

Preparation, thermal, structural and electrical studies of dichlorohexa (anthranilamide) cobalt(II) and dichloro (anthranilamide) copper(II)

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Abstract

The chloro compounds of anthranilamide with cobalt and copper were prepared in aqueous solution. Solid compounds were isolated and characterised by analysis, magnetic moments, and vibrational and electronic spectra. They have octahedral structures. Thermogravimetry and differential thermal analysis show that the compounds lose organic ligand and halogen to give the metal oxide. Electrical conductivities at room temperature show ohmic behaviour and lie in the range from $4.50 \times 10^{-8} \Omega^{-1} \text{m}^{-1}$ (for the cobalt complex) to $8.80 \times 10^{-8} \Omega^{-1} \text{m}^{-1}$ (for the copper complex). The temperature dependence of conductivity was determined for the compounds and was used to provide a measure of the activation energies for conduction.

INTRODUCTION

This paper is a continuation of work previously reported by us on the complexes formed between anthranilamide and the chlorides of cobalt, nickel and copper [1]. In the earlier studies the complexes were obtained from ethanolic solution, whereas in the present study the complexes were isolated from aqueous solution.

The stereochemistry of the anthranilamide complexes was again 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 and copper with anthranilamide were prepared by adding 25 cm³ of a warm solution of anthranilamide (0.02 mol in water) to 25 cm³ of a warm solution of the hydrated metal halide

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(0.01 mol in water). The complexes precipitated on cooling and were filtered, purified by repeated washing with boiling water, 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 obtained using a Carbo Erba elemental analyser.

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

The electronic spectra were obtained using a Beckmann Acta MIV spectrophotometer as solid diffuse reflectance spectra. Magnetic measurements were carried out by the Gouy method using $\text{Hg}[\text{Co}(\text{SCN})_4]$ 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 $10^\circ\text{C min}^{-1}$. In all cases, the $20\text{--}800^\circ\text{C}$ temperature range was studied.

Electrical measurements of the compounds were carried out on discs of diameter 13 mm and thickness of approximately 1 mm formed by compressing powdered compound in a hydraulic press which was set to apply a force of 100 kN. An electrode of 5.9 mm was placed concentrically on each of the 2 flat faces of every disc by applying conductive silver paint through masks. Details of the methods used for the electrical measurements have been previously described [1].

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

TABLE 1
Analyses of compounds (in %)

Compound		Metal	Carbon	Nitrogen	Hydrogen
$\text{Co}(\text{C}_7\text{H}_8\text{N}_2\text{O})_6\text{Cl}_2$	Theory	6.22	53.28	17.75	5.11
	Found	6.32	53.16	17.66	5.02
$\text{Cu}(\text{C}_7\text{H}_8\text{N}_2\text{O})\text{Cl}_2$	Theory	23.48	31.07	10.35	2.98
	Found	23.06	30.86	10.14	2.66

TABLE 2

Electronic spectra and magnetic moments

Compound	Band position/ cm ⁻¹	d-d transition	μ /BM
Co(C ₇ H ₈ N ₂ O) ₆ Cl ₂	8403	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	5.02
	13072	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$	
	19230	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	
Cu(C ₇ H ₈ N ₂ O)Cl ₂	13889	${}^2E_g(D) \rightarrow {}^2T_{2g}(D)$	1.56

magnetic moments of the compounds are listed in Table 2. The bands at 8403, 13 702 and 19 230 cm⁻¹ in the electronic spectrum of the cobalt complex, together with the magnetic moment of between 4.8 and 5.2 BM, suggest that the cobalt atoms are in an octahedral environment [2]. The copper complex has a single broad band in its electronic spectrum between 10 000 and 15 000 cm⁻¹, suggesting that this complex also has an octahedral environment [3]. The magnetic moment for the complex is 1.56 BM indicating some spin–spin interaction.

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 assignments. In the cobalt and copper 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, while the $\nu(\text{CO})$ and $\nu(\text{NH})$ bands due to the amide group move to higher wavenumbers on complexation. This would suggest that in these complexes the nitrogen atom of the amine group is coordinated to a metal ion, while no bonds are formed between the oxygen and nitrogen atoms of the amide group and the metal ions [4, 5]. Metal–halogen and metal–nitrogen vibrations are also listed in Table 3.

