THERMAL DECOMPOSITION OF 4,6-DIAMINO-1,2-DIHYDRO-2-THIOPYRIMIDINE AND ITS COMPLEXES WITH Co^{II}, Co^{III}, Ni^{II} AND Cu^{II} IONS

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ABSTRACT

The thermal behaviour of 4,6-diamino-1,2-dihydro-2-thiopyrimidine (HDATP) and its complexes with Co^{II}, Co^{III}, Ni^{II} and Cu^{II} ions has been studied by thermogravimetric and differential scanning calorimetric techniques. IR spectroscopy applied to the complexes previously heated in air atmosphere allowed elucidation of the decomposition steps and the nature of the intermediate products. The enthalpies of the corresponding decomposition processes were calculated.

INTRODUCTION

Pyrimidine derivatives are widely distributed in living organisms, which has stimulated research into the coordination modes of pyrimidine to metal ions in order to establish the role of metal ions in biological systems [1–4]. Moreover, numerous sulphur-substituted pyrimidines have found applications as clinically useful drugs; for instance, pyrimidine-2-thione and its derivatives have been demonstrated to possess antitumour and antithyroid activity [5,6]. To complement a previously published series of papers devoted to the synthesis and characterisation of metal complexes from pyrimidine-2-thione and 2-thiopurine derivatives [7–20], we describe here the thermal behaviour of a series of 4,6-diamino-1,2-dihydro-2-thiopyrimidine (HDATP) complexes with Co^{II}, Co^{III}, Ni^{II} and Cu^{II} ions.

EXPERIMENTAL

The pyrimidine derivative (HDATP) was prepared by a previously reported method [21]. All the chemicals used in this work were analytical reagent grade.

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TABLE 1

Analytical data of HDATP and its isolated complexes

Compound	Colour	Found (calculated) (%)				
		C	H	N	S	M
HDATP·$\frac{1}{2}$H$_2$O	White	31.8 (31.8)	4.4 (4.6)	37.1 (37.1)	–	–
[Co(DATP)$_3$]·H$_2$O	Brown	28.7 (28.8)	3.4 (3.4)	33.0 (33.6)	–	11.9 (11.8)
[Co(HDATP)$_2$(H$_2$O)$_2$]-(NO$_3$)$_2$	Pink	19.0 (19.1)	3.2 (3.2)	27.6 (27.8)	–	12.8 (11.7)
[Co(HDATP)(H$_2$O)$_2$]-(NO$_3$)$_2$	Violet	13.8 (13.3)	3.1 (2.8)	22.8 (23.3)	–	15.8 (16.3)
[Ni(DATP)$_2$]	Yellow	28.1 (28.2)	2.6 (2.9)	32.4 (32.9)	18.5 (18.8)	18.0 (17.2)
[Ni(HDATP)$_2$(NO$_3$)$_2$]	Yellow	20.6 (20.6)	2.5 (2.6)	29.4 (30.0)	12.6 (13.7)	12.5 (12.6)
[Cu(DATP)$_2$]	Light brown	28.1 (27.8)	2.9 (2.9)	32.5 (32.4)	–	– (18.4)

Thermal studies were carried out on a Mettler TG 50 thermobalance and a Mettler DSC 20 differential scanning calorimeter. Thermogravimetric curves were registered in dynamic conditions using a flow rate of 100 ml min^{-1} of pure air, with sample masses between 4.002 mg and 10.321 mg and a heating rate of 10 or 20°C min^{-1}. DSC curves were obtained in a static air atmosphere, using sample masses between 1.058 mg and 4.530 mg and a heating rate of 10°C min^{-1}. The temperature ranges investigated were 35–850°C (TG) and 25–600°C (DSC).

The IR spectra of the residues from pyrolytic processes were recorded in KBr medium (4000–250 cm^{-1}) and polyethylene medium (600–180 cm^{-1}) using a Perkin–Elmer 983G spectrophotometer.

The preparative methods for the isolated complexes Co(DATP)$_3$·H$_2$O, Co(HDATP)$_x$(NO3)$_2$·2H$_2$O (x = 1,2), M(DATP)$_2$(M $\equiv$ Ni^{II}, Cu^{II}) and Ni(HDATP)$_2$·(NO$_3$)$_2$ were described in a previous paper [20]. Their chemical analyses are detailed in Table 1.

