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Preparation, structural characterisation, thermal and electrical studies of the chloro complexes of cobalt, nickel and copper with acrylamide

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Abstract

The chloro compounds of cobalt, nickel and copper with acrylamide have been prepared. Spectral and magnetic data have been used to deduce the stereochemistry of the compounds. The thermal behaviour of acrylamide and its complexes with cobalt, nickel and copper have been studied by thermogravimetry and differential thermal analysis. The cobalt complex forms an intermediate complex before the metal oxide is produced. The nickel and copper complexes undergo decomposition with loss of the organic ligand and chlorine to give the metal oxides.

Electrical conductivities for the compounds at room-temperature are in the range $5.8 \times 10^{-8}\ \Omega^{-1}\ m^{-1}$ (for the cobalt compound) to $3.1 \times 10^{-5}\ \Omega^{-1}\ m^{-1}$ (for the copper compound). The current-voltage characteristic for the uncomplexed acrylamide is ohmic whereas its complexes exhibit hysteresis which is attributed to orientation of the polar complexed molecules in the applied electric field. The temperature dependences of conductivity have been determined for the compounds and are used to measure the activation energies for conduction.

INTRODUCTION

The compound acrylamide has three donor sites which can form bonds with metal ions: the nitrogen atom of the amine group, the double bond between the carbon atoms and the oxygen of the carboxyl group.

$H_2C{=}CHCONH_2$
Acrylamide (C_3H_5NO)

This paper reports the thermal analysis and electrical studies of acrylamide and its complexes with the transition metals cobalt, nickel and copper. Spectral and magnetic studies have been used to characterise each metal complex and to interpret the type of coordination which takes place with the metal ion.

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EXPERIMENTAL

Preparation of the complexes

The compounds were all prepared by mixing hot ethanolic solutions of acrylamide and the appropriate metal halide in an approximately 2:1 molar ratio. The precipitated complexes were filtered, washed with warm ethanol and air dried.

Apparatus

The concentration of the 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 infrared spectra were recorded using KBr discs over the wavenumber range 4000–600 cm^{-1}, and using polyethylene discs over the 600–200 cm^{-1} range, on a Perkin–Elmer infrared spectrophotometer, model 598. The electronic spectra were recorded as solid diffuse reflectance spectra using a Beckman Acta MIV spectrophotometer.

Measurements of magnetic moments were made using the Gouy method with $Hg[Co(SCN)_4]$ as calibrant.

The thermal analysis studies were made on a Stanton Redcroft model STA 1500 thermobalance. Thermogravimetry (TG) and differential thermal analysis (DTA) traces were obtained at a heating rate of 10°C min^{-1} in static air. The 20–800°C range was studied in all cases. The intermediate compound was isolated from the starting material by heating the starting material at a fixed temperature on the thermobalance until a constant weight was obtained.

Electrical measurements of the compounds were carried out on discs 13 mm in diameter and of thickness in the range 0.93–1.33 mm, formed by compressing powdered compound in a hydraulic press which was set to apply a force of 100 kN. An electrode of diameter 4.9 mm was placed concentrically on each of the two flat faces of every disc by applying conductive silver paint through masks. Measurements of current were obtained using a Keithley 610C electrometer. For room-temperature conductivity determinations 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. Temperature dependence measurements of conductivity for each compound were obtained by placing each disc in turn in an electrically heated oven and heating over the approximate temperature range of 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

TABLE 1

Analyses of the compounds

Compound	Colour	Theory (%)				Found (%)			
		Metal	Carbon	Nitrogen	Hydrogen	Metal	Carbon	Nitrogen	Hydrogen
$Co(C_3H_5NO)_2Cl_2$	Blue	21.67	26.47	10.29	3.68	21.36	26.26	10.12	3.24
$Co(C_3H_5NO)Cl_2$ [a]	Blue	29.33	17.92	6.97	2.49	29.08	17.56	6.66	2.29
$Ni(C_3H_5NO)_2Cl_2$	Yellow	21.60	26.49	10.30	3.68	21.34	26.39	10.02	3.32
$Cu(C_3H_5NO)_2Cl_2$	Green	22.97	26.03	10.12	3.62	22.57	25.73	9.87	3.28

[a] Thermal decomposition product.

