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Preparation, structural characterisation, thermal and electrical studies of complexes of cobalt, nickel and copper with methyl-3-pyridyl-carbamate

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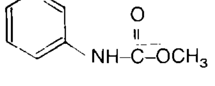
Abstract

The thiocyanate compound of cobalt(II), and the chloro compounds of cobalt(II), nickel(II) and copper(II) with methyl-3-pyridyl-carbamate were prepared in ethanolic solution from which solid compounds were isolated. The suggested structure for the cobalt compounds is tetrahedral, while for the nickel and copper compounds it is octahedral. The techniques of thermogravimetry and differential thermal analysis show that the chloro compounds of cobalt, nickel and copper form intermediate compounds before the metal oxide is produced. The thiocyanate compound of cobalt undergoes decomposition with loss of organic ligand and the formation of cobalt thiocyanate, which then decomposes to give an oxide of cobalt.

Room-temperature electrical measurements are reported for the uncomplexed ligand and its metal chloride compounds. All compounds were found to exhibit ohmic behaviour.

INTRODUCTION

This work is a continuation of previously reported thermal and electrical studies on pyridines and transition metals [1–4]. The present work reports the structural properties, thermal and electrical studies for the compounds formed by complexing cobalt, nickel and copper with methyl-3-pyridyl-carbamate.



Methyl-3-pyridyl-carbamate ($C_7H_8N_2O_2$).

Thermogravimetry and differential thermal analysis were used to study the thermal stability and thermal decomposition. Spectral and magnetic measure-

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ments were used to infer structure and d.c. electrical measurements were used to obtain the electrical conductivity.

EXPERIMENTAL

Preparation of the complexes

The compounds were prepared as reported in the literature [5].

Analytical, magnetic, spectral and thermal measurements

The analysis of the metal ion was determined using a Perkin-Elmer 373 atomic absorption spectrophotometer and carbon, hydrogen and nitrogen analyses were obtained using a Carlo Erba elemental analyser. Magnetic moments of the compounds were assessed by the Guoy method using $Hg[Co(SCN)_4]$ as calibrant. Electronic spectra were obtained on a Beckmann Acta MIV spectrophotometer as solid diffuse reflectance spectra. Infrared spectra, using KBr discs in the range 4000–600 cm^{-1} and polyethylene discs in the range 600–200 cm^{-1}, were recorded by a Perkin-Elmer infrared spectrophotometer model 598. The thermal analysis measurements were performed using a Stanton Redcroft model STA 1500 thermobalance. The thermogravimetry (TG) and differential thermal analysis (DTA) traces were obtained at a heating rate of 10°C min^{-1} in static air. In all cases the 20–800°C temperature range was studied.

Electrical measurements

The electrical measurements carried out on the prepared compounds comprised of measuring current as a function of voltage at room temperature to obtain the electrical conductivity σ of the compounds. For such measurements the compounds were formed into discs of diameter 13 mm and thickness of approximately 1 mm, by compressing the powdered compound in a hydraulic press set to apply a force of 100 kN.

The disc thickness was accurately measured by a micrometer. Circular electrodes of known diameter were formed concentrically on the flat faces of the disc by applying silver conductive paint through masks. The disc was then stored in a desiccator for several days before being tested.

The room-temperature dark current was measured for a series of applied d.c. voltages using a Keithley 610C electrometer. To test that the electrodes were ohmic and non-blocking, the voltage was increased in stages from zero to 30 V and then decreased in corresponding stages; this procedure was then repeated in reverse polarity. Agreement, within a maximum of ±10%, between the four current readings was regarded as confirmation that the electrodes were not significantly rectifying.

RESULTS AND DISCUSSION

The analytical results for the metal complexes are given in Table 1. These analyses agree with the given formulae proposed for the compounds.