The fact that the compounds were isolated from solution as powders and not as single crystals meant that no complete structure determination could be made. However, spectroscopic and magnetic data enable us to predict that the cobalt complex consists of six molecules of anthranilamide covalently bonded to a cobalt atom through the nitrogen atom of the amine group. The chloride ions are attached by ionic bonding to give [Co(C₇H₈N₂O)₆]Cl²⁻. The copper complex is considered to consist of two parallel chains 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 the chloro complexes of anthranilamide with cobalt and copper are shown in Figs. 1 and 2. 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.

TABLE 3(a)

Infrared spectra (4000–200 cm^{-1})

Compound	$\nu_{\text{NH}}(\text{NH}_2)$	$\nu_{\text{NH}}(\text{CONH}_2)$	$\nu(\text{C}=\text{O})$
$\text{C}_7\text{H}_8\text{N}_2\text{O}$	3410(s) 3320(s)	3180(s)	1656(s)
$\text{Co}(\text{C}_7\text{H}_8\text{N}_2\text{O})_6\text{Cl}_2$	3402(s) 3316(s)	3182(s)	1660(s)
$\text{Cu}(\text{C}_7\text{H}_8\text{N}_2\text{O})\text{Cl}_2$	3380(s) 3318(s)	3196(s)	1662(s)

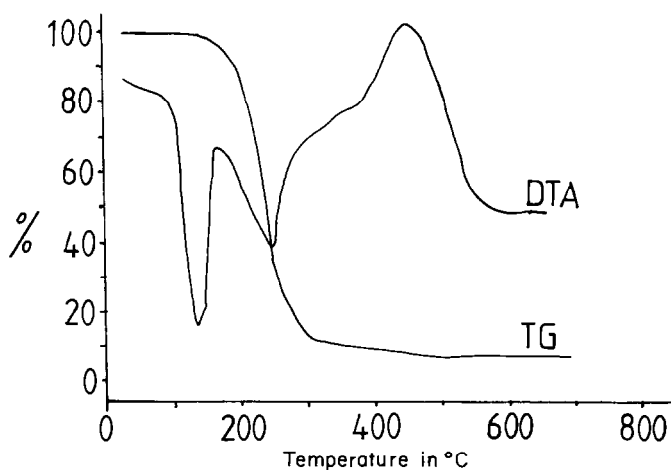
TABLE 3(b)

Infrared spectra (4000–200 cm^{-1})

Compound	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{Cl})$	$\nu(\text{M}-\text{N})$
$\text{C}_7\text{H}_8\text{N}_2\text{O}$	–	–	–
$\text{Co}(\text{C}_7\text{H}_8\text{N}_2\text{O})_6\text{Cl}_2$	–	–	238(m)
$\text{Cu}(\text{C}_7\text{H}_8\text{N}_2\text{O})\text{Cl}_2$	–	260(m)	234(m)

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

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 complexes of cobalt and copper are shown in Fig. 3. The I – V characteristics of the compounds are linear and, hence, Ohm's law is obeyed for the compounds. The electrical conductivities, Table 5, are calculated from the gradients of the I versus V plots, with the assumption that the current flow is perpendicular in direction to the electrodes.

Fig. 1. TG and DTA trace for $\text{Co}(\text{C}_7\text{H}_8\text{N}_2\text{O})_6\text{Cl}_2$; sample weight, 8.83 mg.

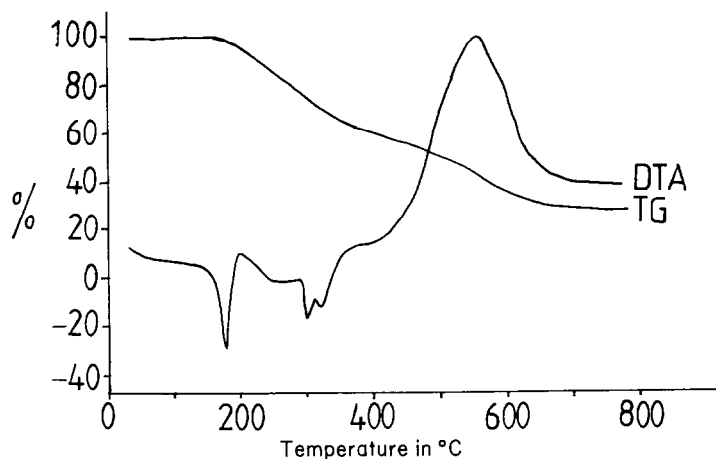


Fig. 2. TG and DTA trace for $\text{Cu}(\text{C}_7\text{H}_8\text{N}_2\text{O})\text{Cl}_2$; sample weight, 9.38 mg.

