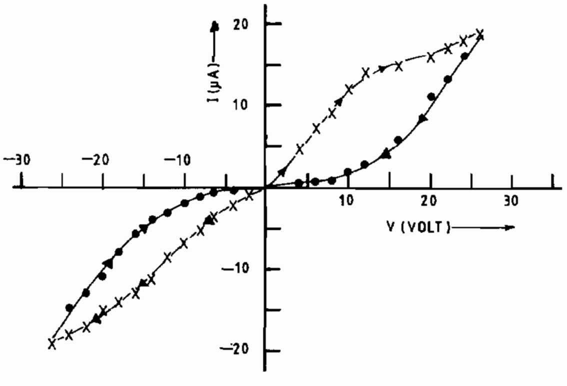

Fig. 1. Room temperature plot of current (*I*) *vs.* voltage (*V*) for a $Ni(HPAA)_2Cl_2$ disc of thickness 0.94 mm. x, increasing |*V*|; ●, decreasing |*V*|.

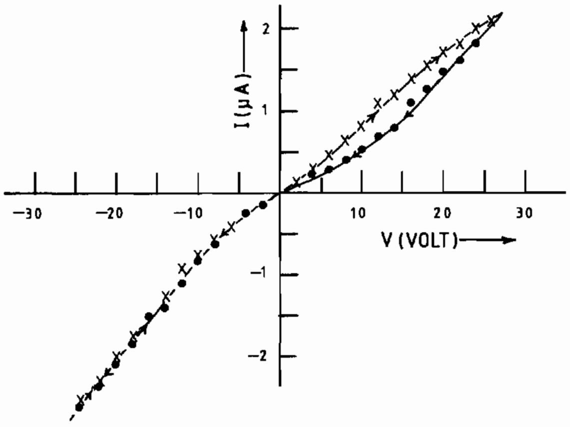

Fig. 2. Room temperature plot of current (*I*) *vs.* voltage (*V*) for a $Co(HPAA)_2Cl_2$ disc of thickness 0.30 mm. x, increasing |*V*|; ●, decreasing |*V*|.

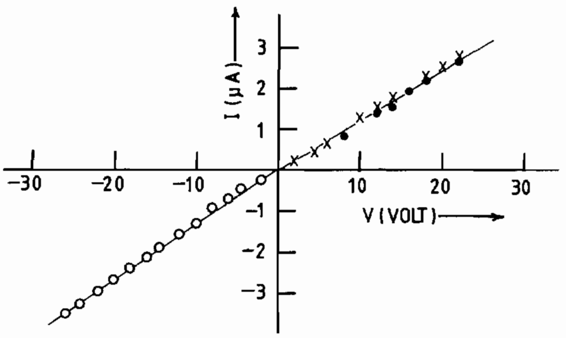

Fig. 3. Room temperature plot of current (*I*) *vs.* voltage (*V*) for a $Cu(HPAA)_2Cl_2$ disc of thickness 1.05 mm. x, increasing *V*; ●, decreasing *V*; both for $V > 0$. o, coincident data for |*V*| increasing and decreasing with $V < 0$.

Electrical Conduction

The room temperature current (*I*) *versus* voltage (*V*) characteristics for the nickel, cobalt and copper compounds are shown in Figs. 1, 2 and 3 respectively. For the nickel and cobalt compounds a striking feature is the hysteresis exhibited in these curves. During the first application of an increasing voltage the current exceeds its value for any given voltage compared with the current when the voltage is decreasing (first quadrant in Figs. 1 and 2). For increase and subsequent decrease of voltage under reversed polarity, *i.e.* in the third quadrant of the plots, the same effect can be seen for the nickel compound although the enclosed area is less than that in the first quadrant. In the case of the cobalt compound, Fig. 2, the area enclosed by the curve in the third quadrant has collapsed essentially to zero. The *I*

TABLE IV. Electrical Properties of the Compounds

Compound	σ^a (Ω^{-1} m^{-1})	$\oint_{Q1} I dV/I_m V_m{}^b$	ΔE^c (eV)
$Co(HPAA)_2Cl_2$	1.8×10^{-6}	0.11	0.25
$Ni(HPAA)_2Cl_2$	3.7×10^{-5}	0.33	
$Cu(HPAA)_2Cl_2$	7.8×10^{-6}	0.03	
$Zn(HPAA)_2Cl_2$	2.4×10^{-6}	0.08	

[a] σ = electrical conductivity. Data is for room temperature and based on the mean gradient of I *versus* V graphs in the third quadrant. [b] Data is for room temperature. The range of integration is clockwise around the closed loop of I *versus* V plots in the first quadrant. V_m = maximum applied voltage (26 volt); I_m = current flowing for the maximum applied voltage. [c] ΔE is the parameter appearing in the equation $\sigma = \sigma_0 \exp(-\Delta E/2kT)$ and is found from the gradient of the linear section of the ln σ *versus* $1/T$ plot.

versus V curve for the zinc compound, which has not been presented, is qualitatively similar to that for the cobalt compound. For the copper compound the hysteresis in both polarities is small but again is qualitatively similar. In view of this small hysteresis no attempt has been made to show the enclosed areas in Fig. 3.

