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THERMAL DECOMPOSITION OF SULPHONAMIDE DERIVATIVE COMPLEXES. II. THERMAL BEHAVIOUR OF COMPLEXES OF ACETAZOLAMIDE * WITH Ni(II), Co(II), Zn(II), Cd(II), Hg(II) and Ag(I)

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ABSTRACT

The thermal behaviour of complexes of acetazolamide (Acm) with Ni(II), Co(II), Zn(II), Cd(II) Hg(II) and Ag(I) has been studied using TG and DTA techniques in flowing air and nitrogen atmospheres, and IR spectroscopy. The complexes decompose in two steps: (A) deammination or dehydration, and (B) pyrolytic decomposition. In the second step, different behaviours are observed. Degradation of the ligand of the $Ni(Acm)_2(NH_3)_4$, $Zn(Acm)_2(NH_3)_2$, $Co(Acm)_2(NH_3)_2$ and $Cd(Acm)\cdot 1.5\ H_2O$ complexes leads to the metal oxide (in air) or sulphide (in nitrogen). During the formation of these compounds in air, the DTA curves show important exothermic peaks attributable to oxidation processes such as the formation of sulphates. In this sense, $CoSO_4$ and $CdSO_4$ can be isolated at intermediate stages of the degradation. The sulphates presumably originate not from the Acm sulphonamido moiety but from oxidation of a thiadiazole (tdz) derivative. This behaviour is similar to that which has been previously observed for Cu(II)–Acm complexes. Thermal degradation of $K_2Ni_2(Acm)_3\cdot 5H_2O$ gives a mixture of potassium sulphate and nickel(II) oxide (in air) or nickel(II) sulphide (in nitrogen). In the case of the Ag(I) and Hg(II) complexes, the formation of sulphides in both air and nitrogen atmospheres is tentatively proposed as an intermediate stage of the pyrolysis. Finally, the HgS sublimates and the Ag_2S decomposes to give Ag.

INTRODUCTION

Interest in the coordination behaviour of acetazolamide (Acm) arises from its ability to inhibit the carbonic anhydrase, a Zn(II) metalloenzyme. This inhibition occurs through interaction of Acm with the metal ion at the active site.

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* Acetazolamide is 5-acetamido-1,3,4-thiadiazole-2-sulphonamide.

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In previous papers [1–4] we have reported on the synthesis and characterization of several complexes of Acm with metal ions, and on the thermal decomposition of the copper(II) complexes [5]. The TG and DTA curves obtained indicated that thermal degradation occurs in different ways in air and in nitrogen atmospheres. As a continuation of this work, the present paper reports the results of thermal decomposition studies of complexes of Acm with Zn(II), Co(II), Ni(II), Cd(II), Hg(II) and Ag(I).

EXPERIMENTAL

Apparatus

TG analyses were performed in air and nitrogen atmospheres using Perkin–Elmer 3600 and DTA 1700 instruments, at heating rates of 5, 10 and 20 °C min^{-1}. DSC curves were obtained under the same experimental conditions. Peak integration and subsequent enthalpy calculations were performed using the Perkin–Elmer system 7/4 partial-area integration program. The latent heat of fusion of pure indium metal ($\Delta H = 28.4$ J g^{-1}) was used for calibration. Thermolytic reactions were obtained with samples varying in weight from 3.0 to 5.0 mg.

IR spectra were obtained using KBr pellets on a Perkin–Elmer Model 843 spectrophotometer.

Samples

The complexes $\text{Co(Acm)}_2(\text{NH}_3)_2$, $\text{Ni(Acm)}_2(\text{NH}_3)_4$, $\text{Zn(Acm)}_2(\text{NH}_3)_2$, $\text{Cd(Acm)} \cdot 1.5\ \text{H}_2\text{O}$, $\text{Ag}_2(\text{Acm})(\text{NH}_3)$, Ag_2Acm and $\text{Hg(Acm)} \cdot 0.5\ \text{H}_2\text{O}$ were prepared according to methods previously reported [1,2,4].

RESULTS AND DISCUSSION

Thermal decomposition of the acetazolamide complexes takes place in two stages: (A) deammination or dehydration, and (B) pyrolytic decomposition.

(A) Deammination or dehydration

Deammination

Figures 1, 2 and 3 show TG and DTA curves for the $\text{Ni(Acm)}_2(\text{NH}_3)_4$, $\text{Co(Acm)}_2(\text{NH}_3)_2$ and $\text{Zn(Acm)}_2(\text{NH}_3)_2$ compounds, respectively.

