Thermochimica Acta, 170 (1990) 139–145
Elsevier Science Publishers B.V., Amsterdam

THERMAL, SPECTRAL AND MAGNETIC STUDIES ON 4-HYDROXYPTERIDINE COMPOUNDS OF MANGANESE(II), COBALT(II), NICKEL(II) AND COPPER(II)

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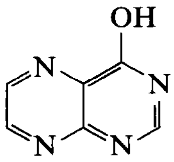
(Received 7 March 1990)

ABSTRACT

The chloro compounds of 4-hydroxypteridine with manganese, cobalt, nickel and copper were prepared in ethanolic solution, from which the solid compounds were isolated. The suggested structure for the cobalt compound is tetrahedral, while for the manganese, nickel and copper compounds it is octahedral. The thermal behaviour of these compounds has been studied by thermogravimetry and differential thermal analysis techniques. The compounds of cobalt and nickel are hydrated. Thermal decomposition studies show that these compounds lose water of crystallisation followed by organic ligand to give the metal oxide. The compounds of manganese and copper are anhydrous. Thermal decomposition studies show that these compounds lose organic ligand to form the metal oxide.

INTRODUCTION

The compound 4-hydroxypteridine has five donor atoms which can form bonds with metal ions: the two nitrogen atoms of the pyrazine ring, and the two nitrogen atoms and the hydroxyl oxygen in the pyrimidine ring.



4-Hydroxypteridine ($C_6H_4N_4O$).

This compound, which is illustrated in the enolic form, can also exist in the ketonic form [1]. This paper reports the thermal analysis studies of 4-hydroxypteridine and of the complexes formed by it and the transition metals manganese, cobalt, nickel and copper. Spectral and magnetic studies have been used to characterise each metal complex and to interpret the type of coordination which takes place with the metal ion.

EXPERIMENTAL

Preparation of the complexes

A solution of 4 g of metal halide in 60 cm^3 of ethanol was obtained by warming until the ethanol boiled. To the boiling solution was added 3 g of 4-hydroxypteridine dissolved in ethanol. This solution was then refluxed for 2 h, cooled and diethyl ether was added with stirring. The precipitated complex was filtered off and dried in a desiccator over calcium chloride for 24 h.

Apparatus

The concentration of metal ion was obtained by means of 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 for the range 4000–600 cm^{-1} and polyethylene discs from 600–200 cm^{-1} on a Perkin–Elmer IR spectrophotometer model 598.

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

Magnetic measurements were carried out by the Gouy method using $Hg[Co(SCN)_4]$ as the calibrant.

The thermal analysis studies were carried out 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. In all cases, the 20–800°C temperature range was studied.

RESULTS AND DISCUSSION

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

TABLE 1

Analyses and magnetic moments of the compounds

Compound [a]	Colour		M (%)	C (%)	N (%)	H (%)	μ (B.M.)
$Mn(C_6H_4N_4O)_2Cl_2$	White	Calc.	13.97	34.14	26.54	1.91	5.84
		Expt.	13.47	34.29	26.41	1.80	
$Co(C_6H_4N_4O)Cl_2 \cdot 1.5H_2O$	Blue	Calc.	19.32	23.62	18.37	2.31	4.62
		Expt.	19.04	23.44	18.15	2.20	
$Ni(C_6H_4N_4O)Cl_2 \cdot 2.5H_2O$	Green	Calc.	18.18	22.32	17.35	2.81	2.96
		Expt.	18.36	22.18	17.51	2.66	
$Cu(C_6H_4N_4O)Cl_2$	Green	Calc.	22.48	25.50	19.82	1.42	1.76
		Expt.	22.29	25.38	19.66	1.30	

[a] $C_6H_4N_4O$, 4-hydroxypteridine.

TABLE 2

Electronic spectra

Compound	Band position (cm^{-1})	d–d Transition
$Co(C_6H_4N_4O)Cl_2 \cdot 1.5H_2O$	7692	$^4A_2(F) \rightarrow {}^4T_1(F)$
	15151 16000	$^4A_2(F) \rightarrow {}^4T_1(P)$
$Ni(C_6H_4N_4O)Cl_2 \cdot 2.5\ H_2O$	8920	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$
	14810	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$
$Cu(C_6H_4N_4O)Cl_2$	13889	$^2E_g(D) \rightarrow {}^2T_{2g}(D)$

magnetic moments are in Table 1 and the bands in the electronic spectra of the complexes are listed in Table 2. In the electronic spectrum of the manganese compound, no bands due to d–d transitions were observed. The compound has a magnetic moment μ of 5.84 B.M. The positions of the bands in the electronic spectra of the cobalt and nickel compounds would suggest that the cobalt ion is in a tetrahedral environment whereas the nickel ion is in an octahedral environment [2,3]. In the spectrum of the nickel compound the band corresponding to the d–d transition $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ is not observed, owing to the presence of a charge transfer band which extends into this part of the spectrum. The values obtained for the magnetic moments of the cobalt and nickel compounds are also indicative of the cobalt atom being in a tetrahedral environment and the nickel atom in an octahedral environment [2,3]. The copper compound has a broad absorption band between 10000 and 15000 cm^{-1}. This suggests an octahedral environment for the copper atom [2]. The broadness of the band results from Jahn–Teller distortion, which is due to an odd number of electrons in the $d_{x^2-y^2}$ orbital [4]. The band is made up of composite bands involving transitions from the other d-orbitals to the $d_{x^2-y^2}$ orbital. The magnetic moment for the copper compound is similar to the spin-only value.