The molecular magnetic moments and the bands in the electronic spectra of the complexes are listed in Table 2. The position of the bands in the cobalt complexes would suggest that the cobalt ion is in a tetrahedral environment in these compounds [6]. The value obtained for the magnetic moment of each of the compounds supports this suggestion [7]. The position of the bands in the electronic spectrum of the nickel complex is clearly indicative of an octahedral environment for the nickel ion [8]. The magnetic moment obtained for this compound agrees with this suggestion [8]. The position of the band in the electronic spectrum of the copper compound would suggest that the copper atom is in an octahedral environment [9]. The magnetic moment for this compound is lower than the spin-only value, indicating some copper–copper magnetic interaction.

TABLE 1

Analyses of metal complexes in %

Compound	Colour		Metal	Carbon	Nitrogen	Hydrogen
$Co(C_7H_8N_2O_2)_2(CNS)_2$	Blue	Theory	12.29	45.70	17.53	3.36
		Found	12.09	44.86	17.36	3.12
$Co(C_7H_8N_2O_2)_2Cl_2$	Blue	Theory	13.57	38.72	12.90	3.71
		Found	13.46	38.41	12.66	3.44
$Ni(C_7H_8N_2O_2)_2Cl_2$	Green	Theory	13.52	38.75	12.91	3.71
		Found	13.36	38.24	12.73	3.86
$Cu(C_7H_8N_2O_2)_2Cl_2$	Green	Theory	14.48	38.32	12.77	3.67
		Found	14.09	38.02	12.49	3.38

TABLE 2

Electronic spectra and magnetic measurements

Compound	Band position in cm^{-1}	d–d Transitions	μ/BM
$Co(C_7H_8N_2O_2)_2(CNS)_2$	6309	$^4A_2(F) \rightarrow {}^4T_2(F)$	4.02
	15873	$^4A_2(F) \rightarrow {}^4T_1(F)$	
	18830	$^4A_2(F) \rightarrow {}^4T_1(P)$	
$Co(C_7H_8N_2O_2)_2Cl_2$	6329	$^4A_2(F) \rightarrow {}^4T_2(F)$	4.15
	14706	$^4A_2(F) \rightarrow {}^4T_1(F)$	
	17180	$^4A_2(F) \rightarrow {}^4T_1(P)$	
$Ni(C_7H_8N_2O_2)_2Cl_2$	8265	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	3.26
	13889	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	
	23810	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	
$Cu(C_7H_8N_2O_2)_2Cl_2$	13986	$^2E_g(D) \rightarrow {}^2T_{2g}(D)$	1.59

TABLE 3

Infrared spectra (4000-200 cm^{-1})

Compound	ν(NH)	ν(C=O)	Ring vibrations		ν(M-Cl)	ν(M-N)
$C_7H_8N_2O_2$	3241(s) 3186(s)	1723(s)	1585(s)	1554(s)	–	–
$Co(C_7H_8N_2O_2)_2(NCS)_2$	3095(s) 3082(s)	1725(s)	1617(s)	1558(s)	–	240(s) 320(s)
$Co(C_7H_8N_2O_2)_2Cl_2$	3095(s) 3080(s)	1725(s)	1618(s)	1557(s)	316(s)	231(m)
$Ni(C_7H_8N_2O_2)_2Cl_2$	3095(s) 3073(s)	1723(s)	1617(s)	1556(s)	246(s)	259(m)
$Cu(C_7H_8N_2O_2)_2Cl_2$	3098(s) 3072(s)	1721(s)	1614(s)	1555(s)	286(s)	256(m)

Key: s, strong; m, medium.

