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THE PREPARATION, CHARACTERISATION AND THERMAL ANALYSIS STUDIES ON COMPLEXES OF COBALT(II), NICKEL(II), COPPER(II) AND ZINC(II) WITH PHENANTHRIDINE

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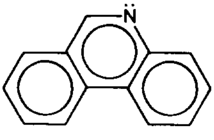
ABSTRACT

A series of chloro and bromo complexes of cobalt, nickel, copper and zinc with phenanthridine have been prepared. The chloro and bromo complexes of cobalt and zinc, and the bromo complex of nickel have tetrahedral structures. The chloro and bromo complexes of copper have tetragonal structures while the chloro complex of nickel has a polymeric octahedral structure. The stereochemical configurations were deduced using spectral and magnetic studies. The decomposition of each complex has been investigated using thermogravimetry and differential thermal analysis.

INTRODUCTION

This work is a continuation of previously reported structural and thermal analysis studies on complexes of the substituted pyridines and some first row transition metal ions [1–10]. In this paper we report the thermal, spectral and magnetic studies of the chloro and bromo complexes of cobalt, nickel, copper and zinc with phenanthridine. Phenanthridine has one donor site in the ring system for complexing to a metal: the nitrogen atom of the aromatic ring system.



Phenanthridine ($C_{13}H_9N$)

Spectral and magnetic measurements have been used to characterise each metal complex and to interpret the type of coordination which takes place

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with the metal ion. Thermogravimetry and differential thermal analysis studies have been carried out on each of the complexes.

EXPERIMENTAL

Preparation of the complexes

The compounds were all prepared by mixing hot ethanolic solutions of the ligand and the appropriate metal halide in an approximately 2 : 1 molar ratio. Precipitation occurred immediately in all cases except for the complex of nickel chloride which formed very slowly after heating on a boiling water bath. A better yield of this compound was obtained by mixing a solution of the ligand in diethyl ether with a solution of nickel chloride in methanol.

The compounds were isolated by filtration under suction, washing with a 1 : 1 solution of ethanol and ether, and drying, firstly by suction of air and then in an oven at 80 ° C for 1 h.

Apparatus

The concentration of the metal ion was determined using a Perkin–Elmer 373 atomic absorption spectrophotometer. The carbon, hydrogen and nitrogen analyses were made using a Carlo Erba elemental analyser.

The IR spectra were recorded using KBr discs over the wavenumber range 4000–600 cm^{-1} and using polyethylene discs over the 600–200 cm^{-1} range on a Perkin–Elmer IR spectrophotometer model 598. The electronic spectra were recorded as solid diffuse reflectance spectra using a Beckman Acta MIV spectrophotometer. Measurements of magnetic moments were made using the Gouy method with $Hg[Co(SCN)_4]$ as calibrant. Each magnetic moment was corrected for diamagnetism using Pascal's constants [11].

The thermal analysis measurements were made on a Stanton Redcroft model STA 1500 thermobalance. Thermogravimetry (TG) and differential thermal analysis (DTA) curves were obtained at a heating rate of 6 ° C min^{-1} in static air. The 20–700 ° C temperature range was studied in all cases. Intermediate compounds were isolated from the starting materials by heating them at a fixed temperature on the thermobalance until a constant weight was obtained.

RESULTS AND DISCUSSIONS

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

TABLE 1

Analysis of the compounds

Compound [a]	Theory (%)				Found (%)			
	Metal	Carbon	Nitrogen	Hydrogen	Metal	Carbon	Nitrogen	Hydrogen
$Co(C_{13}H_9N)_2Cl_2$	12.06	63.94	5.74	3.72	12.23	63.61	5.66	3.64
$Co(C_{13}H_9N)Cl_2$ [b]	19.06	50.52	4.53	2.92	20.82	50.66	4.41	2.57
$Co(C_{13}H_9N)_2Br_2$	10.21	54.10	4.85	3.15	10.04	54.26	4.31	3.07
$Ni(C_{13}H_9N)Cl_2$	19.01	50.55	4.54	2.94	18.69	49.73	4.49	2.85
$Ni(C_{13}H_9N)_2Br_2$	10.17	54.12	4.86	3.15	10.12	53.96	4.89	3.03
$Ni(C_{13}H_9N)Br_2$ [b]	14.76	39.25	3.52	2.28	14.41	38.63	3.77	2.01
$Cu(C_{13}H_9N)_2Cl_2$	12.89	63.35	5.68	3.68	12.61	63.09	5.61	3.73
$Cu(C_{13}H_9N)Cl_2$ [b]	20.25	49.77	4.46	2.89	20.20	49.41	4.11	2.56
$Cu(C_{13}H_9N)_2Br_2$	10.92	53.67	4.82	3.12	10.73	53.21	4.83	3.09
$Zn(C_{13}H_9N)_2Cl_2$	13.21	63.11	5.66	3.67	13.01	62.28	5.68	3.27
$Zn(C_{13}H_9N)Cl_2$ [b]	20.72	49.48	4.44	2.88	20.66	49.13	4.27	2.66
$Zn(C_{13}H_9N)_2Br_2$	11.20	53.50	4.80	3.11	11.09	54.51	4.73	3.24

