Thermochimica Acta, 211 (1992) 85–91
Elsevier Science Publishers B.V., Amsterdam

Thermal, spectral and magnetic studies of the chloro complexes of manganese, cobalt, nickel and copper with 3-pyridinealdoxime

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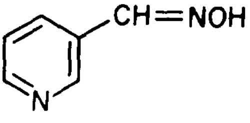
(Received 6 May 1992)

Abstract

Some chloro compounds of manganese, cobalt, nickel and copper with 3-pyridinealdoxime were prepared in ethanolic solution. The compounds have the stoichiometry ML_2Cl_2. Spectral and magnetic studies were used to deduce the stoichiometry. The compounds have polymeric octahedral structures. The thermal behaviour of the compounds was studied by thermogravimetry and differential thermal analysis. Thermal decomposition studies show that the cobalt, nickel and copper compounds each form an intermediate compound before decomposing to the metal halide and finally the metal oxide. The manganese compound decomposes with loss of the organic ligand to give the metal halide, followed by loss of chlorine to give the metal oxide.

INTRODUCTION

In this work, the structural properties and thermal analysis studies of the chloro complexes of manganese, cobalt, nickel and copper with 3-pyridinealdoxime are discussed.



3-Pyridinealdoxime ($C_6H_6N_2O$)

The molecule of 3-pyridinealdoxime has four possible coordination sites: the double bond of the C–N group; the nitrogen atom of the C–N group; the oxygen atom of the OH group; the ring nitrogen atom. Spectral and magnetic studies were used to characterise each complex and

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to interpret the type of coordination taking place to the metal ion. A study of the thermal stability and decomposition of each compound has been carried out using thermogravimetry (TG) and differential thermal analysis (DTA).

EXPERIMENTAL

Preparation of complexes

The complexes of manganese, cobalt, nickel and copper with 3-pyridinealdoxime were prepared by adding a warm ethanolic solution of 3-pyridinealdoxime to a warm ethanolic solution of the metal halide in a 2:1 molar ratio. The precipitated complexes were filtered, purified by repeated washing with boiling ethanol, and dried over calcium chloride.

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 (4000–600 cm^{-1}) and polyethylene discs (600–200 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 $Hg[Co(SCN)_4]$ 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. Intermediate cobalt, nickel and copper complexes were obtained by heating the original complexes on the thermobalance at a fixed temperature until a constant weight was obtained.

RESULTS AND DISCUSSION

The analytical results for the complexes agree with the stoichiometry of the complexes proposed in Table 1. They are of the formula $M(C_6H_6N_2O)_2Cl_2$.

The molecular magnetic moments and the bands in the electronic spectra of the complexes are listed in Table 2. No information is available on the stoichiometry of the manganese complex from the electronic spectrum because no bands corresponding to d–d transitions are observed. The magnetic moment of the manganese complex is 5.94 BM, which is similar to the spin-only value. The cobalt and nickel complexes

TABLE 1

Analyses of compounds

Compound	Method	Metal	Carbon	Nitrogen	Hydrogen
$Mn(C_6H_6N_2O)_2Cl_2$[a]	Theory	15.51	38.94	15.13	3.26
	Found	15.36	38.87	15.04	3.16
$Co(C_6H_6N_2O)_2Cl_2$[a]	Theory	15.75	38.52	14.97	3.23
	Found	15.29	38.12	14.66	3.09
$Co(C_6H_6N_2O)Cl_2$[b]	Theory	23.38	28.60	11.11	2.40
	Found	23.12	28.39	11.02	2.22
$Ni(C_6H_6N_2O)_2Cl_2$[a]	Theory	15.69	38.55	14.98	3.23
	Found	15.29	38.41	14.57	3.07
$Ni(C_6H_6N_2O)Cl_2$[b]	Theory	23.31	28.62	11.12	2.40
	Found	23.07	28.27	11.04	2.27
$Cu(C_6H_6N_2O)_2Cl_2$[a]	Theory	16.77	38.06	14.79	3.19
	Found	16.66	38.01	14.58	3.08
$Cu(C_6H_6N_2O)Cl_2$[b]	Theory	24.76	28.08	10.91	2.35
	Found	24.31	27.66	10.51	2.02

[a] Compound isolated from solution. [b] Compound obtained by heating the corresponding initial compound on thermobalance.

have bands in their electronic spectra which indicates that the metal atoms are in an octahedral environment [1]. The magnetic moment for each compound confirms an octahedral environment [1]. A broad band between 10 000 and 15 000 cm^{-1} in the electronic spectrum of the copper complex indicates that the copper atoms are also in an octahedral environment [1]. The magnetic moment, which is lower than the spin-only value, is indicative of copper–copper magnetic interaction in the complex.

