Thermochimica Acta, 228 (1993) 71–78
Elsevier Science Publishers B.V., Amsterdam

Preparation, structural, thermal and electrical studies of the chloro complexes of cobalt, nickel and copper with 4-pyridinealdoxime

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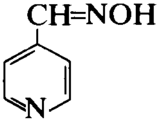
(Received 19 March 1993; accepted 16 April 1993)

Abstract

Some chloro complexes of cobalt, nickel and copper with 4-pyridinealdoxime have been prepared in ethanolic solution. The complexes have stoichiometry ML_2Cl_2. The stereochemical configurations of the complexes have been deduced using spectral and magnetic properties. The cobalt and nickel complexes have octahedral structures while the copper complex has a tetragonal structure. The decomposition of the 4-pyridinealdoxime and its metal complexes have been studied by thermogravimetry and differential thermal analysis. Electrical conductivities at room temperature lie in the narrow range $3.68 \times 10^{-8}\,\Omega^{-1}\,m^{-1}$ (for the copper complex) to $8.89 \times 10^{-8}\,\Omega^{-1}\,m^{-1}$ (for the uncomplexed 4-pyridinealdoxime). The current–voltage characteristics for all the compounds studied are ohmic in nature.

INTRODUCTION

In earlier electrical studies in these laboratories it was found that when a C=C group is present in an organic molecule hysteresis was observed [1–3]. In this work the electrical properties of 4-pyridinealdoxime, which contains a C=N group, and some of its metal complexes are investigated along with structural properties and thermal analysis studies.



4-Pyridinealdoxime ($C_6H_6N_2O$)

Spectral and magnetic studies were used to characterise each of the metal complexes and to interpret the type of coordination which takes place to the metal ion. A study of the thermal stability and decomposition of each

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0040-6031/93/$06.00

compound has been carried out using thermogravimetry (TG) and differential thermal analysis (DTA). Studies involving d.c. electrical measurements were used to obtain information on room temperature electrical conductivity.

EXPERIMENTAL

Preparation of the metal complexes

The metal complexes were prepared by adding a warm ethanolic solution of 4-pyridinealdoxime to a warm ethanolic solution of the metal halide in a 2:1 a molar ratio. The precipitated complexes were filtered, purified by repeated washing with boiling ethanol, and dried over calcium chloride in a desiccator.

Apparatus and measurements

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

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

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 $Hg[Co(SCN)_4]$ as calibrant.

The thermal analysis studies were carried on a Stanton Redcroft STA 1500 thermobalance. The TG and DTA traces were obtained at a heating rate of 10°C min^{-1}. In all cases the 20–800°C temperature range was studied.

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 thicknesses of approximately 1 mm by compressing powdered compound in a hydraulic press set to apply a force of 100 kN. The disc thicknesses were accurately measured by a micrometer. Circular electrodes of known diameter were formed concentrically on the flat faces of each disc by applying a silver conductive paint through masks. The discs were stored in a desiccator for several days before being tested. Use of compressed powder discs for conductivity measurements is widely adopted [4–7] and has been reviewed by Meier [8], who concluded that for materials of relatively low conductivity, errors due to resistance at intergranular contacts were not significant. 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 and this procedure was repeated in reverse polarity. Agreement, within a maximum of ±10%, between the four readings of current was regarded as confirmation that the electrodes were not significantly rectifying.

RESULTS AND DISCUSSION

The analytical results for the metal complexes are listed in Table 1 and show that each of the metal complexes has a stoichiometry $M(C_6H_6N_2O)_2Cl_2$.

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 electronic spectra and the magnetic moments of the cobalt and nickel complexes show that the metal atoms are in an octahedral environment [9]. The copper complex has bands in its electronic spectrum at 14 085 and 19 120 cm^{-1} and a magnetic moment of 2.01 BM.

The wavenumbers of the IR absorption bands for 4-pyridinealdoxime and its metal complexes are shown in Table 3 together with their descriptions and assignments. The bands due to the aromatic ring vibrations are shifted to higher wavenumbers on formation of the complexes. This would suggest that the aromatic ring is coordinated to a metal ion through the ring nitrogen atom [9]. In the IR spectrum of the 4-pyridinealdoxime, a broad band is observed in the 3300–2700 cm^{-1} region. This indicates the presence of hydrogen bonding in the free ligand. On complexation the

TABLE 1

Analyses of metal complexes

Compound		Metal/%	Carbon/%	Nitrogen/%	Hydrogen/%
$Co(C_6H_6N_2O)_2Cl_2$	Theory	15.75	38.52	14.97	3.23
	Found	15.66	38.39	14.82	3.06
$Ni(C_6H_6N_2O)_2Cl_2$	Theory	15.69	38.55	14.98	3.23
	Found	15.46	38.46	14.73	3.12
$Cu(C_6H_6N_2O)_2Cl_2$	Theory	16.77	38.06	14.79	3.19
	Found	16.36	37.92	14.57	3.07

$C_6H_6N_2O$ is 4-pyridinealdoxime.

