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# Thermal, structural and electrical studies of the chloro complexes of cobalt, nickel and copper with anthranilamide

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## Abstract

The chloro compounds of anthranilamide with cobalt, nickel and copper have been prepared in ethanolic solution. Solid compounds have been isolated and characterised by elemental analyses, magnetic moments, vibrational and electronic spectra. They have octahedral structures. Thermogravimetry and differential thermal analysis show that all of the compounds lose organic ligand and halogen to give the metal oxide. Electrical conductivities at room temperature show ohmic behaviour and lie in the narrow range $3.60 \times 10^{-8}$ $\Omega^{-1}$ $m^{-1}$ (for the nickel complex) to $1.00 \times 10^{-7}$ $\Omega^{-1}$ $m^{-1}$ (for the copper complex). The high conductivity of the copper complex, relative to that of the other complexes, is attributed to its polymeric structure. The temperature dependence of conductivity is anomalous. Evidence from IR spectra suggests that such behaviour is a result of premature decomposition which is due to a synergistic effect of applied voltage and temperature.

## INTRODUCTION

Anthranilamide has three donor sites for bonding to metal ions. These are the nitrogen of the amine group and the nitrogen and oxygen of the amide group.

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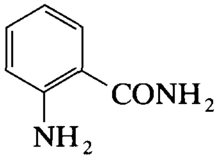

Anthranilamide ($C_7H_8N_2O$).

The stereochemistry of the anthranilamide complexes has been obtained from spectral and magnetic studies. The thermal decomposition of the complexes and their electrical conductivity has also been studied.

## EXPERIMENTAL

### *Preparation of complexes*

The chloro complexes of cobalt, nickel and copper with anthranilamide were prepared by adding 25 $cm^3$ of a warm solution of anthranilamide (0.02 mol in ethanol) to 25 $cm^3$ of a warm solution of the hydrated metal halide (0.01 mol in ethanol). The complexes precipitated on cooling and were filtered, purified by repeated washing with boiling ethanol, 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 using a Carlo Erba elemental analyser.

The IR spectra were obtained using KBr discs (6000–4000 $cm^{-1}$) and polyethylene discs (600–200 $cm^{-1}$) with a Perkin-Elmer IR spectrophotometer model 598.

The electronic spectra were obtained as solid diffuse reflectance spectra using a Beckmann Acta MIV spectrophotometer.

Magnetic measurements were carried out by the Gouy method using $Hg[Co(SCN)_4]$ as calibrant.

The thermal analysis studies were carried out on a Stanton-Redcroft model STA 1500 thermobalance. The TG and DTA curves were obtained at a heating rate of 10°C $min^{-1}$. In all cases the 20–800°C temperature range was studied. The intermediate compound was isolated from its starting material by heating it at a fixed temperature on the thermobalance until a constant weight was obtained.

Electrical measurements of the compounds were carried out on discs of diameter 13 mm and thickness in the range 0.44–0.94 mm formed by compressing powdered compound in a hydraulic press which was set to apply a force of 100 kN. An electrode of 4.9 mm was placed concentrically on each of the 2 flat faces of every disc by applying conductive silver paint

TABLE 1

Analyses of compounds

| Compound | | Metal | Carbon | Nitrogen | Hydrogen |
|---|---|---|---|---|---|
| $Co(C_7H_8N_2O)_2Cl_2$ | Theory | 14.66 | 41.81 | 13.94 | 3.98 |
| | Found | 14.50 | 40.89 | 14.16 | 3.88 |
| $Ni(C_7H_8N_2O)_2Cl_2$ | Theory | 14.62 | 41.83 | 13.94 | 3.98 |
| | Found | 14.38 | 42.36 | 14.06 | 4.06 |
| $Cu(C_7H_8N_2O)_2Cl_2$ | Theory | 15.64 | 41.33 | 13.78 | 3.94 |
| | Found | 15.65 | 41.54 | 14.38 | 3.99 |

through masks. Measurements of current were obtained using a Keithley 610C electrometer. For room temperature conductivity determinations the voltage was increased in 2 V increments from zero to 30 V and then decreased back to zero. This was repeated with reversed polarity. Temperature dependant conductivity measurements were obtained by placing each disc in turn in an electrically heated oven over the approximate temperature range 293–340 K and subsequently 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 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 complexes prepared are listed in Table 1. The analytical results agree with the proposed formulae.