The wavenumbers of the IR absorption bands of methyl-3-pyridyl-carbamate and its metal complexes isolated from ethanolic solution are given in Table 3. The IR spectrum of methyl-3-pyridyl-carbamate is very similar to that of its complexes in the region 4000-600 cm^{-1}. The bands due to the aromatic rings are shifted to higher wavenumbers on formation of the complexes. This would suggest that the nitrogen atom of an aromatic ring is coordinated to a metal ion [10]. Little or no change is observed in the ν(C=O) vibration on complexation. This indicates that the there is no bonding between the oxygen atom of the carboxyl group and the metal atom [11] in each of the complexes. The N-H stretching mode is split by Fermi resonance [12] into two bands of near equal intensity. In all of the complexes, both bands shift to lower wavenumbers as a result of hydrogen bonding. The metal-halide and metal-nitrogen bands observed in the 600-200 cm^{-1} region are also listed in Table 3. The ν(M-Cl) bands in the spectra of the nickel and copper complexes show that the metal ions are in a six-coordinate environment [13] while the corresponding band in the cobalt compound indicates that the cobalt ion is in a four-coordinate environment. The band at 320 cm^{-1} in $Co(C_7H_8N_2O_2)_2(NCS)_2$ has been assigned to a metal-nitrogen stretching mode involving the nitrogen of the NCS anion and further indicates that the cobalt ion is in a tetrahedral environment [14]. The bands in the lower frequency range of 260-230 cm^{-1} have been assigned to the metal-nitrogen stretching vibration of the pyridine ring.

Attempts to isolate single crystals for any of the compounds from ethanolic solution were unsuccessful; thus, without X-ray analysis no definite structures can be described. However, the spectroscopic and magnetic data allow possible structures to be postulated. It is suggested that the structures of the nickel and copper compounds consists of a chain of metal atoms bonded to halogens, with the methyl-3-pyridyl-carbamate molecules above and below the plane of the metal–halogen chain. The cobalt compounds each have tetrahedral structures in which the cobalt atom is bonded to two chloride ions and to two nitrogen atoms, one from each of the methyl-3-pyridyl-carbamate molecules.

The TG and DTA traces, Fig. 1, for methyl-3-pyridyl-carbamate show that it is thermally stable in the temperature range 20–128°C. Its pyrolytic decomposition starts at 128°C and finishes at 598°C with the total elimination of the sample. The DTA trace for methyl-3-pyridyl-carbamate shows an endothermic peak at 122°C corresponding to fusion. The enthalpy of fusion is 28 kJ mol^{-1}. Endothermic and exothermic peaks are then observed in the DTA trace for the decomposition of the methyl-3-pyridyl-carbamate. The TG and DTA traces for the metal complexes are shown in Figs. 2–5 and the thermal decomposition data is given in Table 4. The chloro

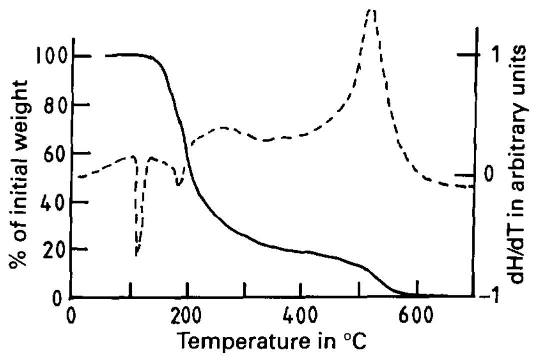

Fig. 1. Thermogravimetric (——, left axis) and differential thermal analysis (– – –, right axis) plots for methyl-3-pyridyl-carbamate of sample weight 8.25 mg.

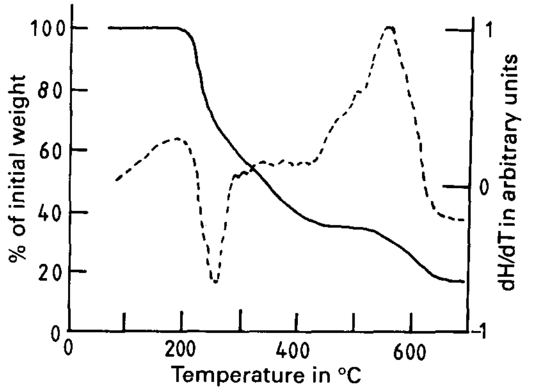

Fig. 2. Thermogravimetric (——, left axis) and differential thermal analysis (– – –, right axis) plots for $Co(C_7H_8N_2O_2)_2(NCS)_2$ of sample weight 8.62 mg.