RESULTS AND DISCUSSION

Elemental analyses, magnetic susceptibilities and spectral studies of the aforementioned complexes [20] suggest that the coordination of HDATP to the metal ions occurs in both anionic (with a negative charge on a cyclic nitrogen atom) and molecular forms through the sulphur atom substituted on C2 and a cyclic nitrogen atom. The resulting structures are [Co(DATP)$_3$] H$_2$O, [Co(HDATP)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ and [Ni(HDATP)$_2$(NO$_3$)$_2$] (octahedral) and [Ni(DATP)$_2$] and [Co(DATP)(H$_2$O)$_2$](NO$_3$)$_2$ (tetrahedral).

The probable modes of decomposition of the pyrimidine derivative and its isolated complexes were deduced from their TG and DSC curves (Figs. 1 and 2), which gave the TG and DSC data summarised in Table 2.

The thermogravimetric curve of HDATP $\cdot \frac{1}{2}$H$_2$O shows a first weight loss in the 120–180°C temperature range, where 6.1% of the initial weight is eliminated. This value is in agreement with the theoretical value calculated
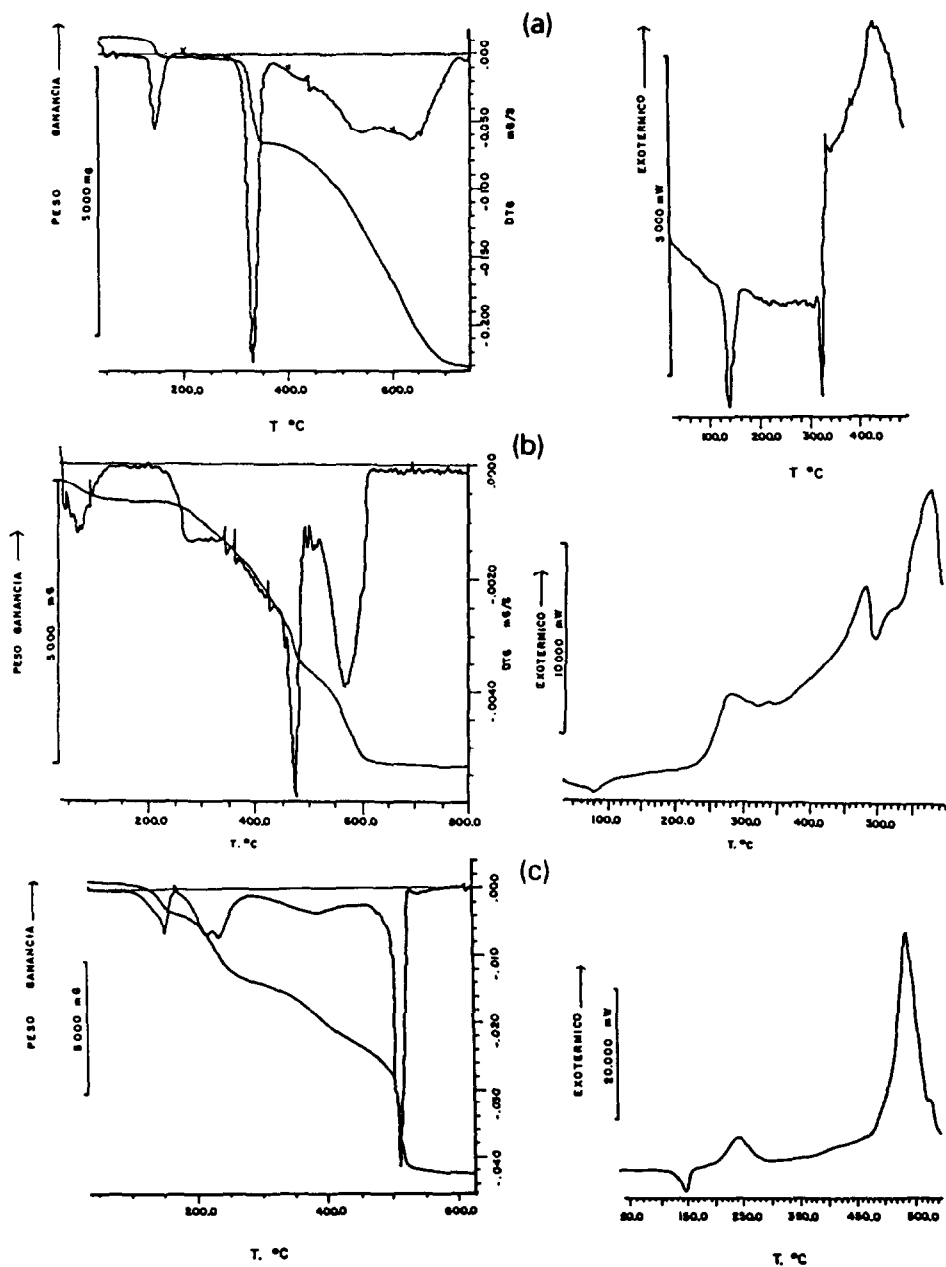

