

## Thermal, structural and electrical studies of the chloro complexes of cobalt, nickel and copper with 2-butoxypyridine

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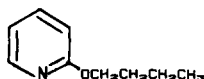
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### Abstract

The chloro compounds of 2-butoxypyridine with cobalt, nickel and copper were prepared in ethanolic solution from which solid compounds were isolated. The suggested structure for the cobalt compound is tetrahedral, whereas for the nickel and copper compounds it is octahedral. The techniques of thermogravimetry and differential thermal analysis show that the copper compound forms an intermediate compound before the metal oxide is formed. The cobalt and nickel compounds decompose with loss of the organic ligand and chlorine to give the metal oxides. Room temperature electrical conductivities of the prepared compounds show near-ohmic behaviour and are in the narrow range of  $2.41 \times 10^{-8}$  to  $6.33 \times 10^{-8} \Omega^{-1} \text{ m}^{-1}$ . The temperature dependence of conductivity shows anomalous behaviour. The similarity in electrical properties of the compounds studied suggests that the conductivities are intrinsically controlled.

### INTRODUCTION

In this paper, the structural characterisation and the thermal and electrical studies of the chloro compounds of cobalt, nickel and copper with 2-butoxypyridine are described and discussed. The molecule of 2-butoxypyridine has two donor sites for bonding to metal ions: the nitrogen atom of the aromatic ring system and the oxygen atom of the butoxy group.



2-Butoxypyridine ( $\text{C}_9\text{H}_{13}\text{NO}$ )

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Spectral and magnetic studies were used to characterise each complex and to interpret the type of coordination which takes place to the metal ion. A study of the thermal decomposition of each compound was carried out using thermogravimetry and differential thermal analysis. Studies involving d.c. electrical measurements were used to obtain information on room temperature electrical conductivity and carrier activation energy.

## EXPERIMENTAL

### *Preparation of the metal complexes*

The complexes were prepared by adding an excess of 2-butoxypyridine to 25 cm<sup>3</sup> of a warm solution of the hydrated metal halide (0.01 mol in ethanol). The complexes which precipitated on cooling were filtered and air dried.

### *Apparatus*

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

The IR spectra were obtained using KBr discs, 4000–600 cm<sup>-1</sup>, and polyethylene discs, 600–200 cm<sup>-1</sup>, on a Perkin-Elmer IR spectrophotometer, model 598.

The electronic spectra were obtained on a Beckmann Acta M IV spectrophotometer as solid diffuse spectra.

Magnetic measurements were carried out by the Gouy method using Hg[Co(SCN)<sub>4</sub>] as calibrant.

The thermal analysis studies were carried out on a Stanton-Redcroft model STA 1500 thermobalance. The TG and DTA traces were obtained at a heating rate of 10°C min<sup>-1</sup>. In all cases, the 20–800°C temperature range was studied. Intermediate compounds were isolated from the starting materials by heating them at a fixed temperature on the thermobalance until a constant weight was obtained.

Electrical conduction measurements were performed under d.c. conditions on discs of the compounds which were prepared by compressing a powdered sample of the complex. These discs were 13 mm in diameter and thicknesses ranged from 1.06 to 1.69 mm. Electrodes 4.9 mm in diameter were formed on the flat surfaces of the discs by applying a silver-based conductive paint. Details of the methods used for electrical measurements have been previously described [1,2].

## RESULTS AND DISCUSSION

The complexes prepared are listed in Table 1. The analytical results agree with the stoichiometry of the complexes.

TABLE 1

Analyses of metal complexes

| Compound                                                     |        | Metal | Carbon | Nitrogen | Hydrogen |
|--------------------------------------------------------------|--------|-------|--------|----------|----------|
| $\text{Co}(\text{C}_9\text{H}_{13}\text{NO})_2\text{Cl}_2$   | Theory | 13.63 | 50.01  | 6.48     | 6.01     |
|                                                              | Found  | 13.42 | 49.66  | 5.68     | 5.92     |
| $\text{Ni}(\text{C}_9\text{H}_{13}\text{NO})_2\text{Cl}_2$   | Theory | 13.59 | 50.04  | 6.48     | 6.02     |
|                                                              | Found  | 13.19 | 49.48  | 6.33     | 5.74     |
| $\text{Cu}(\text{C}_9\text{H}_{13}\text{NO})_2\text{Cl}_2$   | Theory | 14.55 | 49.44  | 6.41     | 5.95     |
|                                                              | Found  | 14.28 | 49.18  | 6.27     | 5.76     |
| $\text{Cu}_3(\text{C}_9\text{H}_{13}\text{NO})_2\text{Cl}_6$ | Theory | 27.01 | 30.61  | 3.97     | 3.68     |
|                                                              | Found  | 26.84 | 30.42  | 3.66     | 3.39     |

