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Thermal, structural and electrical studies of the chloro complexes of cobalt, nickel and copper with 7,8-benzoquinoline

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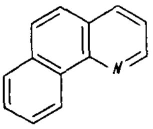
Abstract

The chloro compounds of 7,8-benzoquinoline 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 polymeric octahedral. The techniques of thermogravimetry and differential thermal analysis show that the cobalt compound forms an intermediate compound before the metal oxide is formed. The nickel and copper compounds decompose with loss of organic ligand and chlorine to give the metal oxides. Electrical conductivities for the compounds at room temperature lie in the narrow range $3.09 \times 10^{-8}\ \Omega^{-1}\ \mathrm{m}^{-1}$ (for the copper compound) to $3.59 \times 10^{-7}\ \Omega^{-1}\ \mathrm{m}^{-1}$ (for the cobalt compound). The current–voltage characteristic for the uncomplexed 7,8-benzoquinoline is ohmic, but its complexes exhibit hysteresis. The temperature dependences of conductivity have been determined for the compounds and are used to measure the activation energies for conduction.

INTRODUCTION

In this paper, the structural characterisation, and the thermal and electrical studies of the chloro complexes of cobalt, nickel and copper with 7,8-benzoquinoline are described and discussed. The molecule of 7,8-benzoquinoline has one donor site for bonding to metal ions, namely the nitrogen atom of the aromatic ring system.



7,8-Benzoquinoline ($C_{13}H_9N$)

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The ligand is of interest because it provides an opportunity to study the relationship between the electronic and steric factors involved in monodentate bonding to the metal.

EXPERIMENTAL

Preparation of the complexes

The chloro complexes of cobalt, nickel and copper with 7,8-benzoquinoline were prepared by adding 25 cm^3 of a warm solution of 7,8-benzoquinoline (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 which precipitated on cooling 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 were obtained 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}) on a Perkin–Elmer IR spectrophotometer model 598.

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

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 0.60–1.16 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 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 in 2 V increments from zero to 30 V, and then decreased back to zero. This was repeated with reversed polarity. Temperature-dependence conductivity measurements were obtained by placing each disc in turn in an electrically heated oven over the approximate temperature range 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 were from 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 stoichiometry of the complexes.

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 spectra of the cobalt and nickel complexes and the magnetic moments suggest that the cobalt atoms are in a tetrahedral environment and that the nickel atoms are in octahedral environment [1,2]. The copper compound has a broad band in its electronic spectrum between 10000 and 15000 cm^{-1}, suggesting that the copper atoms are in a six-coordinate environment [2]. 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.

Table 3 lists the main bands in the IR spectra of 7,8-benzoquinoline and its metal complexes. The IR spectrum of the 7,8-benzoquinoline is similar to those of its complexes in the 4000–600 cm^{-1} region except for the bands due to 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 [2]. Metal–chloride and metal–nitrogen bands were assigned and are reported in Table 3.

TABLE 1

Analyses of the compounds

Compound		Metal	Carbon	Nitrogen	Hydrogen
$Co(C_{13}H_9N)Cl_2$ [a]	Theory	19.07	50.52	4.53	2.93
	Found	18.52	50.17	4.19	2.47
$Co_3(C_{13}H_9N)_2Cl_6$ [b]	Theory	23.64	41.75	3.74	2.43
	Found	23.40	41.29	3.38	2.21
$Ni(C_{13}H_9N)Cl_2$ [a]	Theory	19.00	50.56	4.54	2.94
	Found	18.67	50.28	4.44	2.66
$Cu(C_{13}H_9N)_2Cl_2$ [a]	Theory	12.89	63.36	5.68	3.68
	Found	12.86	63.44	5.62	3.26

[a] Initial compound isolated from ethanolic solution.

[b] Intermediate compound produced by heating the corresponding initial compound.

TABLE 2

Electronic spectra and magnetic moments

Compound	Band position (cm^{-1})	d–d Transition	μ (BM)
$Co(C_{13}H_9N)Cl_2$	6250 [a]	$^4A_2(F) \rightarrow {}^4T_2(F)$	4.54
	15038	$^4A_2(F) \rightarrow {}^4T_1(F)$	
	18760	$^4A_2(F) \rightarrow {}^4T_1(P)$	
$Ni(C_{13}H_9N)Cl_2$	9711 [b]	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	3.36
	12195	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	
	26315	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	
$Cu(C_{13}H_9N)_2Cl_2$	10204	$^2E_g(D) \rightarrow {}^2T_{2g}(D)$	1.60

The *Dq* values for the cobalt and nickel complexes are obtained from the first d–d transition. The *Dq* value for the cobalt complex is higher than that observed for T_d symmetry and suggests distortion.