The energy positions of the main bands in the electronic spectra and the magnetic moments of the three compounds prepared directly are listed in Table 2. The position of the bands in the electronic spectra of the cobalt and nickel complexes together with the magnetic moments suggest that the metal atoms are in an octahedral environment [1]. The copper complex has a single broad band in its electronic spectrum at 13071 $cm^{-1}$ suggesting that this complex also has an octahedral environment [1]. The position and broadness of the band is due to Jahn Teller distortion which results from an odd number of electrons in the $d_{x^2-y^2}$ orbital. The band is considered to be a composite band involving transitions from the other d-orbitals to the $d_{x^2-y^2}$ orbital. The magnetic moment obtained for this compound is lower than the spin only value of 1.73 BM indicating some spin–spin magnetic interaction in the compound.

The energies of the main bands in the IR spectra of anthranilamide and its metal complexes are listed in Table 3 together with the descriptions and

TABLE 2

Electronic spectra and magnetic moments

| Compound | Band position (cm$^{-1}$) | d–d transition | $\mu$ (BM) |
|---|---|---|---|
| $Co(C_7H_8N_2O)_2Cl_2$ | 7692 | $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ | 4.84 |
| | 14814 | $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ | |
| | 18518 | $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ | |
| $Ni(C_7H_8N_2O)_2Cl_2$ | 8620 | $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ | 3.16 |
| | 15492 | $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ | |
| | 26428 | $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ | |
| $Cu(C_7H_8N_2O)_2Cl_2$ | 13071 | $^2E_g(D) \rightarrow {}^2T_{2g}(D)$ | 1.62 |

assignments. In the cobalt and nickel complexes the bands due to the N–H vibrations of the amine group are at lower wavenumbers in the complexes than in the free ligand. This suggests that in these complexes the nitrogen atom of the amine group is coordinated to a metal ion [2]. The bands due to the $\nu$(C=O) and $\nu$(N–H) vibrations of the amide group are found to move to lower and higher wavenumbers respectively on complexation. This suggests that the oxygen atom of the carbonyl group is coordinated to a metal ion [3]. In the copper complex the $\nu$(N–H) bands due to the amine group move to lower wavenumbers while the $\nu$(C=O) and $\nu$(N–H) bands due to the amide group move to higher wavenumber on complexation. This would suggest that the nitrogen atoms of the amine groups have formed bonds with the copper atoms, while no bonding occurs between the oxygen and nitrogen atoms of the amide group and the copper atoms [2,3]. Metal–oxygen, metal–halogen and metal–nitrogen vibrations are observed for the cobalt and nickel complexes, whereas metal–halogen and metal–nitrogen vibrations are observed for the copper complex. The assignments made for the metal–halogen and metal–oxygen vibrations are consistent with the metal ions being in an octahedral environment in the complexes [2,3]. The fact that the compounds were isolated from solution as powders and not as single crystals meant that no complete structure determination

TABLE 3

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

| Compound | $\nu_{NH}(NH_2)$ | $\nu_{NH}(CONH_2)$ | $\nu$(C=O) | $\nu$(M–O) | $\nu$(M–Cl) | $\nu$(M–N) |
|---|---|---|---|---|---|---|
| $C_7H_8N_2O$ | 3410(s) 330(s) | 3178 (s) | 1656(s) | | | |
| $Co(C_7H_8N_2O)_2Cl_2$ | 3382(s) 3306(s) | 3236(s), 3183(s) | 1640(s) | 288(s) | 272(sh) | 228(w) |
| $Ni(C_7H_8N_2O)_2Cl_2$ | 3372(s) 3312(s) | 3220(s), 3182(s) | 1642(s) | 292(s) | 278(sh) | 230(w) |
| $Cu(C_7H_8N_2O)_2Cl_2$ | 3370(s) 3317(s) | 3180(s), 3230(s) | 1668(s) | | 266(m) | 242(w) |

[a] Key: s, strong; m, medium; w, weak; sh, shoulder.