It can be seen from the TG curve in Fig. 1 that the Ni(II) compound is stable up to 130 °C. Deammination then occurs, between 130 and 195 °C, in

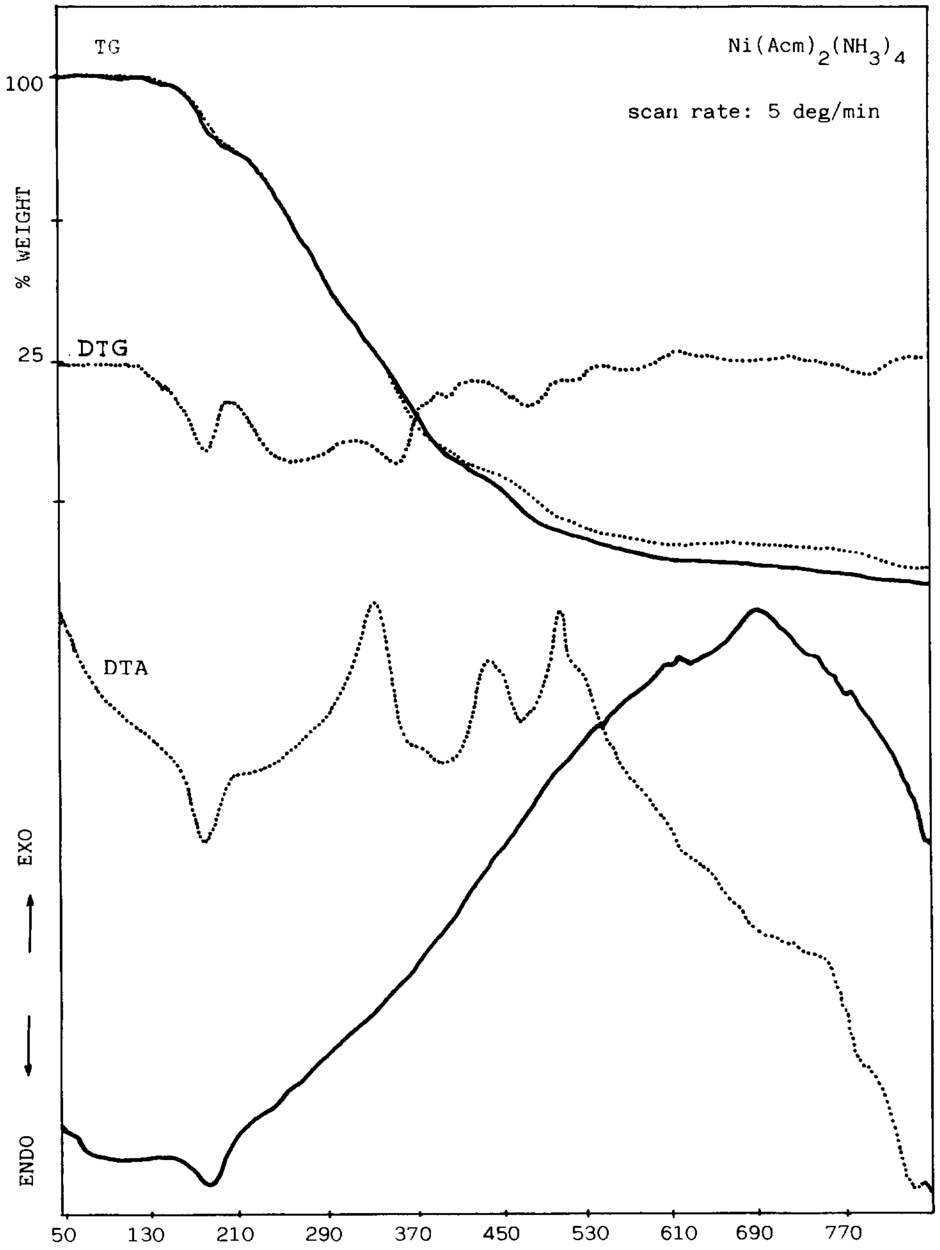

Fig. 1. Ni(Acm)$_2$(NH$_3$)$_4$: TG/DTA curves in nitrogen (———) and in air (······); and DTG curve in air.

a single step perfectly separated in the curve from the ligand degradation. The DTA curve shows the corresponding endothermic peak in the range 150–215 °C (see Table 1). The deammination temperature range is consistent with the fact that the ammonia is coordinated with the metal ion, as corroborated by the crystal structure of the compound [2].