TABLE 2

Electronic spectra and magnetic moments

Compound	Colour	Band position/cm^{-1}	μ/BM
$Co(C_6H_6N_2O)_2Cl_2$	Pink	9091 15674 19120	5.21
$Ni(C_6H_6N_2O)_2Cl_2$	Lime green	8197 13986 19608	3.42
$Cu(C_6H_6N_2O)_2Cl_2$	Dark green	14085 19120	2.01

broad band is replaced by a sharp band indicating that the hydrogen bonding has been removed. The reduction in the ν(C=N) vibration in the complexes as compared to the free ligand is expected due to conjugation to the ring system. The ν(M–Cl) bands in the IR spectra of the metal complexes show that the metal ions are in a six-coordinate environment [9, 10]. The ν(M–N) bands are also listed in Table 3.

The metal complexes were isolated from ethanolic solution as powders so that no definite structures can be described. However the spectroscopic and magnetic data enable us to predict possible structures. The poor solubility, particularly of the cobalt and nickel complexes in polar and non-polar solvents indicates that they have polymeric structures [9]. It is suggested that the structures of the cobalt and nickel compounds is a chain of metal atoms bonded to halogens with the 4-pyridinealdoxime molecules above and below the plane of the metal halogen chain, yielding a polymeric structure. The copper complex is considered to have a tetragonal structure with the complex having a planar arrangement of ligands with the apical positions being free so that the copper might coordinate to halogens of further $Cu(C_6H_6N_2O)_2Cl_2$ groups [11].

TABLE 3

Infrared spectra (4000–200 cm^{-1})

Compound	$\nu_{O-H}(H_2O)$	Ring vibrations	ν(C=N)	ν(M–Cl)	ν(M–N)
$C_6H_6N_2O$	3300–2700 (br, s)	1600 (s) 1420 (s)	1515 (m)		
$Co(C_6H_6N_2O)_2Cl_2$	3346	1604 (s) 1425 (s)	1498 (m)	222 (m)	258 (m)
$Co(C_6H_6N_2O)_2Cl_2$	3350	1614 (s) 1424 (s)	1500 (m)	230 (m)	260 (m)
$Cu(C_6H_6N_2O)_2Cl_2$	3380	1616 (s) 1422 (s)	1500 (m)	280 (s)	255 (m)

Key: br, broad; s, strong; m, medium.

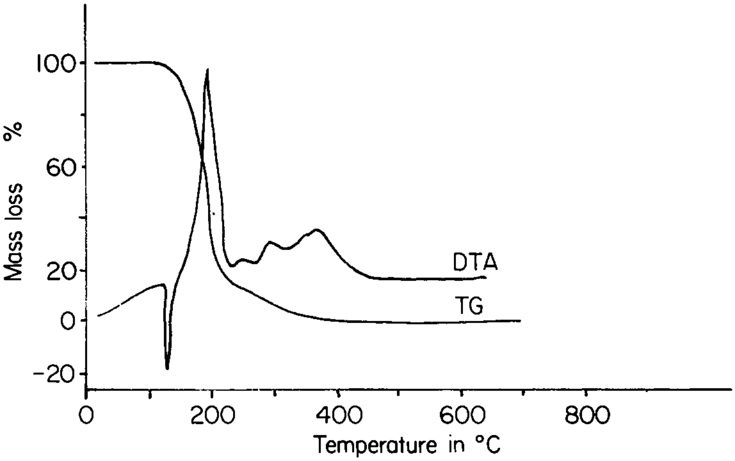

Fig. 1. TG and DTA trace for 4-pyridinealdoxime. Sample mass, 7.39 mg.