TABLE 4

Decomposition processes of the metal complexes

Starting material	Decomposition temp./°C	Residue/%	
		Calc.	Found
$\text{Co}(\text{C}_7\text{H}_8\text{N}_2\text{O})_6\text{Cl}_2$	132–500 (Endo/Exo)	8.5	8.4
$\text{Cu}(\text{C}_7\text{H}_8\text{N}_2\text{O})\text{Cl}_2$	162–724 (Endo/Exo)	29.4	29.2

Key: Endo, endothermic; Exo, exothermic (obtained from DTA curve).

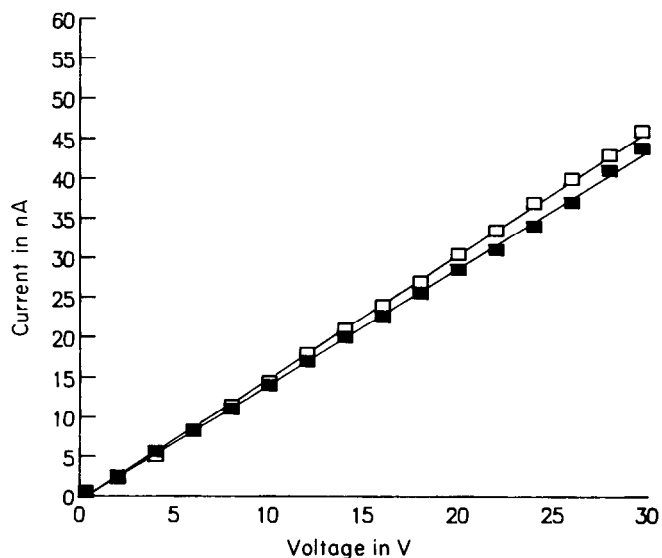


Fig. 3. Room temperature plot of current (I) versus voltage (V) for discs of \square , $\text{Co}(\text{C}_7\text{H}_8\text{N}_2\text{O})_6\text{Cl}_2$; and \blacksquare , $\text{Cu}(\text{C}_7\text{H}_8\text{N}_2\text{O})\text{Cl}_2$. In each case, the plot is based on the mean current at any given voltage V , with V increasing and decreasing in both polarities.

TABLE 5

Electrical properties of the compounds

Compound	$\sigma \times 10^{-8}/(\Omega^{-1}\text{m}^{-1})^a$	$\Delta E/\text{eV}^b$	
		Heating	Cooling
$\text{C}_7\text{H}_8\text{N}_2\text{O}$	7.0	0.92	0.98
$\text{Co}(\text{C}_7\text{H}_8\text{N}_2\text{O})_2\text{Cl}_2^c$	5.1	1.23	1.00
$\text{Co}(\text{C}_7\text{H}_8\text{N}_2\text{O})_6\text{Cl}_2$	4.5	1.16	1.03
$\text{Cu}(\text{C}_7\text{H}_8\text{N}_2\text{O})_2\text{Cl}_2^c$	10.0	1.25	1.36
$\text{Cu}(\text{C}_7\text{H}_8\text{N}_2\text{O})\text{Cl}_2$	8.8	1.18	1.43

^a Room temperature (20°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 $\ln \sigma$ against T^{-1} was used to determine ΔE . Separate results are given for heating and cooling cycles. Ref. 1.