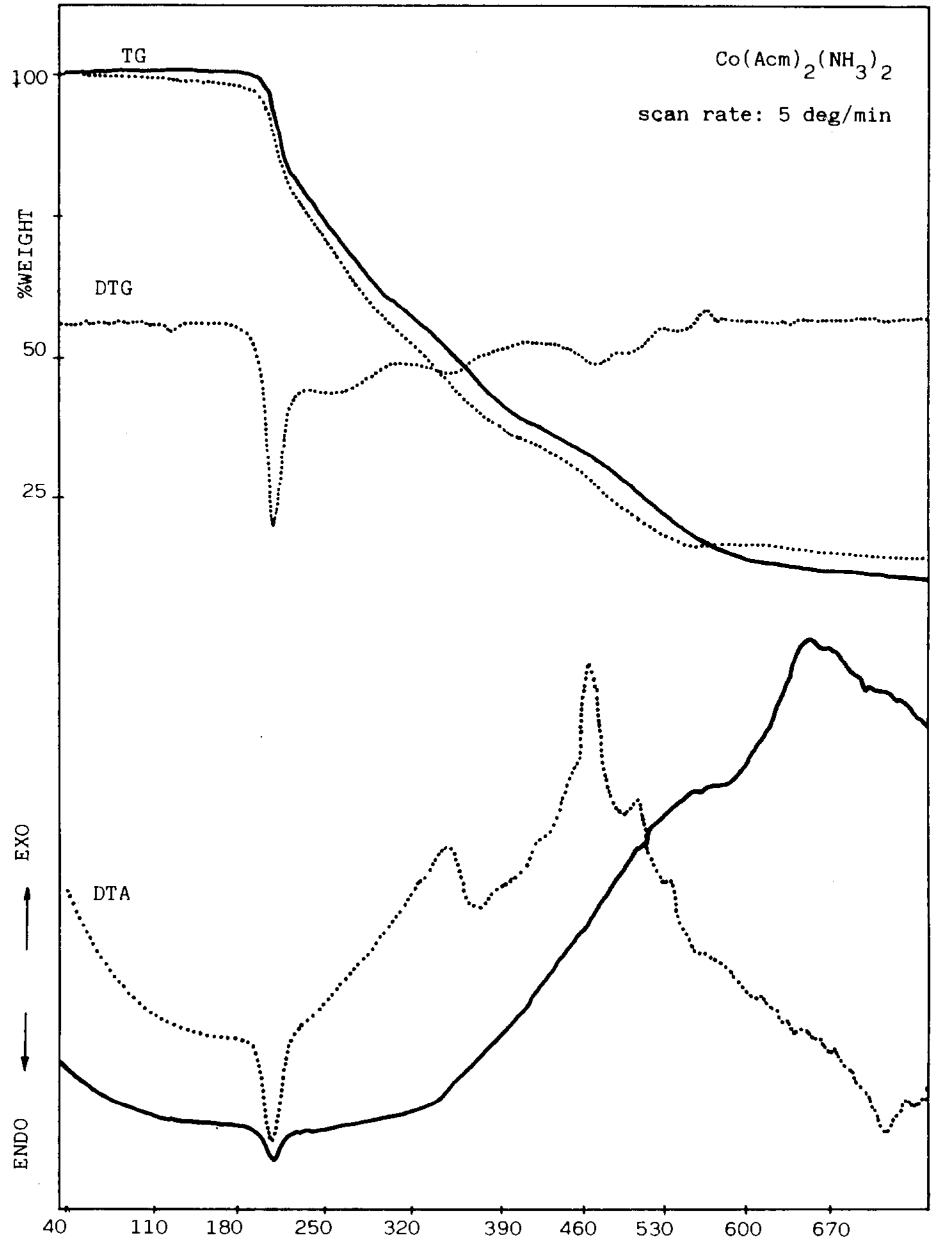

Fig. 2. Co(Acm)$_2$(NH$_3$)$_2$: TG/DTA curves in nitrogen (———) and in air (· · · · · ·); and DTG curve in air.

The Co(II) and Zn(II) compounds are stable up to 180 and 200 °C, respectively, when deammination begins. Thus, the TG curves show that these complexes are stable at higher temperatures than the Ni(II) complex. However, with the Zn(II) and Co(II) complexes deammination overlaps with pyrolytic decomposition, and it is not possible to separate the two processes.