TABLE 2

Electronic spectra and magnetic moments

Compound	Band position (cm^{-1})	d–d Transition	μ (BM)
$Mn(C_6H_2N_2O)_2Cl_2$	–	–	5.94
$Co(C_6H_6N_2O)_2Cl_2$	9804	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	4.90
	15 748	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	
	18 939	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	
$Ni(C_6H_6N_2O)_2Cl_2$	8402	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	3.16
	13 986	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	
	24 271	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	
$Cu(C_6H_6N_2O)_2Cl_2$	13 850	$^2E_g(D) \rightarrow {}^2T_{2g}(D)$	1.59

TABLE 3

IR spectra (400–200 cm^{-1})

Compound	ν(O–H) [a]	Ring vibrations [a]	ν(C=N) [a]	ν(M–Cl) [a]	ν(M–N) [a]
$C_6H_6N_2O$	3300–2710 (br,s)	1585 (s), 1412 (s)	1515 (s)	–	–
$Mn(C_6H_6N_2O)_2Cl_2$	3440 (s)	1600 (s), 1430 (s)	1498 (s)	230 (w)	290 (m)
$Co(C_6H_6N_2O)_2Cl_2$	3430 (s)	1602 (s), 1428 (s)	1491 (s)	232 (w)	292 (m)
$Ni(C_6H_6N_2O)_2Cl_2$	3440 (s)	1602 (s), 1430 (s)	1488 (s)	229 (w)	290 (m)
$Cu(C_6H_6N_2O)_2Cl_2$	3380 (s)	1604 (s), 1428 (s)	1489 (s)	248 (w)	282 (m)

[a] Key: br, broad; m, medium; s, strong; w, weak.

The wavenumbers of the IR absorption bands for 3-pyridinealdoxime and its metal complexes are shown in Table 3 together with their description 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 nitrogen atom in the aromatic ring is coordinated to a metal ion [1]. In the IR spectra of the 3-pyridinealdoxime, a broad band is observed in the 3300–2710 cm^{-1} region. This indicates the presence of hydrogen bonding in the free ligand. On complexation the 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, owing to conjugation to the ring system. The ν(M–Cl) bands in the spectra of the complexes show that the metal ions are in a six-coordinate environment [1]. The ν(M–N) bands are also listed in Table 3.

Single crystals of the compounds could not be isolated from ethanolic solution, thus no definite structures can be described. However, the spectroscopic and magnetic data enable us to predict possible structures.

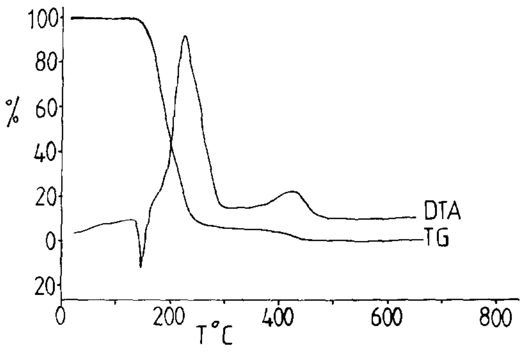

Fig. 1. TG and DTA trace for 3-pyridinealdoxime; sample weight = 13.88 mg.

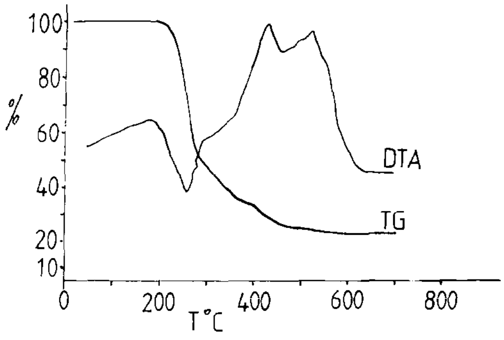

Fig. 2. TG and DTA trace for $Mn(C_6H_6N_2O)_2Cl_2$; sample weight = 3.55 mg.

The poor solubility of the complexes in polar and non-polar solvents indicates that they have polymeric structures [1]. It is suggested that the structure of the complexes is a chain of metal atoms bonded to halogen atoms, with the 3-pyridinealdoxime molecules above and below the plane of the metal–halogen chain, yielding a polymeric structure.

The TG and DTA traces for 3-pyridinealdoxime and its manganese,

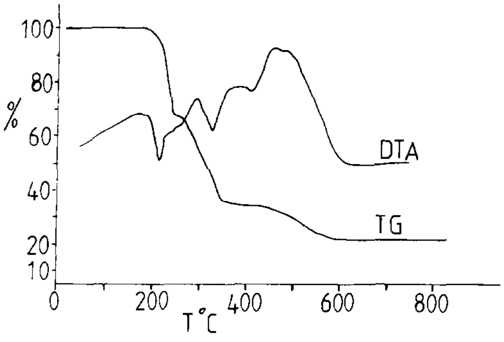

Fig. 3. TG and DTA trace for $Co(C_6H_6N_2O)_2Cl_2$; sample weight = 6.17 mg.