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 analytical data agree with the given formulae proposed for the complexes.

The wavenumbers of the IR absorption bands as well as their descriptions and assignments are given in Table 2 for acrylamide and its complexes isolated from ethanolic solution. The IR spectrum of acrylamide is almost identical to those of its complexes in the 4000–600 cm^{-1} region except for the bands due to the $\nu(NH_2)$ vibrations which move to lower wavenumbers on complexation. This would suggest that bonding is taking place between the metal atom and the nitrogen of the amine group [1]. The fact that little change is observed in the wavenumber of the $\nu(C=C)$ and $\nu(C=O)$ vibrations would suggest that no bonding takes place between these groups and the metal atom. Metal–halogen and metal–nitrogen bands are assigned for the complexes and are reported in Table 2.

The electronic spectra and magnetic measurements, see Table 3, would suggest that for the cobalt complex the cobalt atoms are in a tetrahedral

TABLE 2

Infrared spectra (4000–200 cm^{-1}) [a]

Compound	$\nu(NH_2)$	$\nu(C=O)$ [b]	$\nu(C=C)$	$\nu(M-Cl)$	$\nu(M-N)$
C_3H_5NO	3342 (s), 3180 (s)	1668 (s)	1612 (s)		
$Co(C_3H_5NO)_2Cl_2$	3332 (s), 3170 (s)	1666 (s)	1614 (s)	358 (vs)	236 (w)
$Ni(C_3H_5NO)_2Cl_2$	3333 (s), 3172 (s)	1668 (s)	1614 (z)	266 (m)	220 (w)
$Cu(C_3H_5NO)_2Cl_2$	3330 (z), 3168 (s)	1667 (s)	1612 (z)	320 (z)	238 (w)

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

[b] The assignment of this frequency to the carbonyl group is not intended to imply that the absorption is due only to the C=O bond.

TABLE 3

Electronic spectra and magnetic moments

Compound	Band position (cm^{-1})	μ (BM)
$Co(C_3H_5NO)_2Cl_2$	7300	4.20
	14598	
	17857	
$Ni(C_3H_5NO)_2Cl_2$	7194	2.76
	13389	
	23148	
$Cu(C_3H_5NO)_2Cl_2$	6410	2.02
	24986 (sh) [a]	

[a] sh, shoulder.

environment [2]. The position of the cobalt chloride bands in the IR spectrum of this complex supports the suggested tetrahedral configuration for the complex [2]. The electronic spectrum and magnetic moment of the nickel complex are indicative of the nickel atom in an octahedral environment [3]. The nickel–chloride band in the IR spectrum of this complex supports the suggestion of an octahedral configuration for the complex [3]. Two bands are observed in the electronic spectrum of the copper complex, one below 10000 cm^{-1} and the other above 20000 cm^{-1}. This would suggest that the copper atom is in a tetrahedral environment [4]. The magnetic moment is 2.02 BM indicating no magnetic spin–spin interaction in the complex. The copper–chloride band in the far-IR spectrum of the complex agrees with the suggestion of a tetrahedral environment for the copper atom [5].

The fact that the complexes were isolated as powders and not as single crystals means that no complete structure determination was carried out. However, the spectroscopic and magnetic data enable us to propose structures. In the cobalt and copper compounds two chloride ions and two acrylamide molecules make up the tetrahedral environment around the metal ions. The nickel complex has an octahedral structure. The poor solubility of this complex in both polar and non-polar solvents would suggest that it has a polymeric structure [3]. It is thus postulated that for this complex the nickel atoms are bonded to halogen atoms to give a chain in which each halogen acts as a bridge between the metal atoms. The acrylamide molecules are bonded to the nickel atoms above and below the plane of the chain.