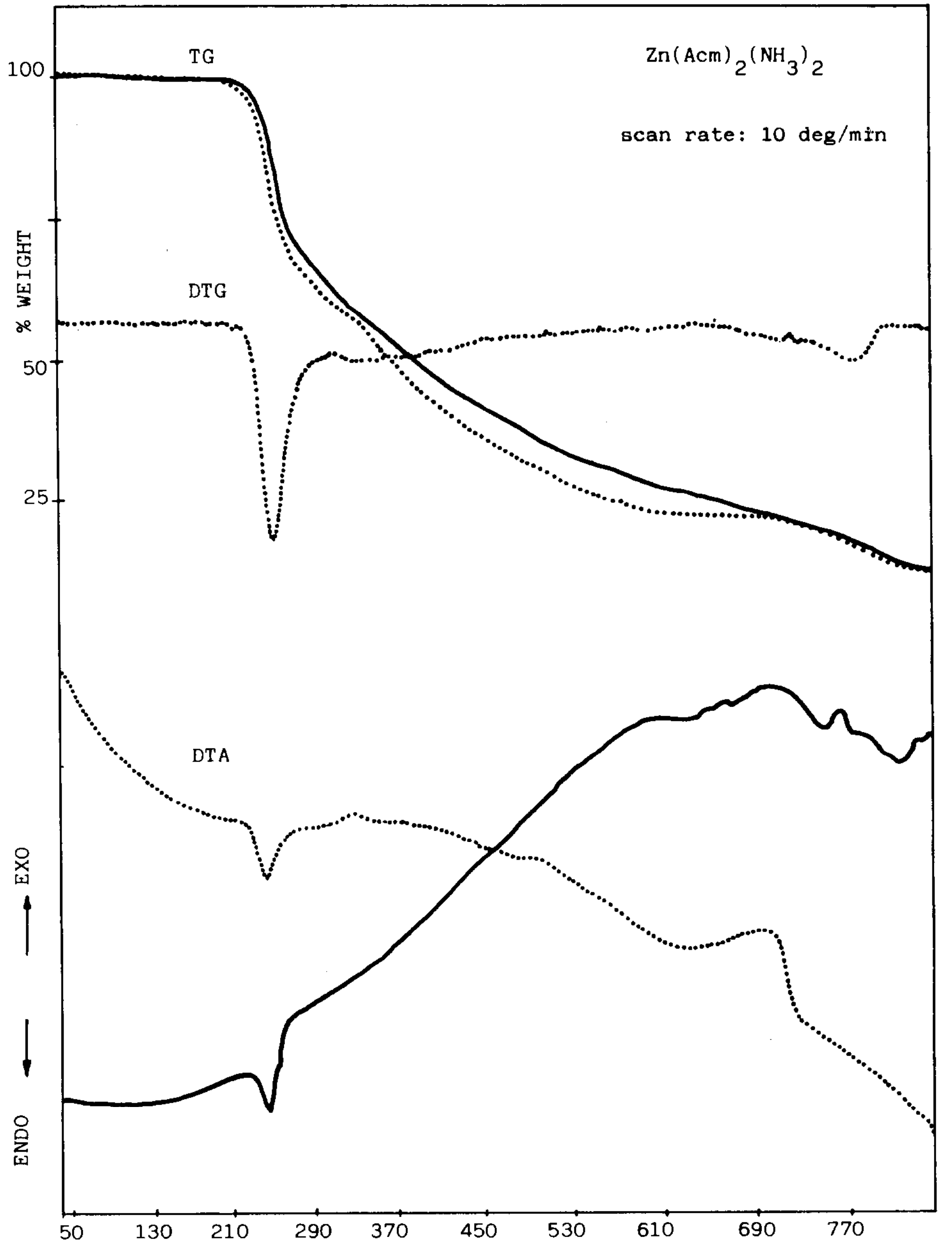

Fig. 3. Zn(Acm)$_2$(NH$_3$)$_2$: TG/DTA curves in nitrogen (———) and in air (······); and DTG curve in air.

The DTA curves exhibit an endothermic peak between 180 and 230 °C for the Co(II) complex, and between 215 and 290 °C for the Zn(II) complex. As was the case for the Ni(II) complex, but here more clearly, the deammination temperatures suggest coordination of the ammonia with the metallic