The wavenumbers of the IR absorption bands for 4-hydroxypteridine and for its chloro complexes isolated from ethanolic solution are given in Table 3, together with the descriptions and assignments. The cobalt and nickel compounds show a strong absorption band in the region 3700–2000 cm^{-1}, ν_{O-H}, indicating the presence of water of crystallisation.

The IR spectrum of 4-hydroxypteridine would suggest that it exists in the ketonic form as the free ligand, since bands are observed at 1710 cm^{-1} and 3400 cm^{-1} which correspond to the $\nu_{C=O}$ and ν_{N-H} vibrations respectively. In the metal complexes the $\nu_{C=O}$ band is observed to move to lower wavenumber, indicating that complexation has taken place [5]. The trend in the bands due to the aromatic ring vibrations, which are reported in Table 3, is to higher wavenumber on the formation of the complexes. This would indicate the presence of metal–nitrogen bands in these compounds [2]. The ν_{M-X} and ν_{M-O} vibrations have been identified and are listed in Table 3.

TABLE 3

Infrared spectra (4000–200 cm^{-1})

Compound	$\nu_{O-H}(H_2O)$	ν_{N-H}	$\nu_{C=O}$	Ring vibrations	ν_{M-X}	ν_{M-O}	ν_{M-N}
$C_6H_4N_4O$	–	3400(m)	1710(s)	1586(s) 1389(s)	–	–	–
$Mn(C_6H_4N_4O)_2Cl_2$	–	3380(s)	1642(s)	1586(s) 1389(s)	255(m)	282(w)	–
$Co(C_6H_4N_4O)Cl_2 \cdot 1.5H_2O$	3700–2000 (br, s)	–	1660(s)	1605(s) 1407(s)	302(s)	284(m)	238(w)
$Ni(C_6H_4N_4O)Cl_2 \cdot 2.5H_2O$	3700–2350 (br, s)	–	1665(s)	1608(s) 1410(s)	255(m)	270(w)	212(w)
$Cu(C_6H_4N_4O)Cl_2$	–	3382(s)	1670(s)	1609(s) 1408(s)	252(m)	265(m)	224(w)

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

The compounds isolated from solution were all obtained as powders, and without X-ray analysis no definite structures can be deduced. However, spectroscopic and magnetic data, along with the chemical composition of the compounds, allow us to postulate possible structures. The poor solubility of the manganese, nickel and copper compounds in polar and non-polar solvents indicates that they have polymeric structures [2]. It is thus suggested that the structure of the manganese compound is a chain of manganese atoms bonded to halogens with the oxygen atom of 4-hydroxypteridine molecules bonding to manganese atoms above and below the plane of the metal–halogen chain. The nickel and copper compounds consists of parallel chains of metal atoms bonded to halogens with the 4-hydroxypteridine molecules as bridging units between adjacent chains, forming a sheet structure, with an oxygen atom and a nitrogen atom of the ring system being bonded to the copper and nickel atoms. The cobalt compound has a tetrahedral structure in which the cobalt atom is bonded to two chloride ions and to a nitrogen atom and an oxygen atom of the aromatic ring.

The TG and DTA curves for 4-hydroxypteridine and the complexes with manganese, cobalt, nickel and copper are given in Figs. 1–5. The TG curve for 4-hydroxypteridine shows that this compound is thermally stable in the temperature range 20–298 ° C. Its pyrolytic decomposition begins at 298 ° C and finishes at 623 ° C with total elimination of the sample. The DTA curve of 4-hydroxypteridine shows an endothermic peak at 285 ° C due to melting. The enthalpy of fusion is 7 kJ mol^{-1}. The 4-hydroxypteridine then decomposes immediately, producing exothermic peaks at 365 ° C and 572 ° C respectively

The TG and DTA curves for the complexes formed between 4-hydroxypteridine and manganese, cobalt, nickel and copper are given in Figs. 2–5.

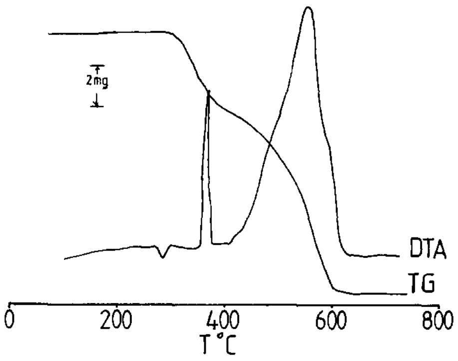


Fig. 1. TG and DTA curves for 4-hydroxypteridine. Sample weight = 13.54 mg.

