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THERMAL, SPECTRAL AND MAGNETIC STUDIES OF SOME FIRST ROW TRANSITION METAL COMPLEXES OF 1,4-BIS(4-AMINOCYCLOHEXYL) BUTADIYNE

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ABSTRACT

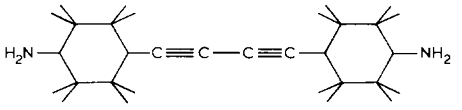
Some new compounds of 1,4-bis(4-aminocyclohexyl) butadiyne with cobalt(II), nickel(II) and copper(II) have been prepared in ethanolic solution The compounds which have been characterised by analyses, magnetic moments, vibrational and electronic spectra, have polymeric octahedral structures The thermal behaviour of these compounds has been studied by thermogravimetry (TG) and differential scanning calorimetry (DSC) techniques Thermal decomposition studies show that the hydrated compounds lose water followed by organic ligand to give the metal oxide, while the anhydrous compounds lose organic ligand to give the metal oxide (The crystal structure of 1,4-bis(4-aminocyclohexyl) butadiyne is also discussed)

INTRODUCTION

Diacetylenes were first reported in the literature in the late 19th century [1,2], but the current intense interest in these compounds and the organic polymers formed from them began with the work of Wegner [3,4]

The phenomena of complete crystallinity and the presence of a conjugated main chain in the polymer system have stimulated the preparation of a large number of polydiacetylenes [5–9]

In this paper we report the thermal analysis studies of 1,4-bis(4-aminocyclohexyl) butadiyne together with the complexes formed between the ligand and the transition metals, cobalt, nickel and copper



1,4 – bis (4-aminocyclohexyl) butadiyne (L)

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Spectral and magnetic studies have been used to characterise each metal complex and to establish the type of coordination involved

EXPERIMENTAL

Preparation of ligand

Copper(I) chloride (0.13 mol), ammonium chloride (0 14 mol) and 20 cm^3 of water were added to a solution of 4-ethynylcyclohexylamine (0 10 mol) in 50 cm^3 of 2 M hydrochloric acid The resulting mixture was shaken under oxygen for 24 h Cold concentrated ammonium hydroxide was added and the resulting slurry was extracted with ether (6 × 100 cm^3) The combined ether extracts were dried (anhydrous potassium carbonate) and evaporated to give a yellow–brown solid, which on recrystallisation from ethanol–water yielded metallic white crystals

Preparation of metal complexes

The ligand (0 01 mol) was dissolved in warm ethanol and the metal halide or thiocyanate (0 1 mol), in the minimum of warm ethanol, was added to this solution The mixture was stirred on a water bath until the metal complex precipitated The precipitate was filtered, washed with warm ethanol and dried

Apparatus

The concentration of the metal ion was obtained by a Perkin–Elmer 373 atomic absorption spectrophotometer and the carbon, hydrogen and nitrogen analyses were obtained 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}) on a Perkin–Elmer infrared spectrophotometer Model 598

The electronic spectra were obtained on a Beckmann Acta MIV spectrophotometer as solid diffuse reflectane spectra

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

The thermal analyses were carried out on a Stanton Redcroft Model STA 781 thermobalance and a Mettler differential scanning calorimeter (DSC TA 3000) Thermogravimetry curves were obtained at a heating rate of 10 °C min^{-1} in static air In all cases the 20–700 °C range was studied DSC curves were obtained at a heating rate of 10 °C min^{-1} in a stable atmosphere of air in the 30–400 °C range.

RESULTS AND DISCUSSION

The purity of the 1,4-bis(4-aminocyclohexyl) butadiyne was established by melting point, by carbon, hydrogen and nitrogen analyses, and by infrared spectroscopy

The metal complexes prepared are listed in Table 1 The thiocyanate complex of cobalt and the chloride complex of nickel are hydrated, while the chloride complexes of cobalt and copper are anhydrous

The electronic spectra (Table 2) for the chloro complexes of cobalt, nickel and copper suggest that the metal ion is in an octahedral environment [10]. It is normal to observe three spin-allowed d–d transitions for the cobalt and nickel complexes, but only two transitions are observed in the present investigation This is due to the presence of a large charge transfer band which extends into the visible region and masks the third transition. The magnetic moments for the cobalt and nickel complexes (Table 1) support the case for an octahedral environment for the cobalt and nickel ions [10,11] The magnetic moment for the copper complex (Table 1) is lower than the spin-only value and would suggest some copper–copper interaction in this