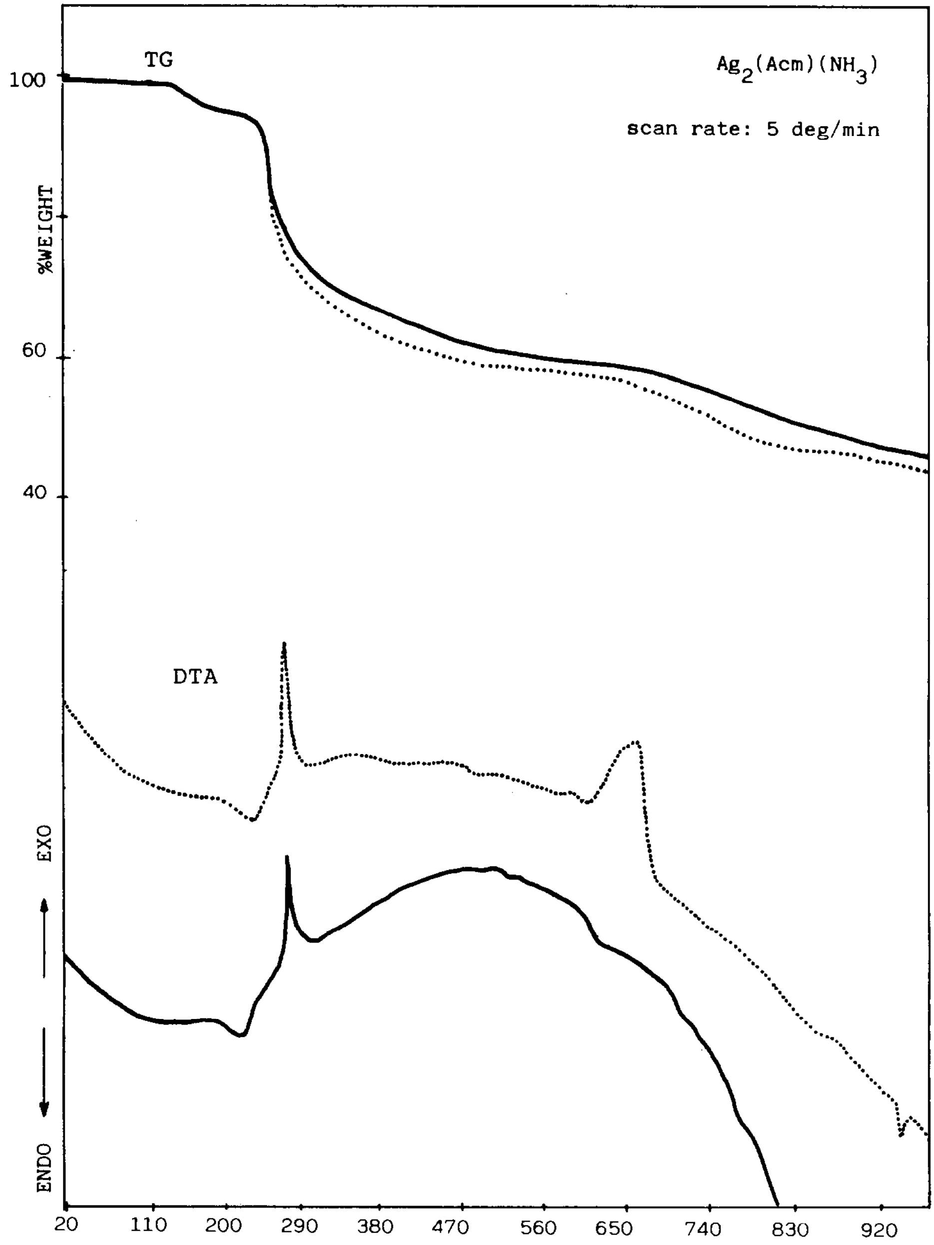

Fig. 4. $Ag_2(Acm)(NH_3)$: TG/DTA curves in nitrogen (———) and in air (· · · · · ·).

ions. Furthermore, the Zn(II) compound seems to bind the ammonia molecules more strongly than does the Co(II) compound.

Figure 4 shows TG and DTA curves for the $Ag_2(Acm)(NH_3)$ compound. Deammination of the $Ag_2(Acm)(NH_3)$ complex occurs between 125 and 190 °C. The corresponding endothermic event in the DTA curve appears in the range 210–280 °C (see Table 1). Although there are no differences

TABLE 1

Deammination and dehydration processes

Compound	Deammination	% weight loss		DTA peak temperature (°C)	ΔH (kJ mol^{-1})
	Starting temperature (°C)	Exp.	Calc.		
$Ni(Acm)_2(NH_3)_4$	130	11.9	11.8	150–215	204.2
$Co(Acm)_2(NH_3)_2$	180	—	–	180–230	167.5
$Zn(Acm)_2(NH_3)_2$	200	—	–	215–290	187.0
$Ag_2(Acm)(NH_3)$	90	3.7	3.8	210–280	54.9
Compound	Dehydration	% weight loss		DTA peak temperature (°C)	ΔH (kJ mol^{-1})
	Temperature range (°C)	Exp.	Calc.		
$K_2Ni_2(Acm)_3 \cdot 5H_2O$	40–230	9.2	9.5	40–230	164.0
$Cd(Acm) \cdot 1.5H_2O$	40–140	7.5	7.8	70–150	11.4
$Hg(Acm) \cdot 0.5H_2O$	30– 90	2.5	2.1	65–140	weak

between the IR spectra of this complex and those of $Ag_2(Acm)$, it can be inferred from the deammination temperature and the ΔH value that the ammonia is not just a crystallization molecule.

Dehydration

TG and DTA curves for the compounds $K_2Ni_2(Acm)_3 \cdot 5H_2O$, $Cd(Acm) \cdot 1.5H_2O$ and $Hg(Acm) \cdot 0.5H_2O$ are shown in Figs. 5–7, respectively.

Dehydration of this complex of Ni(II) occurs between 40 and 230 °C although the most important loss of weight occurs in the range 40–120 °C, which means that several water molecules must be of hydration (see Table 1). The DTA curve shows an undefined endothermic region between 40 and 230 °C.

The compound of Cd(II) loses water molecules in the range 40–140 °C. The DTA curve shows two very weak endothermic peaks centred at 90 and 120 °C, respectively, which indicates the existence of two kinds of water in the complex.

The compound of Hg(II) suffers a weak loss of weight between 30 and 90 °C, attributable to loss of hydration water. The nature of the water molecules could be deduced from the low temperature of the dehydration and the weak endothermic change observed in the DTA curve.

(B) Pyrolytic decomposition

Pyrolytic degradation takes place in two stages: (1) formation of a metal–thiadiazole derivative, and (2) decomposition of the derivative to give the corresponding oxide or sulphide as final product.