[a] $C_{13}H_9N$ = phenanthridine.
[b] Thermal decomposition products.

The wavenumbers of the IR absorption bands as well as their descriptions and assignments are given in Table 2 for the complexes isolated from ethanolic solution. The IR spectrum of phenanthridine is almost identical to that of its complexes in the 4000–625 cm^{-1} region except for the bands due to the ring vibrations of the aromatic ring which move to higher wavenumbers in the complexes. This would suggest that coordination is taking place between the metal and the nitrogen atom in the aromatic ring [4]. Metal–halogen and metal–nitrogen bands are assigned for the complexes and are reported in Table 2.

The electronic spectrum and the magnetic measurements, Table 3, would suggest that for the bromo complexes of cobalt and nickel and the chloro

TABLE 2

IR spectra of the starting materials (4000–200 cm^{-1})

Compound	Ring vibrations			ν_{M-X}	ν_{M-N}
$C_{13}H_9N$	1608(S)	1571(S)	1523(S)	–	–
$Co(C_{13}H_9N)_2Cl_2$	1613(S)	1582(S)	1526(S)	345(S), 310(S)	248(M)
$Co(C_{13}H_9N)_2Br_2$	1613(S)	1582(S)	1525(S)	270(M)	230(W)
$Ni(C_{13}H_9N)Cl_2$	1618(S)	1583(S)	1525(S)	260(M)	230(W)
$Ni(C_{13}H_9N)_2Br_2$	1612(S)	1582(S)	1525(S)	270(S), 240(S)	220(M)
$Cu(C_{13}H_9N)_2Cl_2$	1619(S)	1580(S)	1526(S)	330(M)	220(W)
$Cu(C_{13}H_9N)_2Br_2$	1613(S)	1581(S)	1525(S)	270(M)	220(W)
$Zn(C_{13}H_9N)_2Cl_2$	1613(S)	1584(S)	1527(S)	330(S), 300(S)	220(M)
$Zn(C_{13}H_9N)_2Br_2$	1613(S)	1584(S)	1526(S)	235(S)	205(M)

S, Strong; M, medium; W, weak.

TABLE 3

Electronic spectra and magnetic moments of the starting materials

Compound	Colour	Peak position (cm^{-1})	d–d transition	μ (B.M.)
$Co(C_{13}H_9N)_2Cl_2$	Blue	9170	$^4A_2(F) \rightarrow {}^4T_1(F)$	4.38
		16340	$^4A_2(F) \rightarrow {}^4T_1(P)$	
$Co(C_{13}H_9N)_2Br_2$	Turquoise	8850	$^4A_2(F) \rightarrow {}^4T_1(F)$	4.23
		15870	$^4A_2(F) \rightarrow {}^4T_1(P)$	
$Ni(C_{13}H_9N)Cl_2$	Red-brown	11360	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	3.25
		17240	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	
		21410	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	
$Ni(C_{13}H_9N)_2Br_2$	Blue	9900	$^3T_1(F) \rightarrow {}^3A_2(F)$	3.45
		17090	$^3T_1(F) \rightarrow {}^3T_1(P)$	
$Cu(C_{13}H_9N)_2Cl_2$	Grey	18690	$^2B_1 \rightarrow {}^2A_1$	1.78
$Cu(C_{13}H_9N)_2Br_2$	Yellow-green	16260	$^2B_1 \rightarrow {}^2A_1$	1.76

complex of cobalt, the metal ion is in a tetrahedral environment [3,7]. The metal–halogen bands in the IR spectra of the complexes support a tetrahedral configuration for the compounds [3,12]. The electronic spectrum and magnetic moment of the chloro compound of nickel are indicative of the nickel atom in an octahedral environment [3,7]. The nickel–halogen band in the IR spectrum of the compound supports the suggestion of an octahedral configuration for this compound [3,7]. A single broad absorption band in the electronic absorption spectra of the chloro and bromo compounds of copper would suggest that the copper ion is in a six-coordinate environment [8]. The magnetic moment for each compound is slightly higher than the spin-only value of 1.73 B.M. The copper–halogen bands in the IR spectra of the compounds are indicative of tetragonal structures [13]. The metal–halogen bands in the IR spectra of the chloro and bromo complexes of zinc are indicative of the zinc ion in a tetrahedral environment [12].