TABLE 1

Analyses of compounds and magnetic moments

Compound	Colour	Calc (%)				Found (%)				Magnetic moment (BM)
		M	C	H	N	M	C	H	N	
$Co(CNS)_2L$ $2H_2O$	Dark blue	13 06	47 90	5 32	12 42	12 94	47 87	5 11	12 27	4 36
$CoCl_2L$	Blue	16 05	52 33	5 45	7 63	15 96	52 38	5 23	7 59	5 01
$NiCl_2LH_2O$	Yellow	15 14	49 52	5 67	7 22	15 17	49 49	5 61	7 21	3 46
$CuCl_2L$	Green	16 97	51 27	5 34	7 48	17 01	51 23	5 36	7 46	1 61

L = 1,4-bis(4-aminocyclohexyl)butadiyne

TABLE 2

Electronic spectra (cm^{-1})

Compound	Peak positions	d–d Transitions
$Co(CNS)_2L$ $2H_2O$	8264	${}^4A_2(F) \rightarrow {}^4T_1(F)$
	16393	${}^4A_2(F) \rightarrow {}^4T_1(P)$
$CoCl_2L$	8333	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$
	16129	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$
$NiCl_2L$ H_2O	7142	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$
	15038	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$
$CuCl_2L$	11364	${}^2E_g(D) \rightarrow {}^2T_{2g}(D)$

L = 1,4-bis(4-aminocyclohexyl)butadiyne

TABLE 3

Infrared Spectra (cm^{-1})

Compound	$\nu_{O-H}(H_2O)$	$\nu_{AS}(NH_2)$	$\nu_S(NH_2)$	$\nu_{C\equiv C}$	ν_{CNS}	$\nu_b(NH_2)$	ν_{M-Cl}
L	–	3266 (m)	3319 (m)	2118 (vw)	–	1583 (m)	–
$Co(CNS)_2L$ $2H_2O$	3400–3100 (br,s)	–	–	–	2100 (s)	1620 (m)	–
$Co(CNS)_2L$	–	3100 (m)	3200 (m)	–	2100 (s)	1620 (m)	–
$CoCl_2L$	–	3138 (m)	3217 (m)	–	–	1589 (m)	235 (w)
$NiCl_2L$ H_2O	3400–3100 (br,s)	–	–	–	–	1605 (m)	232(w)
$NiCl_2L$	–	3120 (w)	3210 (w)	–	–	1605 (m)	232 (w)
$CuCl_2$	–	3120 (m)	3210 (m)	–	–	1585 (m)	234 (w)

Key br = broad, s = strong, m = medium, w = weak, vw = very weak L = 1,4-bis(4-aminocyclohexyl)butadiyne

compound [12] The electronic spectrum and the magnetic moment for the thiocyanate complex of cobalt is indicative of a tetrahedral environment in this case [11]

The main bands in the infrared spectra of the compounds are reported in Table 3 The hydrated compounds show a strong broad absorption band in the region 3400–3100 cm^{-1} (ν_{O-H}) indicating the presence of water of crystallisation

A very weak band at 2118 cm^{-1} in the spectrum of 1,4-bis(4-aminocyclohexyl) butadiyne, which has been assigned to the $\nu_{C\equiv C}$ vibration, is not observed in the spectra of the metal complexes The bands due to $\nu_{AS}(NH_2)$ and $\nu_S(NH_2)$ vibrations in the ligand spectrum show a shift to lower frequency in the spectra of the metal complexes This would suggest that coordination takes place between the nitrogen atoms of the amine group and the metal ions [10,13] The assignment of the band at 2100 cm^{-1} to the ν_{CNS} vibration indicates the existence of a terminal –CNS in the cobalt complex [14] Metal–chlorine bands are present for the chloro compounds and indicate the existence of bridging chlorine atoms [10,15] The insolubility of the chloro compounds in both polar and non-polar solvents is indicative of polymeric structures [10]

The fact that the compounds were isolated as powders and not as single crystals prevents complete structure determination However, spectroscopic and magnetic data enable us to predict that in the chloro compounds the metal ions are in an octahedral environment It is thus postulated that the structure of the compounds consists of a chain of metal atoms bonded to chlorine atoms with each chain being linked to adjacent chains by the 1,4-bis(4-aminocyclohexyl) butadiyne molecules The thiocyanate compound has a tetrahedral structure, each nitrogen atom in the 1,4-bis(4-aminocyclohexyl) butadiyne molecule forming a coordinate bond with the cobalt atoms