The TGA and DTA traces for acrylamide and its cobalt, nickel and copper complexes are given in Figs. 1–4. The TG trace for acrylamide, Fig. 1, shows that this compound is thermally stable in the 20–90°C range. Its pyrolytic decomposition starts at 90°C and finishes at around 225°C with the total elimination of the sample. The DTA trace of acrylamide, Fig. 1,

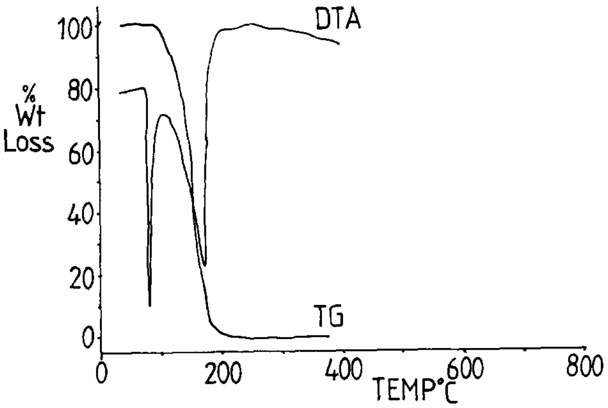

Fig. 1. TG and DTA trace for C_3H_5NO; sample weight = 7.15 mg.

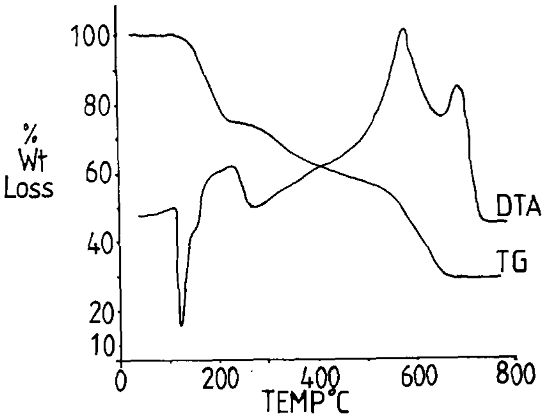

Fig. 2. TG and DTA trace for $Co(C_3H_5NO)_2Cl_2$; sample weight = 12.06 mg.

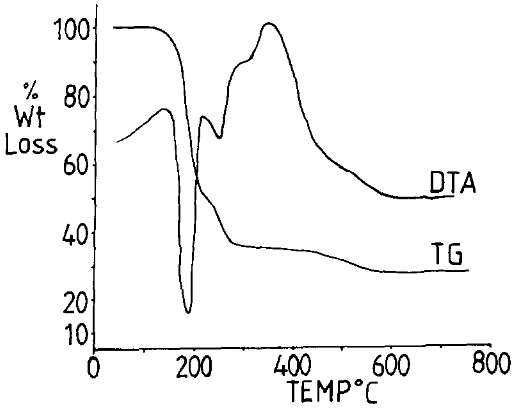

Fig. 3. TG and DTA trace for $Ni(C_3H_5NO)_2Cl_2$; sample weight = 8.68 mg.

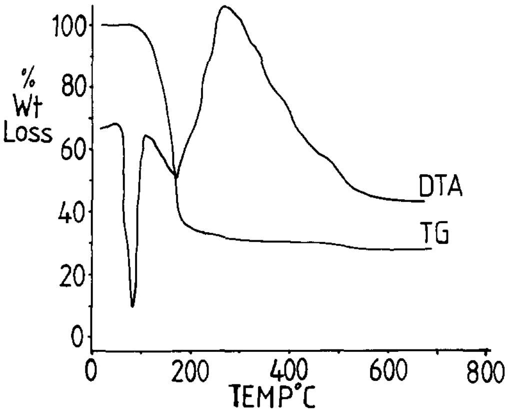

Fig. 4. TG and DTA trace for $Cu(C_3H_5NO)_2Cl_2$; sample weight = 7.76 mg.

displays an endothermic peak at 86°C corresponding to fusion. The value for the fusion enthalpy calculated from the DTA trace is 7 kJ mol^{-1}. The ligand, acrylamide, decomposes immediately producing an endothermic peak at 175°C. The TG and DTA traces for the complexes formed between acrylamide and the chlorides of cobalt, nickel and copper are given in Figs. 2–4. The cobalt complex, $Co(C_3H_5NO)_2Cl_2$, undergoes an endothermic reaction with the loss of one molecule of acrylamide and the formation of the intermediate compound $Co(C_3H_5NO)Cl_2$. This compound then undergoes exothermic reactions with loss of the remaining molecules of acrylamide and chlorine to give Co_3O_4. The nickel and copper complexes do not yield intermediate compounds but undergo endothermic/exothermic reactions with loss of the organic ligand and chlorine to give the metal oxides.