[a] $Dq = 625$.

[b] $Dq = 971$.

The fact that no single crystals were obtained on precipitation of the complexes from ethanolic solution means that no complete crystallographic 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 compound has a binuclear structure in which a four-coordinate environment for each of the cobalt atoms results from two terminal groups (a benzoquinoline molecule and a chloride ion) and two bridging groups (two chloride ions). The nickel compound consists of a double-layer chain structure in which each chloride ion is acting as a bridge between three nickel atoms with the benzoquinoline molecules in trans positions [3]. In the copper complex the polymer chain consists of Cu–Cl atoms with the benzoquinoline molecules bonded above and below the plane of the chain to each copper atom through the lone pair of electrons on the ring nitrogen.

The results of the thermogravimetry studies are shown in Figs. 1–3 and Table 4. The cobalt complex decomposes via an intermediate complex to

TABLE 3

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

Compound	Ring vibrations	ν(M–Cl)	ν(M–N)
$C_{13}H_9N$	1590 (s) 1510 (s)	–	–
$Co(C_{13}H_9N)Cl_2$	1606 (s) 1516 (s)	310 (s), 294 (s)	230 (w)
$Ni(C_{13}H_9N)Cl_2$	1605 (s) 1514 (s)	262 (m)	228 (w)
$Cu(C_{13}H_9N)_2Cl_2$	1608 (s) 1515 (s)	264 (m)	232 (w)

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

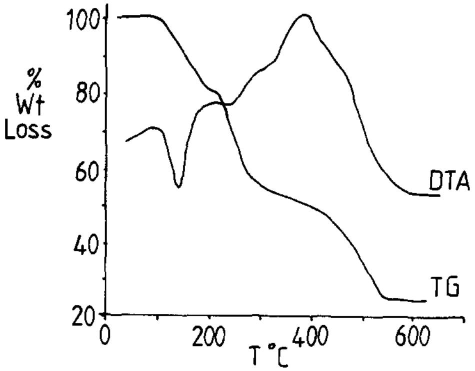

Fig. 1. TG and DTA trace for $Co(C_{13}H_9N)Cl_2$. Sample weight = 6.34 mg.

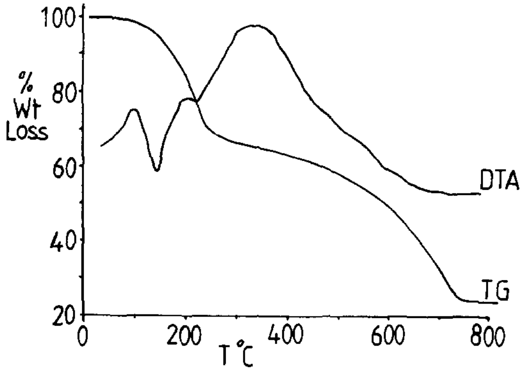

Fig. 2. TG and DTA trace for $Ni(C_{13}H_9N)Cl_2$. Sample weight = 8.32 mg.

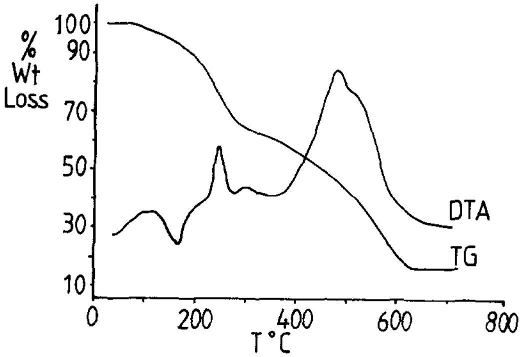

Fig. 3. TG and DTA trace for $Cu(C_{13}H_9N)_2Cl_2$. Sample weight = 9.36 mg.