Fig. 1. TG and DSC curves of: A, HDATP$\cdot\frac{1}{2}$H$_2$O; B, [Co(DATP)$_3$]$\cdot$H$_2$O; C, [Co(HDATP)$_2$(H$_2$O)](NO$_3$)$_2$ and D, Co(HDATP)(NO$_3$)$_2$.
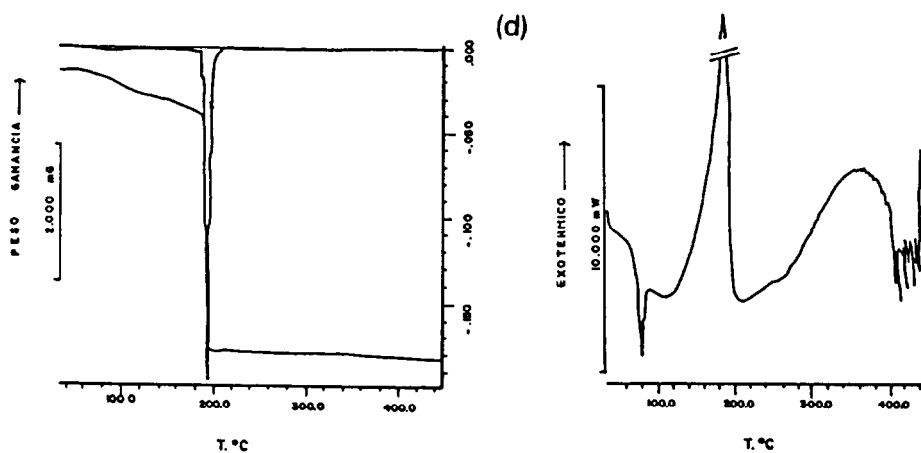
Fig. 1 (continued).

for the total dehydration of the pyrimidine derivative (5.96%). The dehydration process was confirmed by the disappearance of the $\nu(OH)$ band in the IR spectrum of a ligand sample after heating at $200°C$. The expected endothermic effect was observed in the DSC curve at $138°C$. From this effect, the dehydration enthalpy, 25 kJ mol^{-1}, was calculated.

At $324°C$, the DSC plot shows a sharp endotherm, which is assigned to the fusion of the anhydrous HDATP. The enthalpy value (8 kJ mol^{-1}), was lower than that expected for the fusion; this is probably due to the overlap of the said effect with the exothermic effect which accompanies the start of the pyrolysis of the compound.

The compound [Co(DATP)$_3$] · H$_2$O contains water as revealed in the TG curve by a weight loss effect in the 45–110°C range (Fig. 1B). The experimental percentage weight loss (6.1%) is in good agreement with that calculated for a water molecule (5.96%) and the value of 37 kJ mol^{-1} for the dehydration enthalpy is sufficiently low for it to be considered as crystallisation water. Once dehydrated, the complex decomposes pyrolytically in the 325–610°C range, showing three exothermic effects in the DSC curve (Fig. 1B). The pyrolysis process gave Co$_3$O$_4$ as residue (the nature of this was proved by recording its IR spectrum).