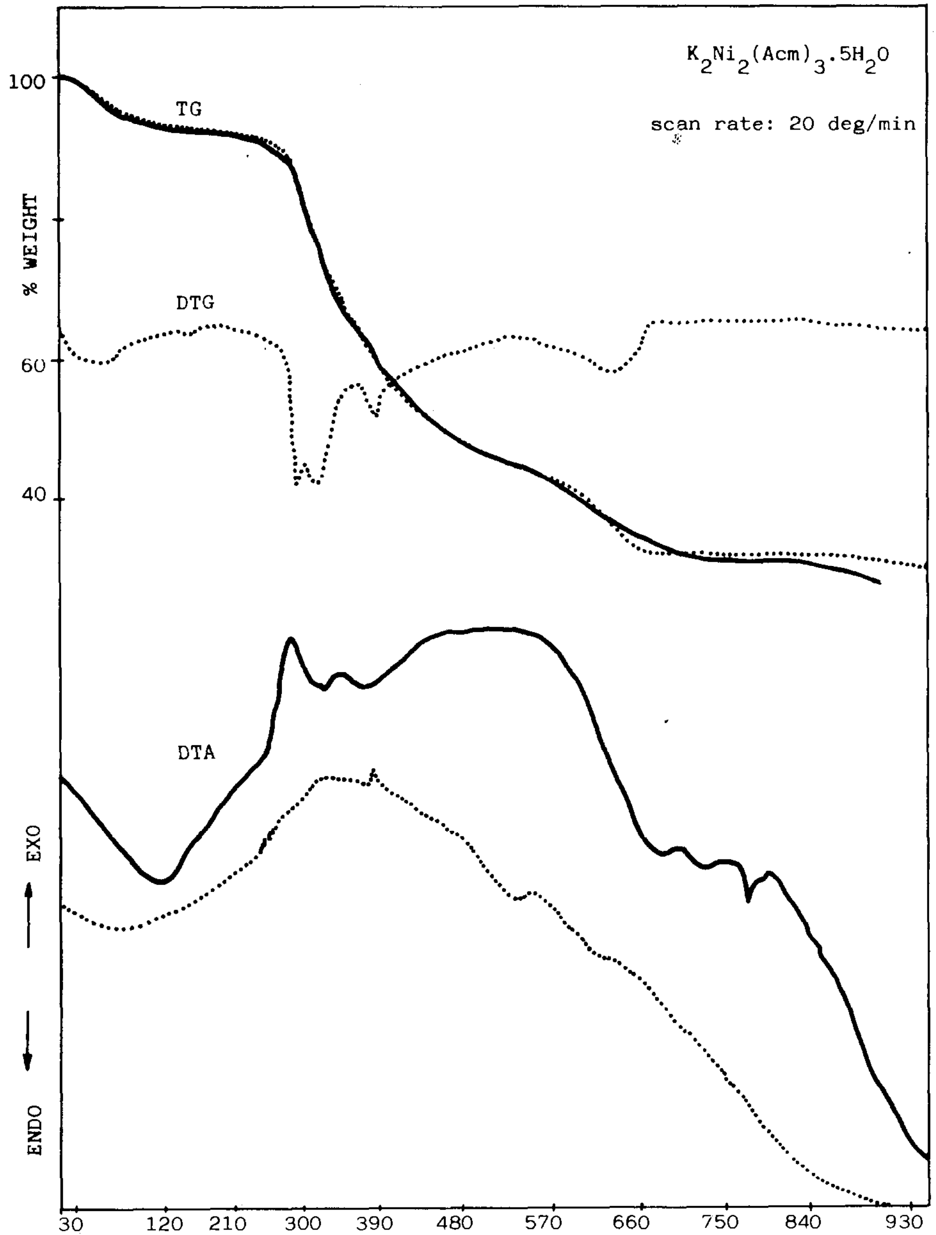

Fig. 5. $K_2Ni_2(Acm)_3 \cdot 5H_2O$: TG/DTA curves in nitrogen (———) and in air (· · · · · ·); and DTG curve in air.

The slopes of the TG curves and the percentages of weight lost suggest that for the $Co(Acm)_2(NH_3)_2$, $Ni(Acm)_2(NH_3)_4$ and $Zn(Acm)_2(NH_3)_2$ complexes the first stage of the ligand decomposition is similar, giving a M(II)–$(tdz)_2$ derivative, as has been observed in the pyrolysis of the Cu–Acm complexes [5]. The formation of these species is also indicated by IR spectra