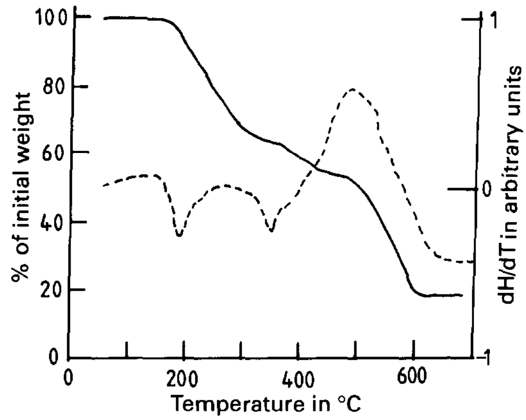

Fig. 3. Thermogravimetric (——, left axis) and differential thermal analysis (– – –, right axis) plots for $Co(C_7H_8N_2O_2)_2Cl_2$ of sample weight 7.24 mg.

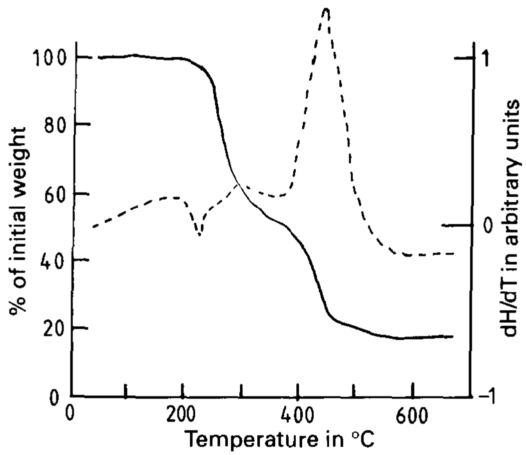

Fig. 4. Thermogravimetric (——, left axis) and differential thermal analysis (– – –, right axis) plots for $Ni(C_7H_8N_2O_2)_2Cl_2$ of sample weight 7.13 mg.

compounds of cobalt, nickel and copper decompose via intermediate compounds to give the metal oxides. The decomposition scheme is

$$Co(C_7H_8N_2O_2)_2Cl_2 \xrightarrow{\text{Endo}} Co(C_7H_8N_2O_2)Cl_2 \xrightarrow{\text{Exo}} Co_3O_4$$

$$Ni(C_7H_8N_2O_2)_2Cl_2 \xrightarrow{\text{Endo}} Ni_3(C_7H_8N_2O_2)_2Cl_6 \xrightarrow{\text{Exo}} NiO$$

$$Cu(C_7H_8N_2O_2)_2Cl_2 \xrightarrow{\text{Endo}} Cu_3(C_7H_8N_2O_2)_2Cl_6 \xrightarrow{\text{Exo}} CuO$$

The compound $Co(C_7H_8N_2O_2)_2(NCS)_2$ decomposes endothermically with loss of the two molecules of methyl-3-pyridyl-carbamate, followed by an exothermic reaction and the formation of Co_3O_4. The observed mass loss for each of the processes compares favourably with the theoretical values

TABLE 4

Thermal decomposition processes for methyl-3-pyridyl-carbamate and its metal complexes

Process	Temp range in % [a]	Enthalpy change [b]	Weight loss		Enthalpy of reaction in kJ mol^{-1} [b]
			Calc.	Found	
$C_7H_8N_2O_2 \rightarrow$ pyrolytic process	128–598	Endo/Exo	100	100	415
$Co(C_7H_8N_2O_2)_2(NCS)_2 \rightarrow Co(NCS)_2$	189–486	Endo	63.5	63.4	168
$Co(NCS)_2 \rightarrow Co_3O_4$	486–668	Exo	19.8	19.7	604
$Co(C_7H_8N_2O_2)_2Cl_2 \rightarrow Co(C_7H_8N_2O_2)Cl_2$	149–352	Endo	35.0	35.1	86
$Co(C_7H_8N_2O_2)Cl_2 \rightarrow Co_3O_4$	352–626	Exo	46.5	46.3	747
$Ni(C_7H_8N_2O_2)_2Cl_2 \rightarrow Ni_3(C_7H_8N_2O_2)_2Cl_6$	191–340	Endo	46.7	46.6	68
$Ni_3(C_7H_8N_2O_2)_2Cl_6 \rightarrow NiO$	340–581	Exo	29.5	29.4	391
$Cu(C_7H_8N_2O_2)_2Cl_2 \rightarrow Cu_3(C_7H_8N_2O_2)_2Cl_6$	189–339	Endo	46.2	46.3	56
$Cu_3(C_7H_8N_2O_2)_2Cl_6 \rightarrow CuO$	339–628	Exo	35.7	35.6	437