The results of the thermogravimetry studies are given in Figs. 1–4 and Table 4. The TG trace for 4-pyridinealdoxime (Fig. 1) shows that this compound is thermally stable in the range 20–127°C. Its pyrolytic decomposition starts at 127°C and finishes at 428°C with the total elimination of the sample. The DTA trace shows a peak at 132°C corresponding to fusion. The decomposition of the 4-pyridinealdoxime produces exothermic effects in the DTA trace. The TG and DTA traces for the metal complexes are shown in Figs. 2–4. The thermal decomposition scheme for the complexes is

$$M(C_6H_6N_2O)_2Cl_2 \xrightarrow{\text{ENDO}} M(C_6H_6N_2O)Cl_2 \xrightarrow{\text{ENDO}} MCl_2 \xrightarrow{\text{EXO}} \text{Metal oxide}$$

for M is Co^{2+}, Ni^{2+}

$$Cu(C_6H_6N_2O)_2Cl_2 \xrightarrow{\text{ENDO}} CuCl_2 \xrightarrow{\text{EXO}} CuO$$

The observed mass losses for these processes compare favourably with the theoretical values in Table 4.

The mean room temperature current I versus voltage V characteristics, obtained under conditions of rising and falling voltage in both polarities, are shown in Fig. 5 for the 4-pyridinealdoxime complexes of nickel and copper chlorides. The current versus voltage relationship for the compounds are shown to be linear throughout the voltage range investigated, indicating that ohmic electrical conduction prevails. Similar I–V characteristics were obtained for free 4-pyridinealdoxime ligand and its cobalt chloride complex. The electrical conductivities for the compounds were determined from the gradient of the I–V characteristics and are given in Table 5. The most striking feature of the room temperature electrical

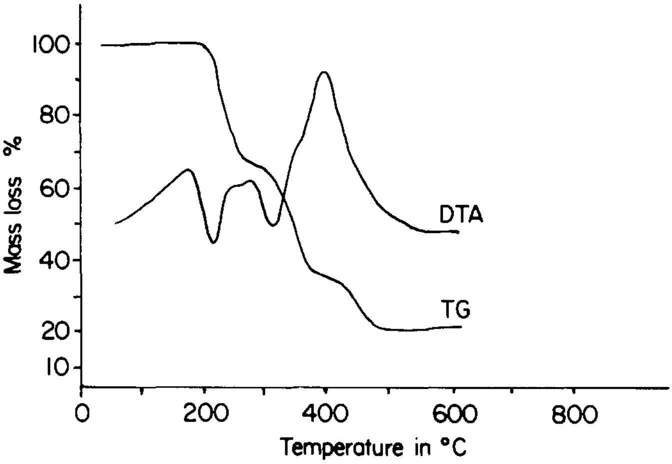

Fig. 2. TG and DTA trace for $Co(C_6H_6N_2O)_2Cl_2$. Sample mass, 6.74 mg.

conductivity measurements is that the metal complexes possess lower conductivities than the uncomplexed 4-pyridinealdoxime. Thus it would appear that complexing the ligand with metal ions produces an apparent reduction in the observed electrical conductivity. Such a phenomenon has been previously observed in the transition metal complexes of 4,7-phenanthroline [12]. It was postulated in these studies that the electrical conduction pathway was predominantly via suitable orbitals belonging to the ligand molecules in close proximity to one another. On coordination, the incorporation of a metal ion would destroy or hinder this conduction path by increasing the internuclear distance between these ligand orbitals and hence result in the lower conductivity values of the metal complexes. It is suggested that a similar effect is operating in the compounds of the

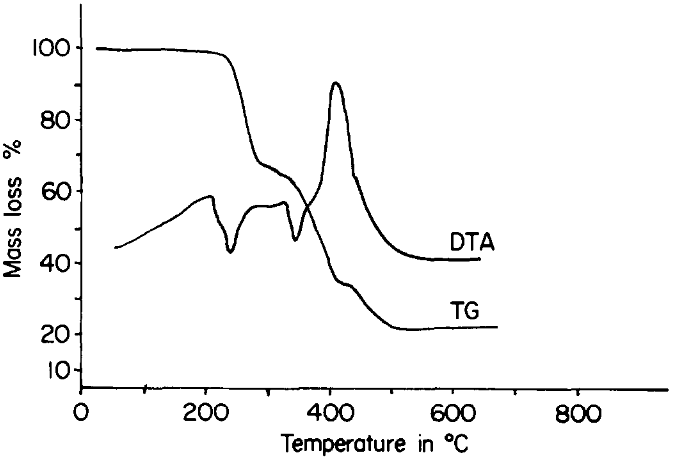

Fig. 3. TG and DTA trace for $Ni(C_6H_6N_2O)_2Cl_2$. Sample mass, 8.37 mg.