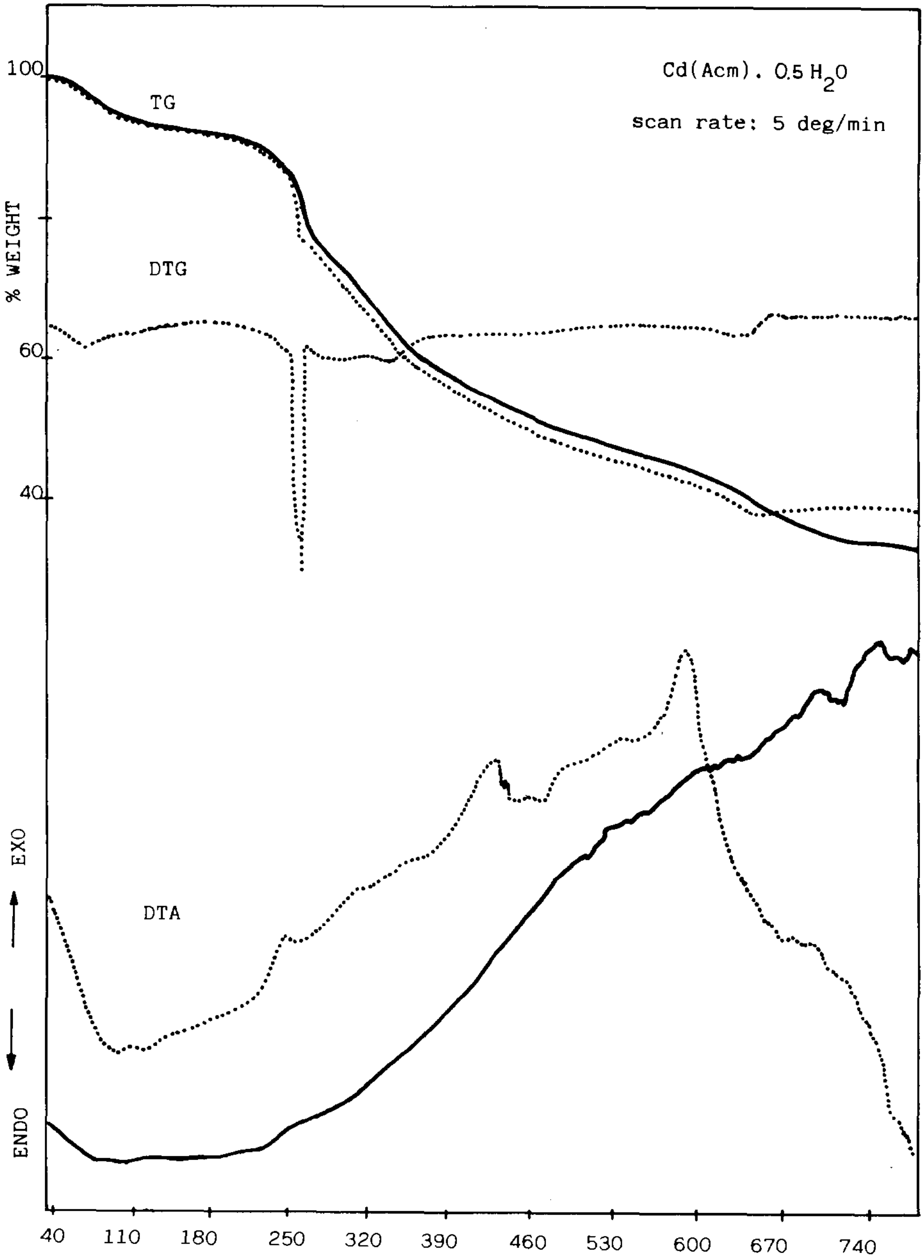

Fig. 6. Cd(Acm)·$1.5H_2O$: TG/DTA curves in nitrogen (———) and in air (······); and DTG curve in air.

of samples taken at the end of this step. The IR spectra show the absence of $st(SO_2)_{asym}$, $st(SO_2)_{sym}$ and st(CO) peaks and the presence of a broad band centred around 1400–1440 cm^{-1}, characteristic of molecules containing "S=C=N" bonds, such as the thiadiazoles [6].