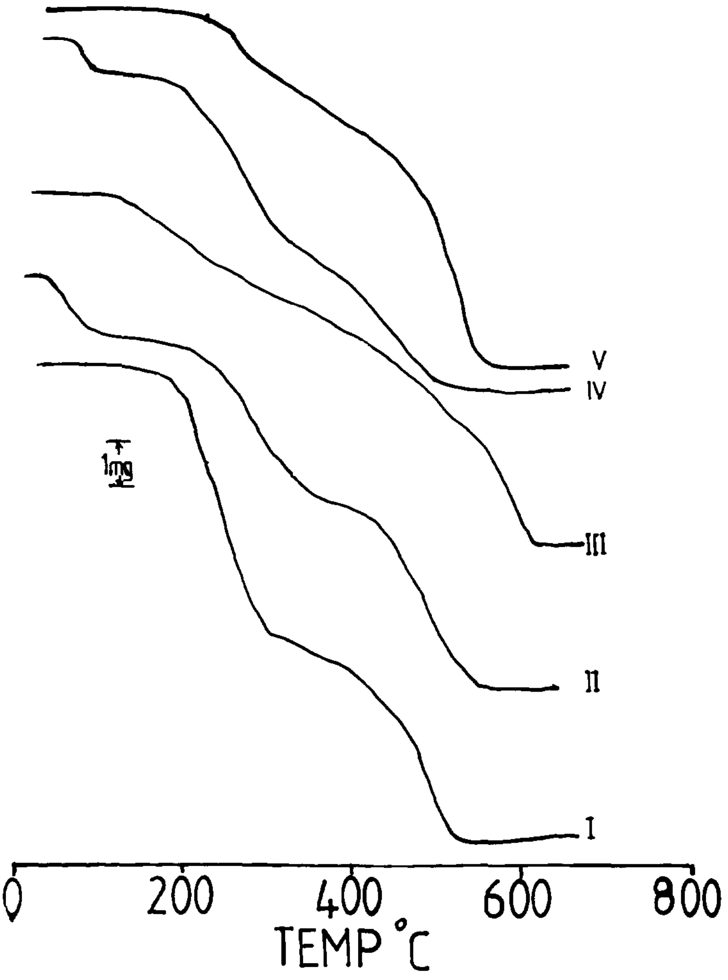

Fig 1 TG curves of I, 1,4-bis(4-aminocyclohexyl) butadiyne (sample weight = 10 18 mg), II, Co(CNS)$_2$(C$_{16}$H$_{24}$N$_2$) 2H$_2$O (sample weight = 10 60 mg), III, CuCl$_2$(C$_{16}$H$_{24}$N$_2$) (sample weight = 9 78 mg), IV, NiCl$_2$(C$_{16}$H$_{24}$N$_2$) H$_2$O (sample weight = 9 24 mg), V, CoCl$_2$(C$_{16}$H$_{24}$N$_2$) (sample weight = 9 90 mg)

The TG and DSC curves (Figs 1 and 2) for 1,4-bis(4-aminocyclohexyl) butadiyne show that the amine is thermally stable over the range 20–132 ° C Its pyrolytic decomposition starts at 132 ° C and finishes at 530 ° C with total elimination of the sample The DSC curve of the 1,4-bis(4-aminocyclohexyl) butadiyne (Fig 2) shows an endothermic peak at 117 ° C corresponding to fusion The value of the fusion enthalpy is 36 28 kJ mol^{-1} Liquid 1,4-bis(4-aminocyclohexyl) butadiyne decomposes with an exothermic peak at 260 ° C The TG and DSC curves for the complexes formed by reaction of 1,4-bis(4-aminocyclohexyl) butadiyne with the chlorides of cobalt, nickel, copper and