The electronic spectra and magnetic measurements are listed in Table 2. The position of the bands in the spectra of the cobalt and nickel complexes together with the magnetic moments, would suggest that the cobalt atoms are in a tetrahedral environment and the nickel atoms are in an octahedral environment in these compounds [3,4]. The copper compound has a broad band in its electronic spectrum between 10 000 and 15 000  $\text{cm}^{-1}$ , suggesting that the copper atoms are in an octahedral environment in the compound [4]. The magnetic moment obtained for the compound is higher than the spin-only value of 1.73 BM, suggesting some orbital contribution to the magnetic moment.

Table 3 shows the main bands in the IR spectra of 2-butoxypyridine and its metal complexes. The IR spectrum of the 2-butoxypyridine is similar to that of its complexes in the 4000–600  $\text{cm}^{-1}$  region. However a difference in the spectra is observed for the ring vibrations which move to higher wavenumbers on complexation. This would suggest that bonding is taking place between the metal atoms and the nitrogen atom of the aromatic ring

TABLE 2

Electronic spectra and magnetic moments

| Compound                                                   | Band position<br>( $\text{cm}^{-1}$ ) | d-d Transition                                                    | $\mu$ (BM) |
|------------------------------------------------------------|---------------------------------------|-------------------------------------------------------------------|------------|
| $\text{Co}(\text{C}_9\text{H}_{13}\text{NO})_2\text{Cl}_2$ | 6944 <sup>a</sup>                     | $^4\text{A}_2(\text{F}) \rightarrow ^4\text{T}_2(\text{F})$       | 4.46       |
|                                                            | 16892                                 | $^4\text{A}_2(\text{F}) \rightarrow ^4\text{T}_1(\text{P})$       |            |
| $\text{Ni}(\text{C}_9\text{H}_{13}\text{NO})_2\text{Cl}_2$ | 7576 <sup>b</sup>                     | $^3\text{A}_{2g}(\text{F}) \rightarrow ^3\text{T}_{2g}(\text{F})$ | 3.38       |
|                                                            | 12658                                 | $^3\text{A}_{2g}(\text{F}) \rightarrow ^3\text{T}_{1g}(\text{F})$ |            |
|                                                            | 22831                                 | $^3\text{A}_{2g}(\text{F}) \rightarrow ^3\text{T}_{1g}(\text{P})$ |            |
| $\text{Cu}(\text{C}_9\text{H}_{13}\text{NO})_2\text{Cl}_2$ | 11765                                 | $^2\text{E}_g(\text{D}) \rightarrow ^2\text{T}_{2g}(\text{D})$    | 2.16       |

<sup>a</sup>  $Dq$  value is 694.

<sup>b</sup>  $Dq$  value is 757. The  $Dq$  value is obtained from the first d-d transition. The  $Dq$  value for the cobalt compound is higher than expected for  $T_d$  symmetry and indicates distortion in the tetrahedral structure.

TABLE 3

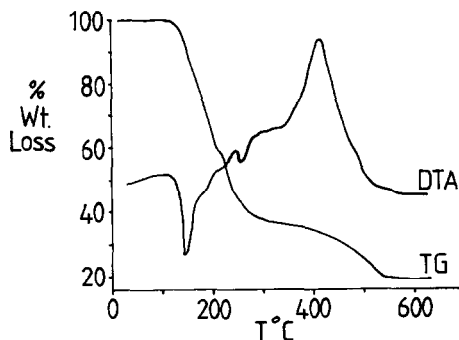
Infrared spectra ( $4000\text{--}200\text{ cm}^{-1}$ )<sup>a</sup>