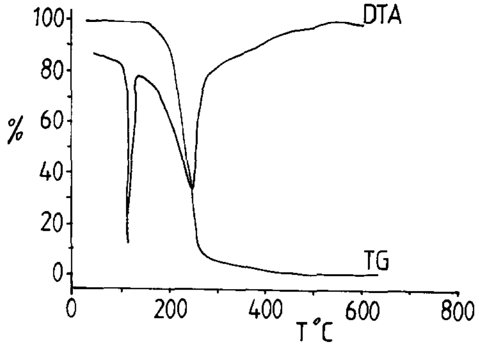

Fig. 1. TG and DTA trace for anthranilamide. Sample mass, 7.20 mg.

could be made. However, spectroscopic and magnetic data enable us to predict that the metal complexes have octahedral structures. In the cobalt and nickel complexes, each metal ion is bonded to two chlorine ions and two anthranilamide molecules (via the amine group and the oxygen atoms of the amide group) to give the six coordinate environment for each metal atom. The copper complex is considered to consist of a chain of copper atoms bonded to halogens with the anthranilamide molecules, bonded by the nitrogen atom of the amine group, above and below the plane of the copper–halogen chains.

The TG and DTA curves for anthranilamide (Fig. 1) show that it is thermally stable in the range 20–148°C. Pyrolytic decomposition commences at 148°C and ends at 420°C with total elimination of the sample. The DTA curve of anthranilamide shows an endothermic peak at 114°C corresponding to fusion. The value of the fusion enthalpy is 35 kJ mol$^{-1}$. Liquid anthranilamide decomposes immediately with an exothermic peak at 250°C. This reaction would appear to be complete by 280°C. However slight decomposition is still observed to take place between 280 and 420°C. It is possible that at 280°C a small amount of tar exists and the decomposition between 280 and 420°C is due to the tar. The TG and DTA curves for the chloro complexes of anthranilamide with cobalt, nickel and copper are shown in Figs. 2–4. The complexes undergo endothermic and exothermic reactions with loss of the organic ligand and halogen to give the metal oxides. This is shown in Table 4. The TG trace (Fig. 3), for the nickel compound would suggest that two anthranilamide molecules are lost followed by chlorine to give nickel oxide (Table 4). The endothermic process observed in the DTA trace is due to bond breaking as the anthranilamide molecules leave, while the two exothermic processes are due to the reaction between the nickel chloride and oxygen. In the case of the cobalt and copper compounds the TG traces (Figs. 2 and 4) show that two steps are again involved in the decomposition process. The DTA traces show that

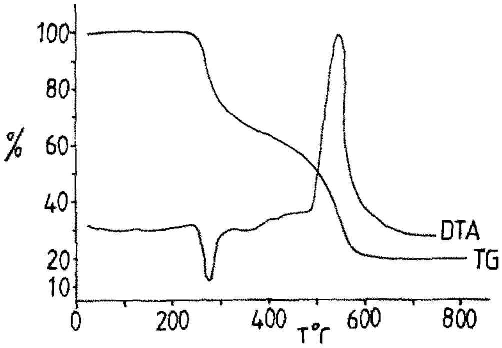

Fig. 2. TG and DTA trace for $Co(C_7H_8N_2O)_2Cl_2$. Sample mass, 8.30 mg.