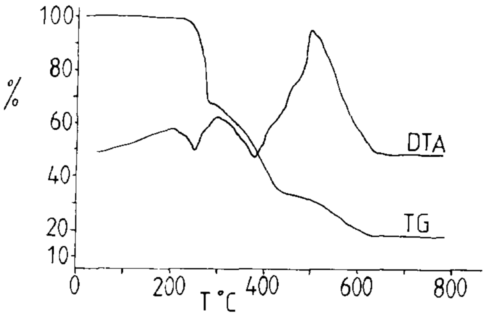

Fig. 4. TG and DTA trace for $Ni(C_6H_6N_2O)_2Cl_2$; sample weight = 8.33 mg.

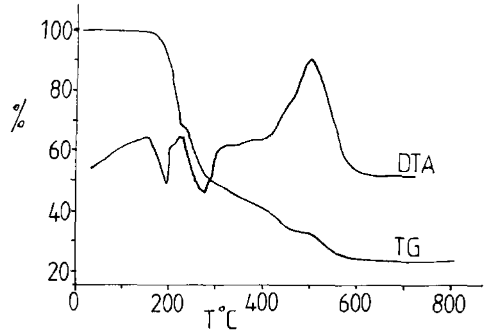

Fig. 5. TG and DTA trace for $Cu(C_6H_6N_2O)_2Cl_2$; sample weight = 7.83 mg.

cobalt, nickel and copper complexes are shown in Figs. 1–5. The TG trace for 3-pyridinealdoxime (Fig. 1) shows that this compound is thermally stable in the 20–147°C range. Its pyrolytic decomposition starts at 147°C and finishes around 472°C with the total elimination of the sample. The DTA trace displays an endothermic peak at 152°C corresponding to fusion. The decomposition of the 3-pyridinealdoxime produces exothermic effects in the DTA trace. The TG and DTA traces for the complexes formed between 3-pyridinealdoxime and the chlorides of manganese, cobalt, nickel and copper are given in Figs. 2–5. The thermal decomposi-

TABLE 4

Decomposition processes of the metal complexes

Process	Temperature range (°C)	Mass loss (%)	
		Calc.	Found
$Mn(C_6H_6N_2O)_2Cl_2 \rightarrow MnCl_2$	189–394 (Endo)	65.98	65.90
$MnCl_2 \rightarrow Mn_2O_3$	394–622 (Exo)	12.70	12.72
$Co(C_6H_6N_2O)_2Cl_2 \rightarrow Co(C_6H_6N_2O)Cl_2$	186–266 (Endo)	32.63	32.66
$Co(C_6H_6N_2O)Cl_2 \rightarrow CoCl_2$	266–397 (Endo)	32.63	32.60
$CoCl_2 \rightarrow Co_3O_4$	397–638 (Exo)	13.29	13.20
$Ni(C_6H_6N_2O)_2Cl_2 \rightarrow Ni(C_6H_6N_2O)Cl_2$	150–294 (Endo)	32.65	32.60
$Ni(C_6H_6N_2O)_2Cl_2 \rightarrow NiCl_2$	294–454 (Endo)	32.65	32.68
$NiCl_2 \rightarrow NiO$	454–656 (Exo)	14.72	14.70
$Cu(C_6H_6N_2O)_2Cl_2 \rightarrow Cu(C_6H_6N_2O)Cl_2$	152–234 (Endo)	32.24	32.20
$Cu(C_6H_6N_2O)Cl_2 \rightarrow CuCl_2$	234–390 (Endo)	32.24	32.26
$CuCl_2 \rightarrow CuO$	390–660 (Exo)	14.53	14.50

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

tion scheme for the cobalt, nickel and copper complexes is

$$Co(C_6H_6N_2O)_2Cl_2 \xrightarrow{\text{Endo}} Co(C_6H_6N_2O)Cl_2 \xrightarrow{\text{Endo}} CoCl_2 \xrightarrow{\text{Exo}} Co_3O_4$$

$$Ni(C_6H_6N_2O)_2Cl_2 \xrightarrow{\text{Endo}} Ni(C_6H_6N_2O)Cl_2 \xrightarrow{\text{Endo}} NiCl_2 \xrightarrow{\text{Exo}} NiO$$

$$Cu(C_6H_6N_2O)_2Cl_2 \xrightarrow{\text{Endo}} Cu(C_6H_6N_2O)Cl_2 \xrightarrow{\text{Endo}} CuCl_2 \xrightarrow{\text{Exo}} CuO$$

The manganese complex undergoes thermal decomposition as

$$Mn(C_6H_6N_2O)_2Cl_2 \xrightarrow{\text{Endo}} MnCl_2 \xrightarrow{\text{Exo}} Mn_2O_3$$

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

REFERENCE

1 J.R. Allan, N.D. Baird and A.L. Kassyk, J. Therm. Anal., 16 (1979) 79.