| Compound                                                   | Ring vibrations   | $\nu(\text{C-O})$ | $\nu(\text{M-Cl})$  | $\nu(\text{M-O})$ | $\nu(\text{M-N})$ |
|------------------------------------------------------------|-------------------|-------------------|---------------------|-------------------|-------------------|
| $\text{C}_9\text{H}_{13}\text{NO}$                         | 1596 (s) 1570 (s) | 1290 (s)          | —                   | —                 | —                 |
| $\text{Co}(\text{C}_9\text{H}_{13}\text{NO})_2\text{Cl}_2$ | 1610 (s) 1578 (s) | 1290 (s)          | 320 (sh)<br>305 (s) | —                 | 226 (w)           |
| $\text{Ni}(\text{C}_9\text{H}_{13}\text{NO})_2\text{Cl}_2$ | 1667 (s) 1634 (s) | 1278 (s)          | 282 (m)             | 268 (m)           | 228 (w)           |
| $\text{Cu}(\text{C}_9\text{H}_{13}\text{NO})_2\text{Cl}_2$ | 1607 (s) 1580 (s) | 1272 (s)          | 288 (m)             | 270 (m)           | 220 (w)           |

<sup>a</sup> s, strong; m, medium; w, weak; sh, shoulder.

[4]. The bands which have been assigned to the  $\nu(\text{C-O})$  vibrations show a shift to lower wavenumbers for the nickel and copper complexes but not for the cobalt complex when comparison is made with that of the free ligand. This indicates that the oxygen atom of the butoxy group is not bonded to the cobalt atoms but that the oxygen atom of the butoxy group is bonded to nickel and copper atoms in these complexes [5]. Metal-chloride, metal-oxygen and metal-nitrogen bands are assigned and are reported in Table 3.

The fact that no single crystals were obtained on precipitation of the complexes from ethanolic solution means that no complete structure determination can be made. However, the spectroscopic and magnetic data enable us to suggest the environment of the metal ion in each of the complexes. The cobalt atoms are in a tetrahedral environment, with each cobalt atom bonded to two chloride ions and to two molecules of the organic ligand through the nitrogen atom of the aromatic ring. The nickel and copper complexes have octahedral structures, with each metal atom bonded to oxygen and nitrogen atoms of two molecules of 2-butoxypyridine. Two chloride ions complete the six-coordinate environment for the metal atom.

Fig. 1. TG and DTA trace for  $\text{Co}(\text{C}_9\text{H}_{13}\text{NO})_2\text{Cl}_2$ . Sample weight = 8.79 mg.

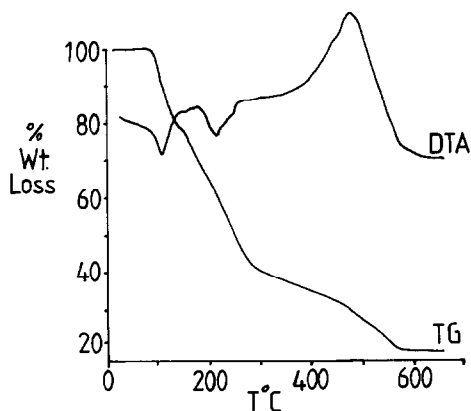
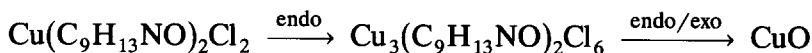


Fig. 2. TG and DTA trace for  $\text{Ni}(\text{C}_9\text{H}_{13}\text{NO})_2\text{Cl}_2$ . Sample weight = 8.76 mg.

The results of the thermogravimetric studies are shown in Figs. 1–3 and Table 4. The copper complex decomposes via an intermediate complex to give  $\text{CuO}$ . The decomposition scheme can be represented as



The cobalt and nickel complexes undergo endothermic and exothermic reactions with loss of the two molecules of 2-butoxypyridine and chlorine to give the metal oxide. An inflexion was observed on the TG curves for these complexes but no complex of simple stoichiometry could be isolated at this stage of the decomposition.