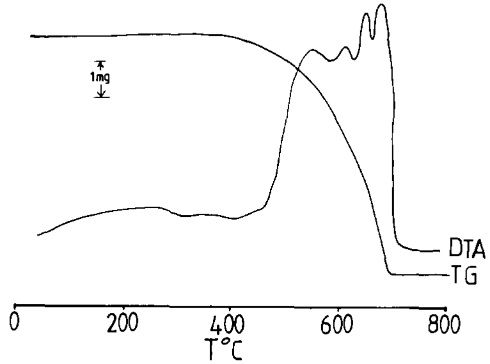


Fig. 2. TG and DTA curves for $Mn(C_6H_4N_4O)_2Cl_2$. Sample weight = 7.71 mg.

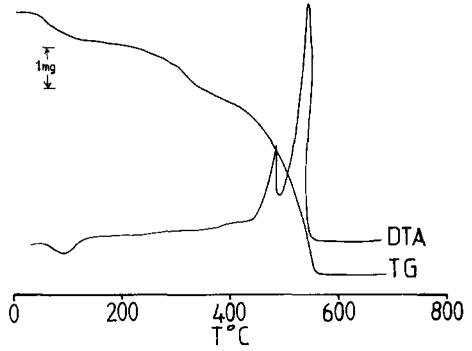


Fig. 3. TG and DTA curves for $Co(C_6H_4N_4O)Cl_2 \cdot 1.5H_2O$. Sample weight = 9.06 mg.

The dehydration process in the cobalt and nickel complexes takes place in one step. The observed weight losses for these processes compare favourably with the theoretical values as shown in Table 4. The dehydration enthalpies have been calculated and are given in Table 4. Decomposition of the

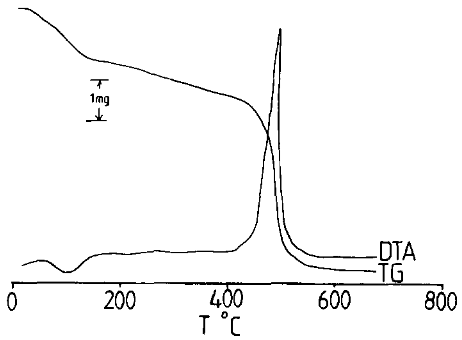


Fig. 4. TG and DTA curves for $Ni(C_6H_4N_4O)Cl_2 \cdot 2.5H_2O$. Sample weight = 8.40 mg.

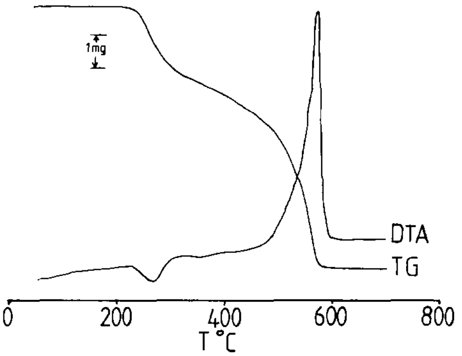


Fig. 5. TG and DTA curves for $Cu(C_6H_4N_4O)Cl_2$. Sample weight = 11.36 mg.

anhydrous complexes follows immediately after the dehydration process, and the residual weights are in good agreement with the values required for the metal oxide; see Table 5. In the DTA traces these decomposition processes correspond to exothermic reactions for the complexes. The manganese and copper complexes, which are anhydrous, undergo ex-

TABLE 4

Dehydration processes of the 4-hydroxypteridine metal complexes

Process	Peak temperature (°C)	Enthalpy change [a]	Weight loss (%)		Enthalpy (kJ mol^{-1})
			Calc.	Found	
$Co(C_6H_4N_4O)Cl_2 \cdot 1.5H_2O \rightarrow Co(C_6H_4N_4O)Cl_2$	105	Endo	8.85	8.38	50
$Ni(C_6H_4N_4O)Cl_2 \cdot 2.5\,H_2O \rightarrow Ni(C_6H_4N_4O)Cl_2$	108	Endo	13.93	14.28	119

[a] Endo, endothermic.

TABLE 5

Decomposition processes of 4-hydroxypteridine and the metal complexes

Process	Temperature range (°C)	Enthalpy change [a]	Residue (%)	
			Calc.	Found
$C_6H_4N_4O$ → pyrolytic process	298–623	Exo	–	–
$Mn(C_6H_4N_4O)_2Cl_2 \rightarrow Mn_2O_3$	402–690	Exo	18.69	18.67
$Co(C_6H_4N_4O)Cl_2 \rightarrow Co_3O_4$	134–551	Exo	26.30	26.60
$Ni(C_6H_4N_4O)Cl_2 \rightarrow NiO$	152–562	Exo	23.14	23.09
$Cu(C_6H_4N_4O)Cl_2 \rightarrow CuO$	220–594	Endo/Exo	28.13	27.46

[a] Endo, endothermic; Exo, exothermic.

othermic and endothermic/exothermic reactions respectively with loss of the organic ligand to give the corresponding metal oxide.

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