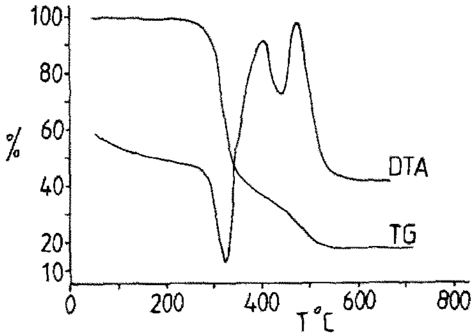

Fig. 3. TG and DTA trace for $Ni(C_7H_8N_2O)_2Cl_2$. Sample mass, 6.12 mg.

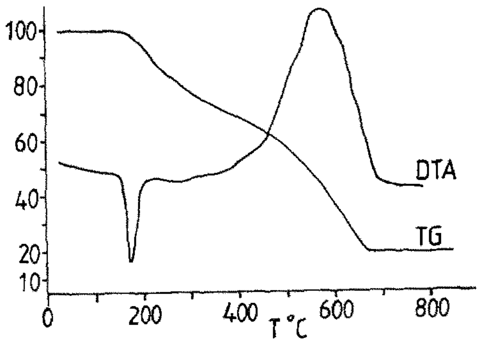

Fig. 4. TG and DTA trace for $Cu(C_7H_8N_2O)_2Cl_2$. Sample mass, 8.54 mg.

TABLE 4

Decomposition processes of the metal complexes

| Starting material | Decomposition temp. (°C) [a] | Mass loss (%) | | Resulting compound |
|---|---|---|---|---|
| | | Calc. | Found | |
| $Co(C_7H_8N_2O)_2Cl_2$ | 238 (endo) | 33.9 | 34.0 | $Co(C_7H_8N_2O)Cl_2$ |
| | 359 (exo) | 80.1 | 80.0 | $Co_3O_4$ |
| $Ni(C_7H_8N_2O)_2Cl_2$ | 212 (endo) | 67.7 | 66.2 | $NiCl_2$ |
| | 440 (exo) | 81.4 | 82.0 | NiO |
| $Cu(C_7H_8N_2O)_2Cl_2$ | 139 (endo) | 22.3 | 22.4 | $Cu_3(C_7H_8N_2O)_4Cl_6$ |
| | 318 (exo) | 80.5 | 80.3 | CuO |

[a] Key: endo, endothermic; exo, exothermic (obtained from DTA curve).

the first process involves bond breaking while in the second process a more complicated reaction involving oxygen appears to occur. The TG trace for the cobalt compound would suggest that one anthranilamide molecule is lost in the first stage followed by the remaining anthranilamide molecule and chlorine to give $Co_3O_4$ in the second stage (Table 4). The TG trace for the copper compound indicates that two thirds of a molecule of anthranilamide is lost followed by the remaining anthranilamide and chlorine to give CuO (Table 4).

The room temperature current $I$ versus voltage $V$ characteristics were obtained under conditions of rising and falling voltage in both polarities. The $I$–$V$ characteristics for the free ligand and its complexes of cobalt, nickel and copper are shown in Fig. 5. The $I$–$V$ characteristics of all compounds are linear and hence Ohm's law is obeyed for all compounds. The electrical conductivities given in Table 5 are calculated from the gradients of the $I$ versus $V$ plots and with the assumption that the current flow is perpendicular in direction to the electrodes.