The room temperature current ( $I$ ) versus voltage ( $V$ ) characteristics were obtained under conditions of rising and falling voltage in both polarities. There is no evidence of blocking behaviour for either electrons

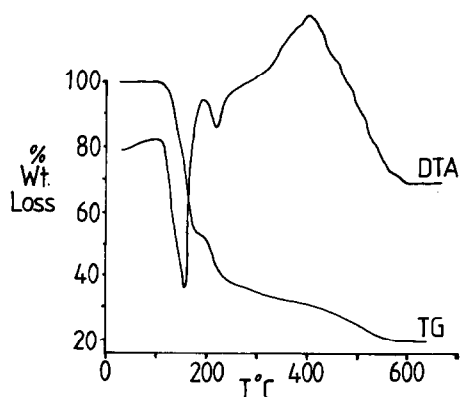


Fig. 3. TG and DTA trace for  $\text{Cu}(\text{C}_9\text{H}_{13}\text{NO})_2\text{Cl}_2$ . Sample weight = 9.64 mg.

TABLE 4

Thermal decomposition products

| Starting material                                          | Decomposition temperature (°C) | Resulting compound                                           | % Weight loss |       |
|------------------------------------------------------------|--------------------------------|--------------------------------------------------------------|---------------|-------|
|                                                            |                                |                                                              | Calc.         | Found |
| $\text{Co}(\text{C}_9\text{H}_{13}\text{NO})_2\text{Cl}_2$ | 110                            | $\text{Co}_3\text{O}_4$                                      | 82.7          | 82.0  |
| $\text{Ni}(\text{C}_9\text{H}_{13}\text{NO})_2\text{Cl}_2$ | 87                             | $\text{NiO}$                                                 | 82.7          | 82.4  |
| $\text{Cu}(\text{C}_9\text{H}_{13}\text{NO})_2\text{Cl}_2$ | 106                            | $\text{Cu}_3(\text{C}_9\text{H}_{13}\text{NO})_2\text{Cl}_6$ | 46.1          | 46.2  |
|                                                            | 196                            | $\text{CuO}$                                                 | 81.8          | 81.8  |

or holes at the contacts because the replication of the current magnitude for a given voltage magnitude is within a few percent.

The  $I$ - $V$  characteristics for the complexes of 2-butoxypyridine, Fig. 4, show a slight departure from Ohm's law within the voltage range 0–5 V. Above 5 V, the  $I$ - $V$  characteristics of the compounds exhibit linearity and, hence, obey Ohm's law. Electrical conductivities for the compounds are given in Table 5 and are calculated from the gradient of the ohmic region of the  $I$  versus  $V$  plots with the assumption that the current flow is perpendicular in the direction to the electrodes. These conductivities are not sufficiently high for device applications but it is presumed that they may be raised by several magnitudes by appropriate doping.

The temperature dependence of conductivity ( $\sigma$ ) for  $\text{Co}(\text{C}_9\text{H}_{13}\text{NO})_2\text{Cl}_2$  is shown in Fig. 5 as a plot of  $\ln \sigma$  versus  $T^{-1}$  where  $T$  is the absolute temperature. Linearity of such plots would indicate that the temperature

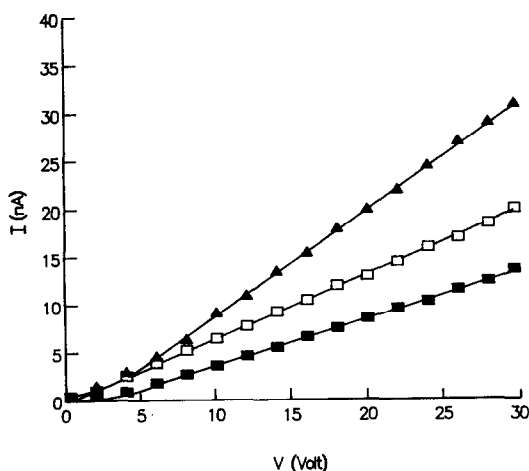


Fig. 4. Room temperature current  $I$  versus voltage  $V$  plot for discs of  $\text{Co}(\text{C}_9\text{H}_{13}\text{NO})_2\text{Cl}_2$  ( $\square$ ),  $\text{Ni}(\text{C}_9\text{H}_{13}\text{NO})_2\text{Cl}_2$  ( $\blacktriangle$ ), and  $\text{Cu}(\text{C}_9\text{H}_{13}\text{NO})_2\text{Cl}_2$  ( $\blacksquare$ ). In each case the plot is based on the mean current at any given voltage  $V$ , with  $V$  increasing and decreasing in both polarities.