Plots of room-temperature current (I) versus voltage (V) characteristics for discs of $Co(C_3H_5NO)_2Cl_2$ and $Ni(C_3H_5NO)_2Cl_2$ are shown in Figs. 5

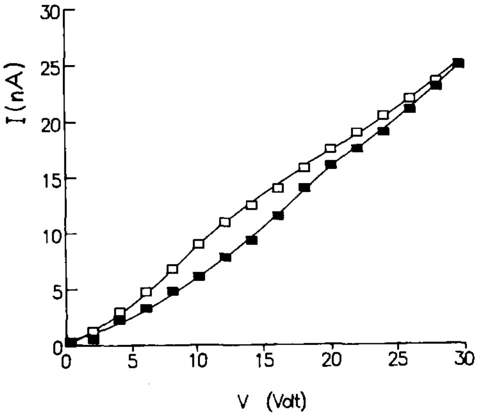

Fig. 5. Room-temperature plot of current (I) versus voltage (V) for a disc of $Co(C_3H_5NO)_2Cl_2$; ■, $|V|$ increasing; □, $|V|$ decreasing.

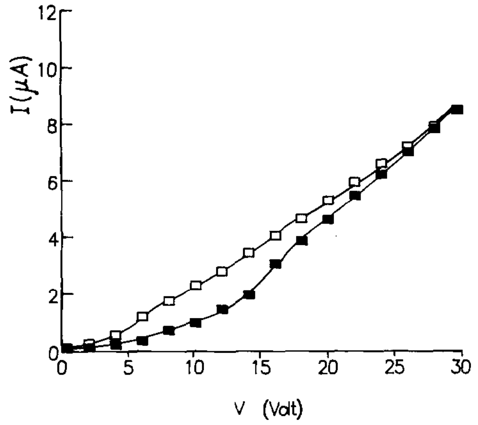

Fig. 6. Room-temperature plot of current (I) versus voltage (V) for a disc of $Ni(C_3H_5NO)_2Cl_2$; ■, $|V|$ increasing; □, $|V|$ decreasing.

and 6. The main feature of these plots is the hysteresis they exhibit. The magnitude of the measured current when the applied voltage was decreased was found to be greater than the value of the current measured during application of increasing voltage. On reversal of the polarity, similar hysteresis effects were obtained on application and removal of the applied voltage for discs of both compounds. The compound $Cu(C_3H_5NO)_2Cl_2$ shows similar qualitative hysteresis characteristics to that shown in Figs. 5 and 6. The presence of hysteresis in the current versus voltage characteristics has previously been observed in metallo-organic compounds of 3-(3-pyridyl)acrylic acid [6,7]. The hysteresis effect is considered to be associated with the presence of an alkene double bond in the structure of the compound. It is postulated that there is a degree of alignment of the polar molecule during application of the applied field and during subsequent removal of this field the molecules only slowly reorientate back to their original positions. Thus the hysteresis effect observed is a result of a semi-permanent distortion of the molecules. Evidence for such a distortion has previously been obtained [8] in other metallo-organic compounds from spectroscopic measurements.

The I versus V characteristic for a disc of the free acrylamide ligand is distinctively different from its complexes in that it shows ohmic behaviour. Thus it appears that the hysteresis effect only occurs when the ligand is complexed to a metal atom.

The room-temperature conductivity values for acrylamide and its complexes are listed in Table 4. Because the complexes exhibit hysteresis, the room-temperature conductivities have been determined from the mean gradient of the I versus V plot with the assumption that the current flows perpendicularly to the electrodes. The measured conductivities show that complexation of acrylamide with nickel and copper chloride yields com-

TABLE 4

Electrical properties of the compounds

Compound	σ [a] (Ω^{-1} m^{-1})	ΔE [b] (eV)	
		Heating	Cooling
C_3H_5NO	2.04×10^{-6}	0.40	0.91
$Co(C_3H_5NO)_2Cl_2$	5.78×10^{-8}	1.03	1.46
$Ni(C_3H_5NO)_2Cl_2$	2.39×10^{-5}	–	1.37
$Cu(C_3H_5NO)_2Cl_2$	3.06×10^{-5}	0.97	1.89

[a] Room-temperature (22°C) conductivity.