The range of room temperature electrical conductivities is from $3.6 \times 10^{-8}\ \Omega^{-1}\ m^{-1}$ for $Ni(C_7H_8N_2O)_2Cl_2$ to $1.0 \times 10^{-7}\ \Omega^{-1}\ m^{-1}$ for $Cu(C_7H_8N_2O)_2Cl_2$. The uncomplexed anthranilamide has an electrical conductivity which falls approximately midway in this range. Due to the relative closeness of the conductivity values of the complexes with the conductivity value for the free anthranilamide, care must be exercised in interpreting any differences in conductivity. However, the observed conductivity values do exhibit an interesting feature in that when compared to the free ligand, both cobalt and nickel complexes yield lower conductivities whilst copper complex yields a higher conductivity. The stoichiometry and stereochemical environment of all the complexes are similar; however, the proposed structures differ in that the cobalt and nickel complexes are considered to be composed of monomer units whereas the copper complex consists of a polymeric chain. Thus it is possible for the copper complex to

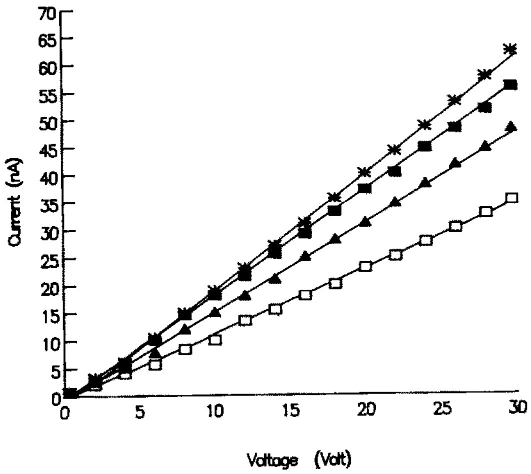

Fig. 5. Room temperature plot of current ($I$) versus voltage ($V$) for discs of ■, $C_7H_8N_2O$; □, $Co(C_7H_8N_2O)_2Cl_2$; ▲, $Ni(C_7H_8N_2O)_2Cl_2$; *, $Cu(C_7H_8N_2O)_2Cl_2$. In each case the plot is based on the mean current at any given voltage $V$, with $V$ increasing and decreasing in both polarities.

be more conductive due to the polymeric chain providing a conduction pathway.

Temperature dependence of the conductivity ($\sigma$) for $Cu(C_7H_8N_2O)_2Cl_2$ is shown in Fig. 6 as a plot of ln $\sigma$ versus $T^{-1}$ where $T$ is the absolute temperature. Linearity of such plots would show the validity of the equation $\sigma = \sigma_0 \exp(-\Delta E/2kT)$, assuming the bond model is applicable, where $\Delta E$ can be considered as the activation energy for releasing free carriers. As shown in Fig. 6, the linearity of the plot is poor and the cooling and heating data do not agree. For a major part of the cooling cycle the measured conductivity is significantly greater than that measured during

TABLE 5

Electrical properties of the compounds

| Compound | $10^8 \sigma$ [a] ($\Omega^{-1}$ $m^{-1}$) | $\Delta E$ [b] (eV) | |
|---|---|---|---|
| | | Heating | Cooling |
| $C_7H_8N_2O$ | 7.0 | 0.92 | 0.98 |
| $Co(C_7H_8N_2O)_2Cl_2$ | 5.1 | 1.23 | 1.00 |
| $Ni(C_7H_8N_2O)_2Cl_2$ | 3.6 | 1.18 | 1.06 |
| $Cu(C_7H_8N_2O)_2Cl_2$ | 10.0 | 1.25 | 1.36 |

[a] Room temperature (20°C) conductivity.

[b] $\Delta E$ 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.

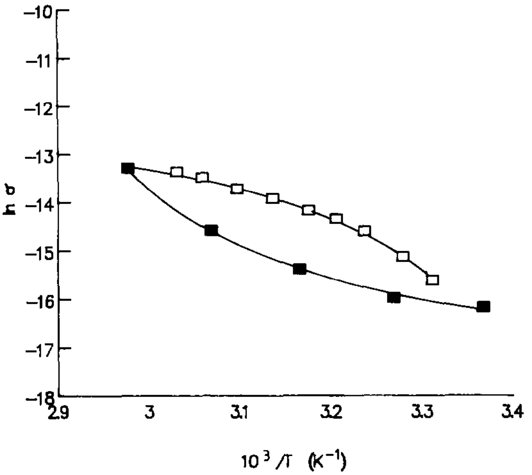

Fig. 6. Plot of ln $\sigma$ versus $10^3/T$ (where $\sigma$ is conductivity in units of $\Omega^{-1}$ $m^{-1}$ and $T$ is the absolute temperature) for a disc of $Cu(C_7H_8N_2O)_2Cl_2$ for ■ a heating cycle and □ a cooling cycle.

the heating cycle. Arrhenius plots for the free ligand and the complexes of cobalt and nickel exhibit the same features.