Key: Endo, endothermic; Exo, exothermic.

[a] From TG trace.

[b] From DTA trace.

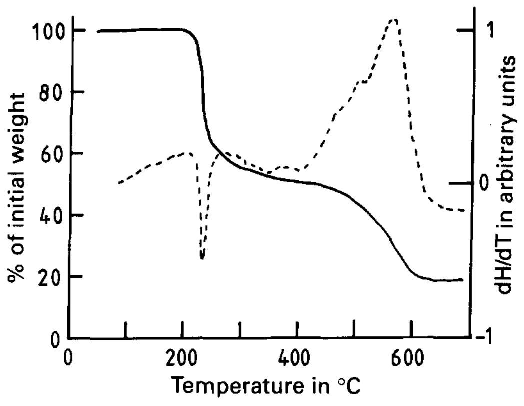

Fig. 5. Thermogravimetric (——, left axis) and differential thermal analysis (– – –, right axis) plots for $Cu(C_7H_8N_2O_2)_2Cl_2$ of sample weight 9.42 mg.

listed in Table 4. The reaction enthalpy for each of the decomposition processes is also listed in Table 4.

The room-temperature current I versus voltage V characteristics were obtained under conditions of rising and falling voltage in both polarities. The current versus voltage relationships for the ligand and the prepared metal complexes of this study were all observed to be linear throughout the voltage range investigated, indicating that ohmic electrical conduction prevailed. From the mean gradients of the $I-V$ characteristics, the electrical conductivities of the compounds were determined and are shown in Table 5.

Comparison of the individual electrical conductivities of the metal chloride complexes with that of the free ligand reveals that complexation of cobalt and nickel with methyl-3-pyridly-carbamate yields compounds with enhanced electrical conductivities. The observed differences in the conductivities between the cobalt and nickel compound may be accounted for in terms of differing molecular structures. The cobalt compound is a tetrahedral monomer whilst the nickel compound is an octahedral polymer. It is suggested that the polymeric nature of the nickel compound provides a

TABLE 5

Room-temperature electrical conductivities of the compounds

Compound	σ in Ω^{-1} m^{-1} [a]
$C_7H_8N_2O_2$	5.72×10^{-7}
$Co(C_7H_8N_2O_2)_2Cl_2$	1.33×10^{-6}
$Ni(C_7H_8N_2O_2)_2Cl_2$	3.41×10^{-5}
$Cu(C_7H_8N_2O_2)_2Cl_2$	6.00×10^{-8}

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

more effective electrical conduction pathway than the monomeric cobalt compound, hence the observed difference in conduction.

However, the nickel and copper compounds are considered to be of similar structure and it is reasonable to expect that their respective conductivities would be comparable. As can be seen from Table 5, this is not the case. Indeed, the copper compound has an observed conductivity value that is significantly less than the uncomplexed methyl-3-pyridyl-carbamate. If the earlier postulation for the electrical conduction in these compounds is valid, then some interaction or barrier must be present within the copper compound which dramatically affects the electrical conduction process. The presence of a large level of impurities acting as traps and recombination centres would inhibit carrier mobility and concentration and, hence, reduce the measured electrical conduction. However the elemental analysis does not show any significant level of impurities. Moreover, a predominant trapping process generally manifests itself in electrical conductivity studies as non-ohmic behaviour [15–17] which was not apparent in this study.

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