The electrical conductivities of $\text{Co}(\text{C}_7\text{H}_8\text{N}_2\text{O})_6\text{Cl}_2$ and $\text{Cu}(\text{C}_7\text{H}_8\text{N}_2\text{O})\text{Cl}_2$ are shown in Table 5. For comparison, Table 5 also contains the previously reported electrical conductivities of the free anthranilamide ligand and its compounds. It is evident from the data shown in Table 5 that there is a similar trend in electrical conductivities of the compounds from the present study to those of the previously reported study. When the electrical conductivities of the compounds are compared to that of the free ligand, it is seen that both the cobalt compounds yield lower conductivities while the copper compounds yield much higher conductivities. Another interesting feature is the closeness (within experimental error) of both the cobalt and the copper compounds. This confirms that the observed values of the electrical conductivities of these compounds relative to the free ligand are correct and not an aberration of the measurement technique.

Though the stereochemical environment of all the complexes is octahedral, their stoichiometry and, more importantly, their proposed structures differ. The cobalt 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 be more conductive due to the polymeric chain providing a conduction pathway. An alternative suggestion to this observed trend would be that the conductivity is controlled by the central metal ions.

The temperature dependence of the conductivity σ for $\text{Cu}(\text{C}_7\text{H}_8\text{N}_2\text{O})\text{Cl}_2$ is shown in Fig. 4 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 band model is applicable, where ΔE can be considered as the activation energy for relasing free carriers. As shown in Fig. 4, 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

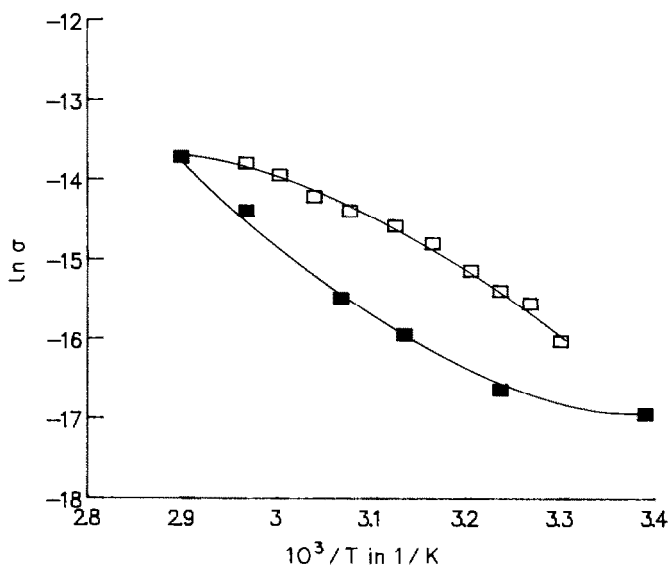


Fig. 4. Plot of $\ln \sigma$ versus $10^3/T$, where σ is conductivity in $\Omega^{-1} \text{m}^{-1}$ and T is the absolute temperature, for a disc of $\text{Cu}(\text{C}_7\text{H}_8\text{N}_2\text{O})\text{Cl}_2$: \square , heating cycle; and \blacksquare , cooling cycle.

the heating cycle. The Arrhenius plot for $\text{Co}(\text{C}_7\text{H}_8\text{N}_2\text{O})_6\text{Cl}_2$ exhibits the same features.

Arrhenius curves with similar characteristics to those described have been found in earlier studies including previous anthranilamide work. A possible explanation for this disparity between the heating and cooling data is the effect of the presence of water in the compounds and its subsequent evaporation. However, as in previous work, this hypothesis was rejected because thermogravimetric and infrared analysis show no evidence of the presence of water and all the compounds were stored above a desiccant for several days prior to electrical measurements.

It is considered significant in the present work, as well as in the previous study of anthranilamide complexes, that the compounds were heated to temperatures which were well below the temperatures found to cause thermal decomposition as determined by thermogravimetric analysis. However, the temperature dependence of conductivity plots indicate that an irreversible physical or chemical change has occurred in these compounds.

Values of ΔE 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. For comparison, ΔE values obtained for cobalt and copper compounds obtained from previous anthranilamide work are also shown. Evidently, in view of the described non-linearity of the plots, caution must be exercised in attaching meaning to the tabulated ΔE values. However,

the observed ΔE values and their trends for both the cobalt and copper compounds in this present study are in good agreement with those values obtained for the cobalt and copper compounds of the previous work, confirming the validity of the data.

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