Values of $\Delta E$ as calculated from the gradients of the best-fittings lines, deduced by linear regression of the data, in the Arrhenius plots are listed in Table 5, where separate results are quoted for both the heating and cooling cycles. Evidently, in view of the described non-linearity of the plots, caution must be exercised in attaching meaning to the tabulated $\Delta E$ values.

Arrhenius curves of similar features to that described have been observed in earlier studies [4–6]. In this present study, the possibility of water being present in the compounds and its effect on conductivity as it evaporated during the heating phase was considered as an explanation for the disparity between the heating and cooling data. However, as in previous work [4–6], this suggestion was rejected. Thermogravimetric and IR analysis showed no evidence for the presence of water and all complexes were desiccated for several days prior to electrical measurement.

It is significant that in the present study, as well as previous studies [4–6], the compounds were heated to temperatures which were well below the temperatures necessary for decomposition as determined by the thermogravimetric analysis. However, the temperature dependence of conductivity plots indicate that an irreversible physical or chemical change has occurred in these compounds. Evidence for such decompositions was obtained by examining a disc of $Cu(C_7H_8N_2O)_2Cl_2$ after temperature dependence measurements. Examination of a cross-section of the disc using a microscope showed a distinct discolouration of the compound, from

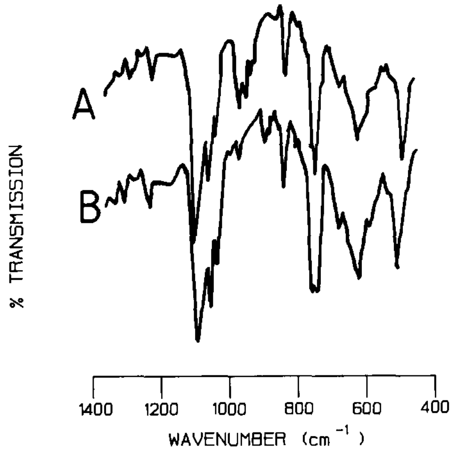

Fig. 7. Infrared spectra of the region 1400–400 cm$^{-1}$ for $Cu(C_7H_8N_2O)_2Cl_2$, (A) before and (B) after measurement of temperature dependance of conductivity.

its original green colour to a brown colour, in the region of the compound between the silver electrodes. This affected region is similar to that expected for the pathway for ideal conduction between both electrodes. Infrared spectra of the original $Cu(C_7H_8N_2O)_2Cl_2$ and the discoloured material from the disc showed that the compounds were similar in terms of major IR bands but they differed slightly in the fingerprint region as shown in Fig. 7. Though no attempt has been made to explain the differences in IR spectra in terms of changes in molecular structures, the differences in these spectra do provide qualitative evidence of decomposition during temperature dependent measurements of conductivity.

From the room temperature measurements of conductivity it is evident that the compounds studied are stable up to an applied voltage of 30 V since they exhibited reproducible ohmic behaviour under conditions of increasing and decreasing voltage in both polarities. Hence the application of a constant 10 V during the temperature dependence measurements would not produce any deteriorating effect.

As previously mentioned, the maximum temperature reached during conductivity measurement was significantly below that for thermal decomposition. It is therefore suggested that although neither the temperature nor the applied voltage alone could cause decomposition of the complexes, the synergistic effect of both the applied voltage and temperature produces premature decomposition of the complexes.

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