[b] 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 σ against T^{-1} was used to determine ΔE. Separate results are given for heating and cooling cycles.

pounds whose conductivities are higher by a factor of 12–15 when compared to the uncomplexed acrylamide. In contrast, the conductivity of the cobalt complex is found to be lower than that of acrylamide by a factor of 35. Similar results were obtained from another disc of the cobalt compound thus indicating that the conductivity is a function of the bulk material and not of the method of electrical contact.

The temperature dependence of the conductivity (σ) for $Cu(C_3H_5NO)_2Cl_2$ is shown in Fig. 7 as a plot of ln σ versus T^{-1} where T is the absolute temperature. Linearity of such a plot would show the validity of the equation $\sigma = \sigma_0 \exp(-\Delta E/2kT)$ where, assuming the band model is applicable, ΔE can be considered as the activation energy for releasing free carriers. However, the current measured during the cooling phase does not agree with that measured during the heating phase even though the

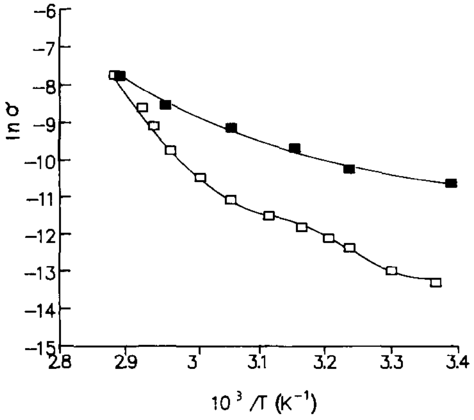

Fig. 7. Arrhenius plot (in the form of ln σ versus $10^3/T$ where σ = conductivity in units of Ω^{-1} m^{-1} and T is the absolute temperature) for a disc of $Cu(C_3H_5NO)_2Cl_2$; ■, points obtained during heating; □, points obtained during cooling.

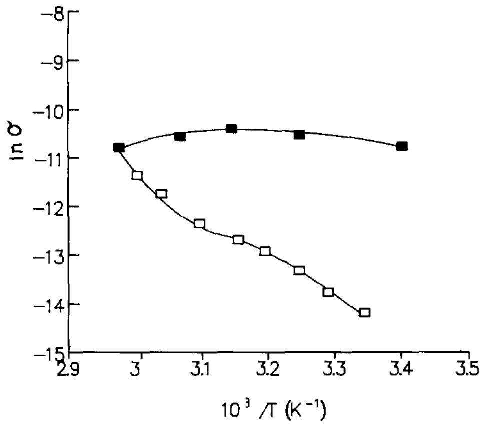

Fig. 8. Arrhenius plot (in the form of ln σ versus $10^3/T$ where σ = conductivity in units of Ω^{-1} m^{-1} and T is the absolute temperature) for a disc of $Ni(C_3H_5NO)_2Cl_2$; ■, points obtained during heating; □, points obtained during cooling.

highest temperature reached was only 346 K which is significantly below the decomposition temperature found from the TG/DTA traces. Uncomplexed acrylamide and its cobalt complex exhibit similar temperature dependences of conductivity to that described for $Cu(C_3H_5NO)_2Cl_2$. Values of ΔE, as calculated from the gradients of the best fitting lines for both the heating and cooling cycles, are listed in Table 4 for each compound. Due to the limited linearity of the temperature dependence plots and the disparity between the heating and cooling data, caution should be exercised in the interpretation of the tabulated ΔE values.

The temperature dependence of conductivity for $Ni(C_3H_5NO)_2Cl_2$ is shown in Fig. 8 and is seen to exhibit negligible change in conductivity with temperature during heating. A possible explanation for this behaviour is that the species of impurity resulting in the room-temperature conductivity is essentially fully ionised at 300 K and the intrinsic mechanism is not significantly activated until temperatures higher than those studied are reached. Evidently, near the maximum temperature attained, a non-reversible change in the electrical properties is produced.

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