The cobalt(II) complexes show a different thermal behaviour (Figs. 1C and 1D). It can be observed that the dehydration process for [Co(DATP)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ takes place in only one step (endothermic effect at 146°C), which suggests that the water molecules are equivalent. The high value for dehydration enthalpy points out that the two water molecules are directly linked to the Co^{II} ion, in accordance with the results obtained from the IR spectra of this complex [20]. After dehydration, the elimination of the free nitrate groups takes place between 180 and 270°C. This process is accompanied by an exothermic effect centred at 242°C; the corresponding
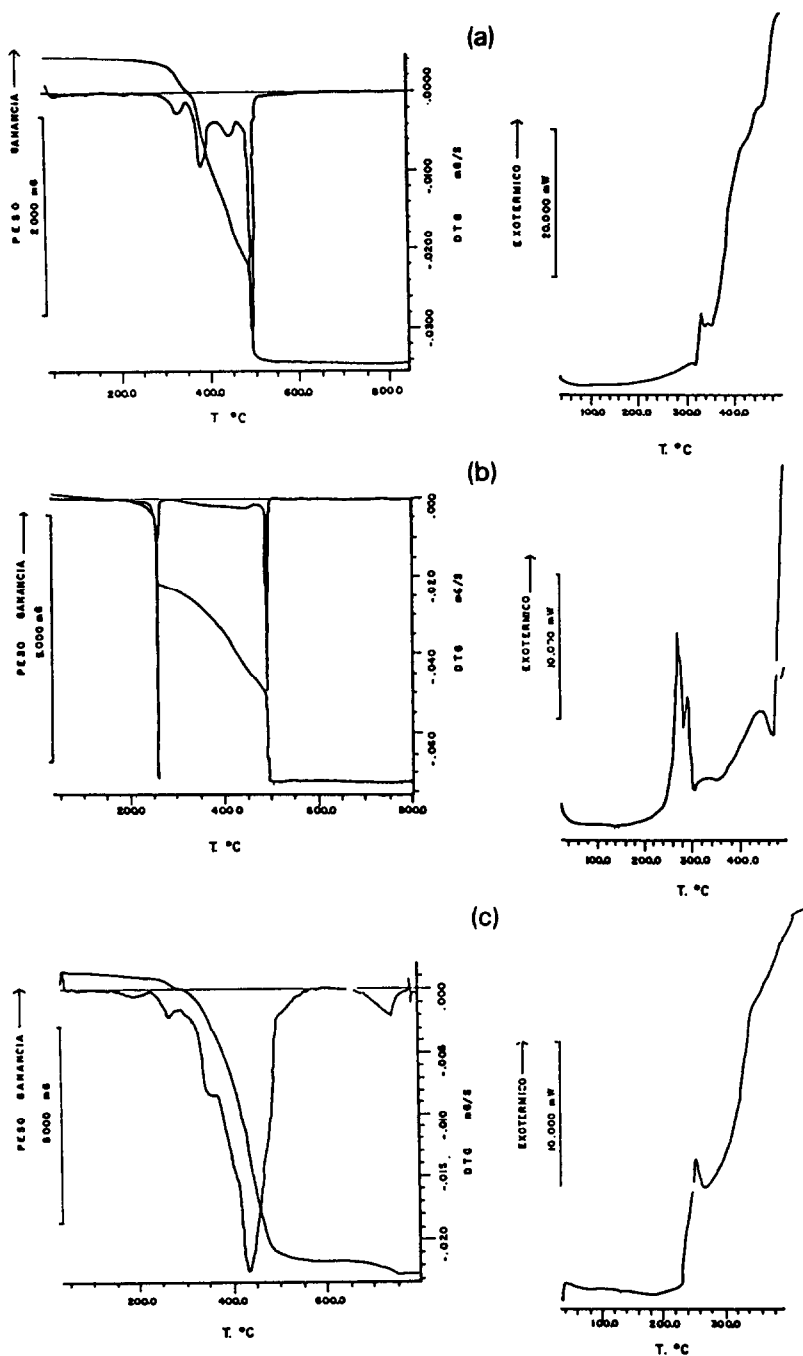
Fig. 2. TG and DSC curves of: A, Ni(DATP)$_2$; B, Ni(HDATP)$_2$(NO$_3$)$_2$; and C, [Cu(DATP)$_2$].

enthalpy value is 336 kJ mol^{-1}. To demonstrate dehydration and loss of nitrate groups, spectra of samples of the complex heated to 185°C and 270°C respectively were recorded. The first spectrum shows the loss of

TABLE 2

Thermoanalytical data for the compound HDATP·$\frac{1}{2}$H$_2$O and its metal complexes.