To quantify the hysteresis in the I *versus* V characteristics the dimensionless ratio $\oint_{Q1} I dV/I_m V_m$ (in which the contour integral is clockwise around the closed loop in the first quadrant, V_m is the maximum applied voltage = 26 volt and I_m is the corresponding current) has been evaluated and listed in Table IV. The integration was performed numerically using Simpson's rule.

Table IV shows the conductivity (σ) for each compound at room temperature. The conductivities have been determined in each case from the mean gradient of the I *versus* V plot in the third quadrant and with the assumption that current flows perpendicularly to the electrodes. The range of room temperature conductivity is from 1.8×10^{-6} Ω^{-1} m^{-1} for the cobalt compound to 3.7×10^{-5} Ω^{-1} m^{-1} for the nickel compound and hence the range of conductivies only spans a factor of 21. This limited conductivity range amongst a series of compounds having the same structure suggests that the observed conductivities are close to the intrinsic values since, if impurities played a major role, one would expect a much wider range as a result of a likely spread in concentrations of donor or acceptor centres.

Consideration has been given to the possibility that hysteresis in the I *versus* V characteristic is a consequence of a chemical change produced by Joule heating. However, a simple calculation shows that the temperature rise during the measurements cannot exceed 0.3 °C, so that thermal degradation is not involved. Furthermore, with V_m = 130 volt for new discs, the resulting conductivities and the shapes of the I *versus* V curves are similar to those for V_m = 26 volt. Hysteresis was not observed in our previously reported work [1–5] on metal complexes of mono and dicarboxylic acid, although these compounds also have polymeric octahedral structures and the measuring conditions were identical. In a recent investigation [15] of another series of complexes, which like the $M(HPAA)_2Cl_2$ series contains an olefinic bond, hysteresis is observed. The evidence therefore suggests that the olefinic bond is the cause of the hysteresis. Possibly, polar molecules orient in the applied field during its first application, but are hindered from subsequent re-randomisation during removal of the field. A current component which is time dependent would be expected if molecules orient and we estimate the time taken to collect the data for each compound was about ten minutes.

Results for the temperature dependences are plotted in Fig. 4 for the copper and zinc compounds and in Fig. 5 for the cobalt compound. These plots are in the form of ln σ *versus* $1/T$ graphs, in which T is the absolute temperature. Equivalent data for the nickel compound were not measured. From the plots it is clear that thermal degradation occurs and is associated with a sharp fall in conductivity. With cooling back to room temperature, the conductivity

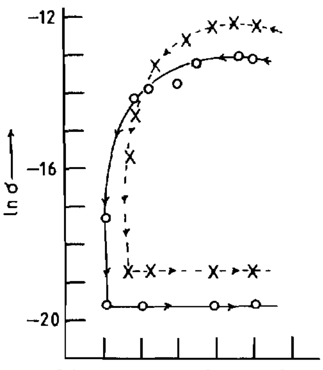

Fig. 4. Plots of ln σ *vs.* $10^3/T$. (σ = conductivity in units of Ω^{-1} m^{-1}, T = absolute temperature). x---, $Cu(HPAA)_2Cl_2$; o——, $Zn(HPAA)_2Cl_2$.

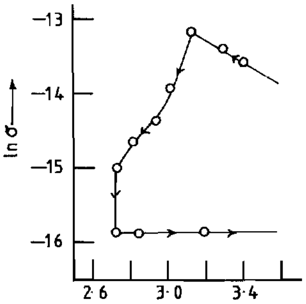

Fig. 5. Plot of ln σ *vs.* $10^3/T$ (σ = conductivity in units of Ω^{-1} m^{-1}, T = absolute temperature) for $Co(HPAA)_2Cl_2$.

of the degraded discs remain constant. For the cobalt compound, Fig. 5, there is a well defined peak which we interpret as the decomposition temperature and read from the graph as 318.5 ± 1.0 K. A thermogravimetric analysis for a further sample of the same compound yielded a decomposition temperature of 318 ± 1.0 K, which is in excellent agreement. We have previously reported [3] the good agreement between the electrical and thermogravimetric methods of determining decomposition temperatures. The compound $Co(HPAA)_2Cl_2$ showed, Fig. 5, a linear range during initial stages of heating. The gradient from this linear section leads to a value of 0.25 eV for the parameter ΔE appearing in the equation $\sigma = \sigma_0 \exp(-\Delta E/2kT)$. If the band model is applicable, as it is believed to be for conductivities as high as those found here [16] and if the free carriers are intrinsically generated, then ΔE can be identified [17] as the energy gap between valence and conduction bands. Thermal stability of the copper and zinc compounds, according to the evidence in Fig. 4, is very poor since the conductivity peaks at only 303 K for both of these compounds.

This paper has described the preparation and some characterisation of the compounds $M(HPAA)_2Cl_2$ in which M is Co, Ni, Cu and Zn. Information relating to the structure has been ascertained using magnetic measurements together with electronic and infrared spectra. Electrical data has been presented in which an unusual hysteresis exists in the *I versus V* characteristics and this effect is believed to be associated with the olefinic bond.

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