TABLE 4

Thermal decomposition products

Starting material	Decomposition temp. (°C)	Resulting compound	Weight loss (%)	
			Calc.	Found
$Co(C_{13}H_9N)Cl_2$	92 (endo)	$Co_3(C_{13}H_9N)_2Cl_6$	19.3	19.2
	218 (exo)	Co_3O_4	75.7	74.9
$Ni(C_{13}H_9N)Cl_2$	52 (endo/exo)	NiO	76.8	76.4
$Cu(C_{13}H_9N)_2Cl_2$	68 (endo/exo)	CuO	83.8	82.6

give Co_3O_4. The decomposition scheme can be represented as

$$Co(C_{13}H_9N)Cl_2 \xrightarrow{\text{endo}} Co_3(C_{13}H_9N)_2Cl_6 \xrightarrow{\text{exo}} Co_3O_4$$

where endo is endothermic and exo is exothermic.

The nickel and copper complexes undergo endothermic and exothermic reactions with loss of the benzoquinoline and chlorine to give the metal oxides.

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 cobalt and nickel compounds are shown in Fig. 4. An interesting feature of these plots is the hysteresis exhibited in the 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 decreased. The same effect was observed for an increase and subsequent decrease of voltage under reversed polarity. The *I*–*V* curve for the copper compound, which has not been presented, is

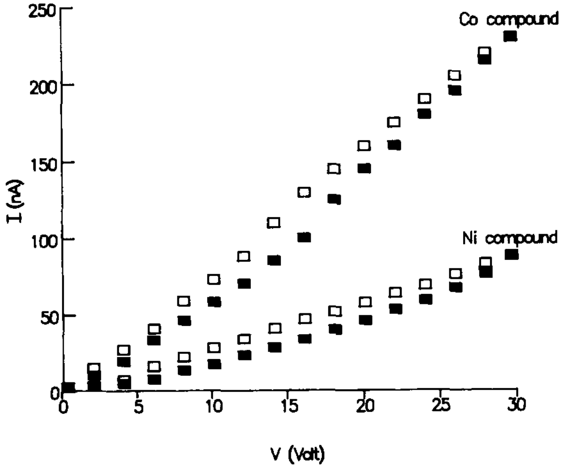

Fig. 4. Room temperature plot of current (*I*) versus voltage (*V*) for discs of $Co(C_{13}H_9N)Cl_2$ and $Ni(C_{13}H_9N)Cl_2$: ■, *V* increasing; □, *V* decreasing.

qualitatively similar to those of the cobalt and nickel compounds, but the hysteresis in both polarities is smaller.

The presence of hysteresis in the current versus voltage characteristics has been previously observed in other metallo-organic compounds studied by this laboratory [4–7]. In these previous studies, the hysteresis effect was considered to be associated with organic ligands which either contained polarisable groups, such as carboxyl C=O and alkene C=C, or contained substituent polar groups which were free to rotate. It was postulated that the hysteresis observed in these studies was due to a degree of alignment and polarisation of the ligand during application of the applied field; during subsequent removal of this field the ligand molecules slowly revert back to their original state. Thus the hysteresis effect observed was a result of a semi-permanent polarisation and distortion of the ligand molecules. Evidence for such a distortion has previously been obtained [8] in other metallo-organic compounds using spectroscopic methods.

The I versus V characteristic for a disc of the free 7,8-benzoquinoline ligand is distinctively different from those of its complexes in that it shows ohmic behaviour. Thus the hysteresis effect only occurs when the ligand is complexed to a metal atom. This observation is similar to that obtained in earlier work [7] where the I versus V characteristics of both the complexed and uncomplexed ligand was studied.

The room temperature conductivity values for 7,8-benzoquinoline and its complexes are listed in Table 5. Because the complexes exhibit hysteresis, the room temperature conductivities were 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 7,8-benzoquinoline yields compounds whose conductivities are not significantly different from that of the uncomplexed ligand. Indeed,

TABLE 5

Electrical properties of the compounds

Compound	$10^8\,\sigma$ [a] ($\Omega^{-1}\,m^{-1}$)	ΔE [b] (eV)	
		Heating	Cooling
$C_{13}H_9N$	14.8	1.68	-
$Co(C_{13}H_9N)Cl_2$	35.9	2.84	1.71
$Ni(C_{13}H_9N)Cl_2$	8.5	1.84	1.43
$Cu(C_{13}H_9N)_2Cl$	3.1	1.21	0.99

[a] Room temperature (20°C) conductivity determined from the mean gradient of the I–V plots.