Compound	Process	Temperature (°C)	ΔH (kJ mol^{-1})	Accumulated weight loss (%)		Residue
				Found	Calculated	
HDATP·$\frac{1}{2}$H$_2$O	$-\frac{1}{2}$H$_2$O	138 (endotherm)	25	6.1	5.96	—
	Fusion	324 (endotherm)	8ᵃ	—	—	—
	Pyrolysis	450 (exotherm)	—	—	—	—
[Co(DATP)$_3$]·H$_2$O	$-$H$_2$O	84 (endotherm)	37	4.3	3.60	Co$_3$O$_4$
	Pyrolysis	275, 480	—	84.4	83.85	—
		574 (exotherm)				
[Co(HDATP)$_2$(H$_2$O)$_2$](NO$_3$)$_2$	$-$2H$_2$O	146 (endotherm)	116	3.1	7.66	Co$_3$O$_4$
	$-$2NO$_3^-$	242 (exotherm)	336	28.9	32.32	—
	Pyrolysis	535 (exotherm)	2491	83.7	84.04	—
[Co(HDATP)(H$_2$O)$_2$](NO$_3$)$_2$	$-$2H$_2$O	81 (endotherm)	—	—	—	Co$_3$O$_4$
	Pyrolysis	195, 370	—	82.0	77.76	—
		(exotherms)				
[Ni(DATP)$_2$]	Pyrolysis	> 300 (exotherm)	—	77.9	78.08	NiO
[Ni(HDATP)$_2$(NO$_3$)$_2$]	$-$2NO$_3^-$	270, 292	—	27.0	26.57	—
		(exotherms)				
	Pyrolysis	443, > 480	—	84.1	83.99	NiO
		(exotherms)				
[Cu(DATP)$_2$]	Pyrolysis	254, > 400	—	77.2	76.98	CuO
		(exotherms)				

ᵃ Overlaps with the exotherm at 450°C.

$\nu(OH)$ and $\nu(M-OH_2)$ bands (which appeared at 3440 cm^{-1} and 555 cm^{-1} in the unheated complex) and the second also that of the $\nu(NO_3)$ band of the free nitrate group (centred in the IR spectrum of $[Co(HDATP)_2(H_2O)_2]$ $(NO_3)_2$ at 1380 cm^{-1}). After elimination of the nitrate groups, the unstable species formed decomposes uninterruptedly up to a temperature of 535°C; this process is accompanied by a strong exothermic effect centred at 520°C. The final product of the pyrolytic decomposition was Co_3O_4 (this was confirmed by IR spectroscopy).

On the other hand, the TG of $[Co(HDATP)(H_2O)_2](NO_3)_2$ (Fig. 1D) shows a progressive and slow weight loss from 60 to 195°C. At this point the total combustion of the sample occurs. The experimental residue was lower than that expected (Table 2) owing to the loss of a part of sample during the pyrolysis. A first step, between 35°C and 120°C, corresponds to the dehydration process (endothermic effect at 81°C). The dehydration weight loss and enthalpy values could not be calculated, since this process overlaps with the pyrolytic decomposition of the anhydrous complex (see Fig. 1D). The TG curve shows that the complex does not undergo any weight loss over 195°C. However, in the CDS curve an exothermic effect appeared at 370°C. This could be due to the fact that the CDS plot was realised with a lower amount of the sample than in the case of the TG plot, and thus the heat evolved at 195°C was not enough for the complete combustion of the sample.

The TG diagram of $[Ni(DATP)_2]$ (Fig. 2A) shows that the complex is stable up to 300°C. This temperature is similar to that of decomposition of the free HDATP, suggesting that the decomposition of the complex starts by the pyrolysis of the ligand molecules. The weight loss continues without interruption up to approximately 500°C, at which temperature the weight of the residue in the crucible was in accordance with the calculated for NiO, this being confirmed by IR spectroscopy (band at 415 cm^{-1}) [22]. The pyrolytic decomposition is reflected in the DSC curve by the presence of several exothermic effects.

IR studies carried out on $[Ni(HDATP)_2(NO_3)_2]$ have shown a direct interaction between the nitrate groups and the Ni^{II} ion [20]. The TG curve of this complex (Fig. 2B) shows a first abrupt weight loss which starts at 200°C. The value found for this is in good agreement with that calculated for the elimination of the nitrate groups. The existence of this process was demonstrated by the fact that the IR bands corresponding to $\nu(ONO)$ and $\nu(Ni-O)$ (at 1382 cm^{-1} and 250 cm^{-1} respectively in the IR spectrum of the ligand [20]) disappear when a sample of the solid complex was heated up to 300°C (the end of the exothermic effect in the DSC curve). When the nitrate groups are eliminated, the TG curve shows that the intermediate is unstable and continues its decomposition up to 500°C to give NiO as the final residue.

The TG curve of $[Cu(DATP)_2]$ (Fig. 2C) shows that the complex is stable

up to appoximately 250°C at which a weight loss starts which continues uninterruptedly up to 550°C. The IR spectrum of a sample of the complex heated at this temperature shows the presence of a mixture of $CuSO_4$ and CuO in the crucible [23]. A second weight loss occurs in the 650–750°C temperature range, which can be attributed to the thermal transformation of $CuSO_4$ into CuO (experimental accumulated weight loss, 77.2%; theoretical, 76.9%).

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