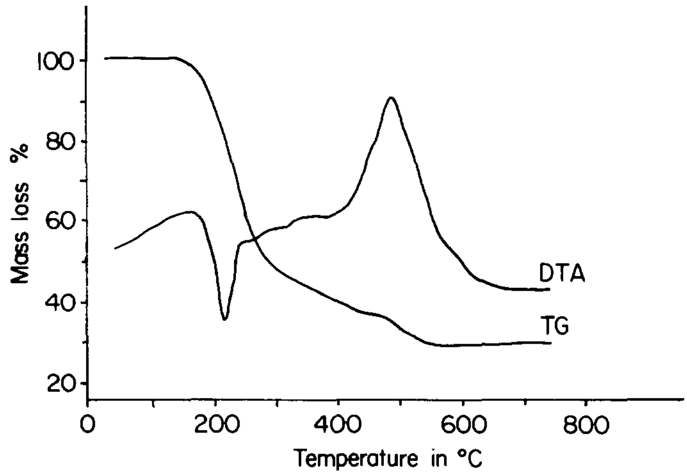

Fig. 4. TG and DTA trace for $Cu(C_6H_6N_2O)_2Cl_2$. Sample mass, 8.23 mg.

TABLE 4

Decomposition processes of metal complexes

Process	Temp. range/°C	Mass loss/%	
		Calc.	Found
$Co(C_6H_6N_2O)_2Cl_2 \rightarrow Co(C_6H_6N_2O)Cl_2$	197–186 (endo)	32.63	32.70
$Co(C_6H_6N_2O)Cl_2 \rightarrow CoCl_2$	286–399 (endo)	32.63	32.74
$CoCl_2 \rightarrow Co_3O_4$	399–508 (exo)	13.29	13.18
$Ni(C_6H_6N_2O)_2Cl_2 \rightarrow Ni(C_6H_6N_2O)Cl_2$	199–298 (endo)	32.65	32.80
$Ni(C_6H_6N_2O)Cl_2 \rightarrow NiCl_2$	298–411 (endo)	32.65	32.72
$NiCl_2 \rightarrow NiO$	411–510 (endo)	14.72	14.68
$Cu(C_6H_6N_2O)_2Cl_2 \rightarrow CuCl_2$	128–440 (endo)	64.48	65.06
$CuCl_2 \rightarrow CuO$	440–542 (exo)	14.53	14.45

Key: endo, endothermic; exo, exothermic.

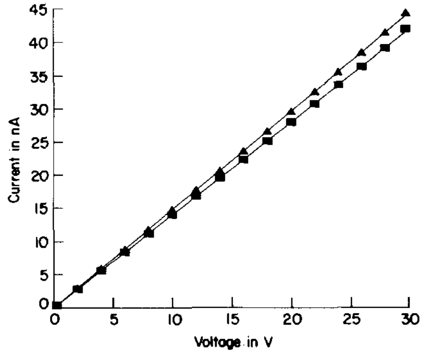

Fig. 5. Room temperature plot of current (I) versus voltage (V) for discs of $Ni(C_6H_6N_2O)_2Cl_2$ (▲) and $Cu(C_6H_6N_2O)_2Cl_2$ (■). In each case the plot is based on the mean current at any given voltage V, with V increasing and decreasing in both polarities.

TABLE 5

Room temperature electrical conductivities

Compound	$10^{-8}\sigma$ [a]/ (Ω^{-1} m^{-1})	Compound	$10^{-8}\sigma$ [a]/ (Ω^{-1} m^{-1})
$C_6H_6N_2O$	8.89	$Ni(C_6H_6N_2O)_2Cl_2$	5.98
$Co(C_6H_6N_2O)_2Cl_2$	5.31	$Cu(C_6H_6N_2O)_2Cl_2$	3.68

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

present studies. The reported electrical conductivities would imply that conduction in these compounds probably occurs by a hopping mechanism.

The limited range of the electrical conductivities of the individual metal complexes of 4-pyridinealdoxime may be attributed to the similarity in sterochemistry and their proposed polymeric nature. As previously discussed, the cobalt and nickel complexes are structurally alike and this is possibly reflected in the closeness of their electrical conductivities. The copper complex differs from the other two compounds by being tetragonal and having different spatial arrangement of ligands and it is possible that this may interfere with the conduction mechanism and hence produce the observed lowest conductivity of the compounds studied.

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