TABLE 5

Electrical properties of the compounds

| Compound                                                   | $10^8 \sigma^a$<br>( $\Omega^{-1} \text{ m}^{-1}$ ) | $\Delta E$ (eV) <sup>b</sup> |         |
|------------------------------------------------------------|-----------------------------------------------------|------------------------------|---------|
|                                                            |                                                     | Heating                      | Cooling |
| $\text{Co}(\text{C}_9\text{H}_{13}\text{NO})_2\text{Cl}_2$ | 5.71                                                | 1.44                         | 1.33    |
| $\text{Ni}(\text{C}_9\text{H}_{13}\text{NO})_2\text{Cl}_2$ | 6.33                                                | 1.50                         | 2.06    |
| $\text{Cu}(\text{C}_9\text{H}_{13}\text{NO})_2\text{Cl}_2$ | 2.41                                                | 1.33                         | 1.33    |

<sup>a</sup> Room temperature (20°C) conductivity.<sup>b</sup>  $\Delta E$  is the activation energy in the equation  $\sigma = \sigma_0 \exp(-\Delta E/2kT)$ . Least-squares fitting of a line to a plot of  $\ln \sigma$  against  $T^{-1}$  was used to determine  $\Delta E$ . Separate results are given for heating and cooling cycles.

dependence of conductivity could be described by the relationship  $\sigma = \sigma_0 \exp(-\Delta E/2kT)$ , in which  $\sigma_0$  is a constant and  $\Delta E$  is the activation energy for a given compound. As seen from Fig. 5, the linearity of the plot is poor and the cooling data do not agree with those for heating. The shape of this curve is considered to be significant in that although on cooling the conductivity decreased as expected, for a similar part of the cycle the measured conductivity was significantly greater for the cooling cycle than that measured during the heating cycle. No explanation is offered for this feature but similar curves have been observed in earlier work [6,7]; this strengthens confidence that the observed shape is genuine rather than an artefact of the measurement technique. Similar Arrhenius plots were obtained for the other two compounds studied.

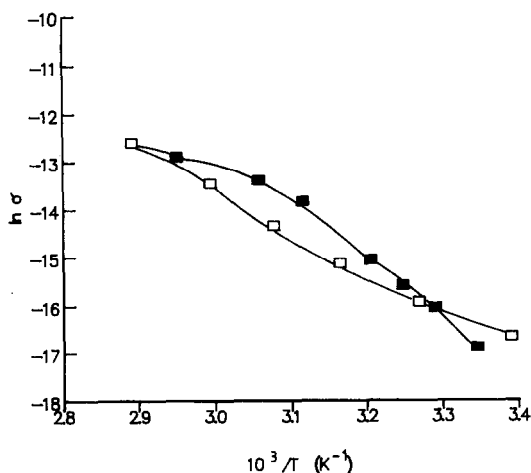


Fig. 5. Plot of  $\ln \sigma$  versus  $10^3/T$  (with  $\sigma$  and  $T$  in units of  $\Omega^{-1} \text{ m}^{-1}$  and K respectively) for a disc of  $\text{Co}(\text{C}_9\text{H}_{13}\text{NO})_2\text{Cl}_2$  for heating cycle ( $\square$ ) and cooling cycle ( $\blacksquare$ ).

Values of  $\Delta E$  as calculated from the gradients of the best-fitting lines, deduced by linear regression of the data, in the Arrhenius plots are listed in Table 5 where separate results are quoted for the heating and cooling cycles. As a result of the described non-linearity of the plots, care must be exercised in attaching meaning to the tabulated  $\Delta E$  values. A possible interpretation for  $\Delta E$ , in terms of band structure, is that it represents the energy gap between valence and conduction bands [8,9]. It is also possible that  $\Delta E$  is the energy barrier to release of a free carrier from donor or acceptor centres [8,9]. Because the measured values of the activation energy for the compounds studied are of similar value, the former explanation is more probable because it would be expected that similar compounds would have similar valence band to conduction band energy gaps. Also the determined values of  $\Delta E$  are exceptionally large for donor or acceptor ionisation energies.

The cobalt, nickel and copper complexes of 2-butoxypyridine are similar in all of the electrical properties studied (Table 5) and this suggests that the conductivities are intrinsically controlled rather than influenced by impurities. Because the electrical conductivities of the individual compounds are of the same magnitude, it is concluded that neither the central metal ion nor the stereochemical environment have any appreciable effect on the conductivity of these compounds.

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