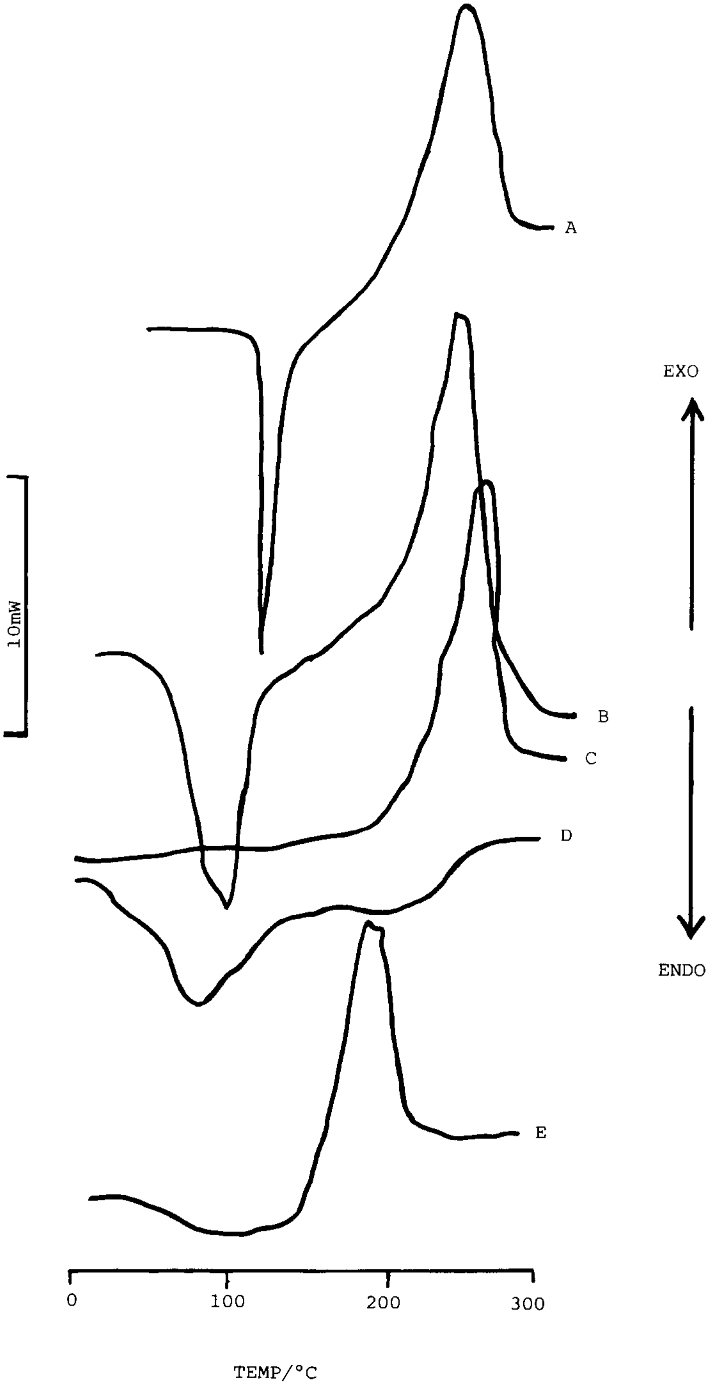

Fig 2 DSC curves of A, 1,4-bis(4-aminocyclohexyl) butadiyne, B, $Co(CNS)_2(C_{16}H_{24}N_2)$ $2H_2O$, C, $CoCl_2(C_{16}H_{24}N_2)$, D, $NiCl_2(C_{16}H_{24}N_2)$ H_2O, E, $CuCl_2(C_{16}H_{24}N_2)$

TABLE 4

Dehydration process for the thiocyanate complex of cobalt and the chloride complex of nickel

Process	Peak temp (° C)	Thermal nature of transformation	Weight loss (%)		Enthalpy (kJ mol^{-1})
			Calc	Found	
$Co(CNS)_2L\ 2H_2O \rightarrow Co(CNS)_2L$	90 3	Endo	7 98	9 43	107 92
$NiCl_2L\ H_2O \rightarrow NiCl_2L$	76 1	Endo	4 64	4 33	27 83

L = 1,4-bis(4-aminocyclohexyl)butadiyne

TABLE 5

Decomposition process of the 1,4-bis(4-aminocyclohexyl) butadiyne and the metal complexes

Process	Temp range (° C)	Thermal nature of transformation	Residue (%)	
			Calc	Found
$C_{16}H_{24}N_2 \rightarrow$ pyrolytic proc	210–530	Exo		
$Co(CNS)_2L \rightarrow Co_3O_4$	120–557	Exo	17 77	16 03
$CoCl_2L \rightarrow Co_3O_4$	137–542	Exo	21 62	20 20
$NiCl_2L \rightarrow NiO$	101–560	Exo	19 26	19 48
$CuCl_2L \rightarrow CuO$	70–612	Exo	21 22	20 40

L = 1,4-bis(4-aminocyclohexyl)butadiyne

the thiocyanate of cobalt are shown in Figs 1 and 2 The thiocyanate complex of cobalt and the chloride complex of nickel first lose water followed by the organic ligand to give the oxide The dehydration of the complexes takes place in one step The observed weight losses for these processes compare favourably with the theoretical values (Table 4) The expected endothermic peak for this type of process is observed in the DSC curve The dehydration enthalpies have been calculated and are listed in Table 4 The decomposition of the anhydrous complexes give residual weights which are in good agreement with the theoretical values for the metal oxides (Table 5). In the DSC curves, these decomposition processes correspond to exothermic peak for the compounds

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