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 for the chloro and bromo compounds of cobalt and zinc and the bromo compound of nickel, the metal ions are in a tetrahedral environment. Two chloride ions and two phenanthridine molecules make up the tetrahedral environment around the metal ions. The chloro compound of nickel has the nickel ions in an octahedral environment. The insolubility of this compound in both polar and non-polar solvents would suggest that it has a polymeric structure [4]. It is thus postulated that for the nickel compound the nickel atoms are bonded to halogen atoms to give a double chain in which each halogen is acting as a bridge between nickel atoms. The phenanthridine molecules are above and below the plane of the double chain. It is suggested that the chloro and bromo compounds of copper have pseudo-planar struc-

TABLE 4

Thermal decomposition products

Starting material	Decomposition temperature (°C)	Resulting compound	Weight loss (%)	
			Calc.	Found
$Co(C_{13}H_9N)_2Cl_2$	174 (endo) [a]	$Co(C_{13}H_9N)Cl_2$	36.67	36.27
	294 (endo)	$CoCl_2$	36.67	36.76
$Co(C_{13}H_9N)_2Br_2$	178 (endo)	$CoBr_2$	62.08	63.04
$Ni(C_{13}H_9N)Cl_2$	160 (endo)	$NiCl_2$	58.01	57.28
$Ni(C_{13}H_9N)_2Br_2$	196 (endo)	$Ni(C_{13}H_9N)Br_2$	31.06	31.92
	282 (endo)	$NiBr_2$	31.06	30.33
$Cu(C_{13}H_9N)_2Cl_2$	184 (endo)	$Cu(C_{13}H_9N)Cl_2$	36.36	36.49
	290 (endo)	$CuCl_2$	36.36	35.42
$Cu(C_{13}H_9N)_2Br_2$	179 (endo)	$CuBr_2$	61.61	60.36
$Zn(C_{13}H_9N)_2Cl_2$	162 (endo)	$Zn(C_{13}H_9N)Cl_2$	36.22	35.33
	316 (endo)	$ZnCl_2$	36.22	34.12
$Zn(C_{13}H_9N)_2Br_2$	186 (endo)	$ZnBr_2$	61.39	60.69

[a] Endo, endothermic reaction.

tures with long bonds being formed from the copper atom to the halides of other groups as is observed in the structure of bispyridine copper(II) chloride [14].

The results of the thermogravimetry and differential thermal analysis are given in Table 4. The temperatures quoted are for the maximum rate of decomposition under the conditions used. The chloro compounds of cobalt, copper and zinc and the bromo compound of nickel, which all have the stoichiometry $M(C_{13}H_9N)_2X_2$, decompose with endothermic reactions via an intermediate compound to give the metal halide. The bromo compounds of cobalt, copper and zinc which have the stoichiometry $M(C_{13}H_9N)_2Br_2$, decompose with endothermic reactions to give the metal bromide. The chloro compound of nickel which has the stoichiometry $Ni(C_{13}H_9N)Cl_2$ decomposes endothermically with loss of the organic ligand to give nickel(II) chloride. The decomposition schemes are

$$M(C_{13}H_9N)_2X_2 \xrightarrow[\text{endo}]{} M(C_{13}H_9N)X_2 \xrightarrow[\text{endo}]{} MX_2$$

$$(M \equiv Co^{2+}, Cu^{2+}, Zn^{2+}; X \equiv Cl^- \text{ and } M \equiv Ni^{2+}; X \equiv Br^-) \qquad (1)$$

$$M(C_{13}H_9N)_2Br_2 \xrightarrow[\text{endo}]{} MBr_2$$

$$(M \equiv Co^{2+}, Cu^{2+}, Zn^{2+}) \qquad (2)$$

$$Ni(C_{13}H_9N)Cl_2 \xrightarrow[\text{endo}]{} NiCl_2 \qquad (3)$$

The metal halides for each of the complexes finally decompose exothermically to give a metal oxide.

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