[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.

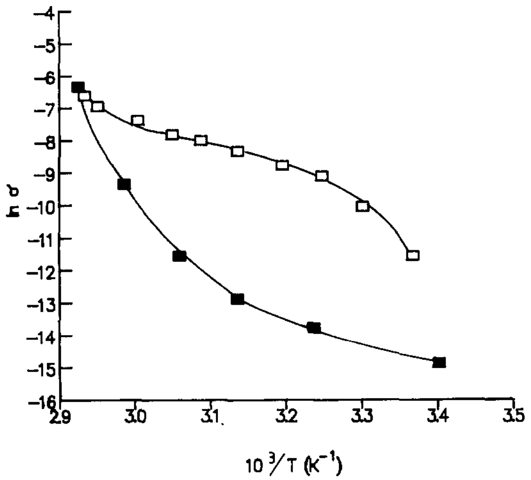

Fig. 5. Arrhenius plot (in the form of ln σ versus $10^3/T$ where σ is the conductivity in units of Ω^{-1} m^{-1} and T is the absolute temperature) for a disc of $Co(C_{13}H_9N)Cl_2$: ■, points obtained during heating; □, points obtained during cooling.

with the exception of the cobalt complex, complexation yielded compounds with conductivities lower than that of the free ligand.

The temperature dependence of the conductivity (σ) for $Co(C_{13}H_9N)Cl_2$ is shown in Fig. 5 as a plot of ln σ 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 from releasing free carriers. As shown in Fig. 5, the linearity of the plot is poor. The observed conductivity on the cooling cycle is found to be greater than that measured during the heating cycle for any given temperature. The compounds of nickel and copper also show similar Arrhenius plots.

The order for the size of the difference between data for the heating and cooling cycles follows that for the degree of hysteresis existing in the room temperature conductivity measurements, i.e.

$$Co(C_{13}H_9N)Cl_2 > Ni(C_{13}H_9N)Cl_2 > Cu(C_{13}H_9N)_2Cl_2.$$

In the case of the nickel and copper compounds, caution should be exercised in attaching significance to this observation, because the maximum temperatures employed in obtaining data on the temperature dependence of the conductivity were in the range in which decomposition occurs and, hence, the composition of these compounds may have been altered. For the cobalt complex, the maximum temperature employed was well below that for decomposition.

The temperature dependence of conductivity for the uncomplexed 7,8-benzoquinoline is shown in Fig. 6. In the temperature range 293–323 K,

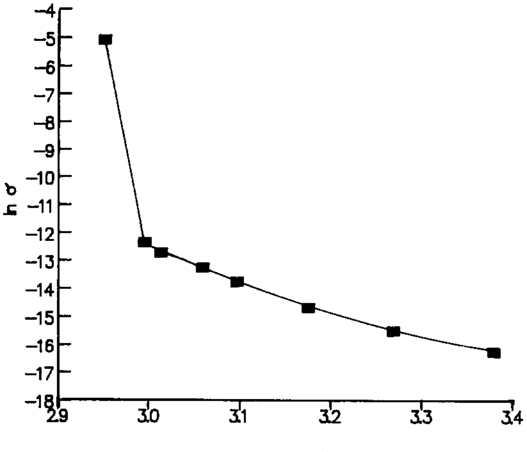

Fig. 6. Arrhenius plot (in the form of ln σ versus $10^3/T$ where σ is the conductivity in units of Ω^{-1} m^{-1} and T is the absolute temperature) for a disc of 7,8-benzoquinoline during the heating cycle.

the plot of the temperature dependence of conductivity is linear and hence obeys the equation $\sigma = \sigma_0 \exp(-\Delta E/2kT)$. The linearity of the plot begins to deviate at 323 K, and at 325 K there is a very sharp increase in the conductivity. The temperature at which this sharp transition occurs is found to correspond to the melting point of 7,8-benzoquinoline.

Values of ΔE for the complexes, calculated from the gradients of the best-fitting lines for both the heating and cooling cycles, are listed in Table 5. Due to the poor linearity of these temperature dependence plots and the disparity between the heating and cooling data, care should be taken when interpreting these tabulated ΔE values. For the uncomplexed ligand, the ΔE value in Table 5 is calculated from the linear section of the plot for the heating cycle only.

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