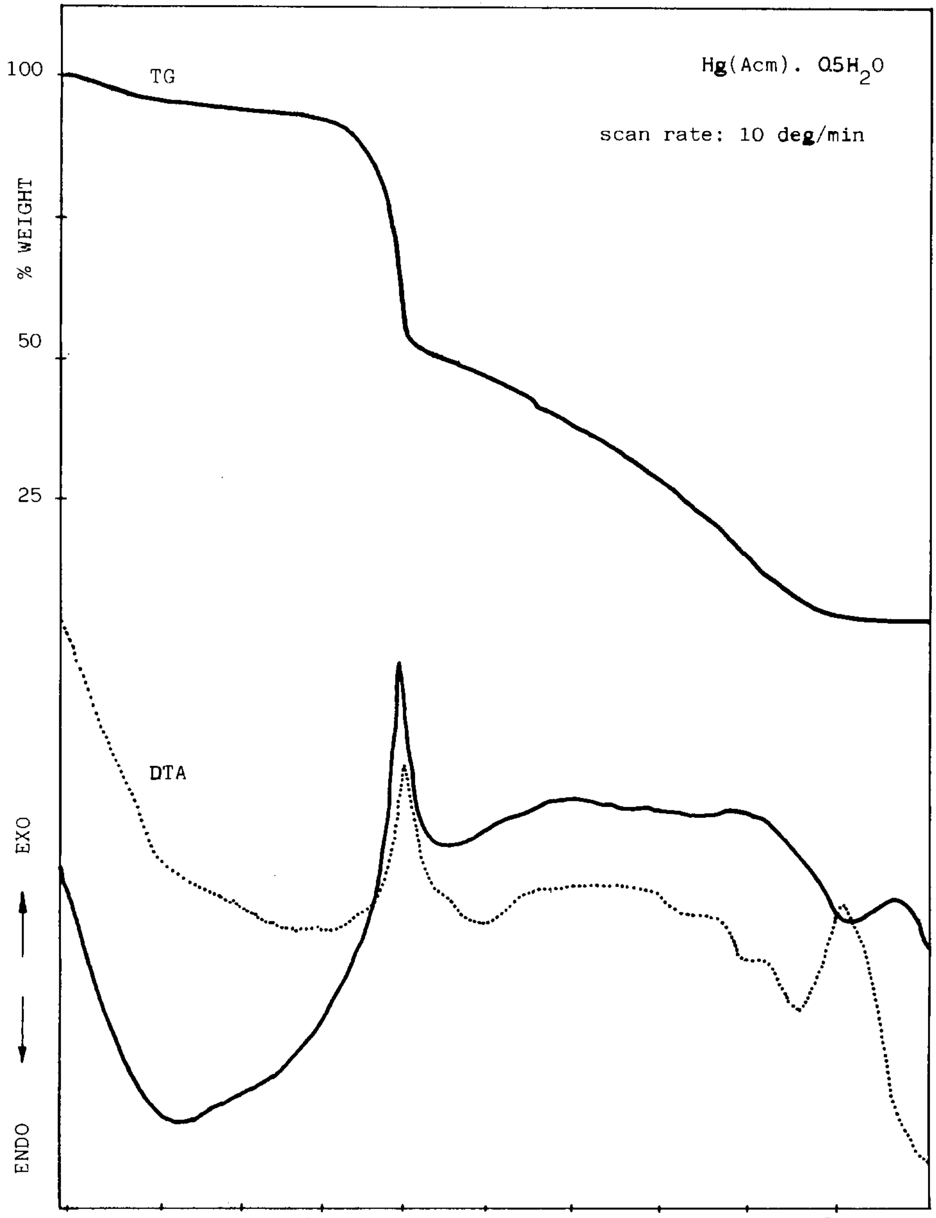

Fig. 7. Hg(Acm)·0.5H_2O: TG curves in nitrogen and in air (———); and DTA curves in nitrogen (———) and in air (······).

The temperatures at which these products were identified and the corresponding percentages of the weights remaining are given in Table 2.

In air, this phase of the ligand degradation gives rise to exothermic peaks in the range 290–390 °C for the Ni(II) complex, and 310–360 °C for the

TABLE 2

First stage of pyrolytic decomposition

Compound	TG T [a] (°C)	% weight remaining			DTA T [b] (°C)	$-\Delta H$ (kJ mol^{-1})
		Exp.	Calc.	For the species		
$Ni(Acm)_2(NH_3)_4$	370	37.4	39.4	"Ni(II)–$(tdz)_2$"	290–390 [c]	773.3
$Co(Acm)_2(NH_3)_2$	370	41.4	42.4	"Co(II)–$(tdz)_2$"	310–360	374.9
$Zn(Acm)_2(NH_3)_2$	330	41.0	43.1	"Zn(II)–$(tdz)_2$"	330–400	27.6
$Cd(Acm)\cdot 1.5H_2O$	330	58.0	61.6	"Cd(II)–(tdz)"	220–270	9.8
$Ag_2(Acm)(NH_3)$	280	76.0	77.4	"Ag(I)–(tdz–SO_2)"	240–280	85.9
$Ag_2(Acm)$	280	80.5	81.9	"Ag(I)–(tdz–SO_2)"	220–280	61.2

[a] Temperature at the end of the process.

[b] Range of the DTA peak.

[c] This peak must include several exothermic events, not only that corresponding to formation of the tdz derivative. Thus, the ΔH value is considerably higher than for the other complexes.

Co(II) complex. The DTA curve for the Zn(II) compound shows a very weak exothermic region between 300 and 430 °C (see Table 2).

Although it would seem from the TG curves that this first stage of the ligand degradation is similar in air and nitrogen atmospheres, the DTA curves in nitrogen do not show any exothermic event, whereas thermal degradation of the Cu(II)–Acm complexes gave rise to an exothermic peak in both atmospheres. The cause may be oxidation processes associated with the breaking of the ligand in the presence of oxygen.

In the second stage of the pyrolytic decomposition, the M(II)–$(tdz)_2$ derivative leads to the formation of metal oxides (in air) or sulphides (in nitrogen) (see Table 3). It is not clear how this species decomposes. The observation of weak–medium bands at around 2100–2200 cm^{-1} in the IR spectra of residues collected at different temperatures and the literature concerning the fragmentation of cyclic structures [7] suggest the formation of intermediate species containing "S=C=N" or "C≡N" groups.

TABLE 3

Final residues in air atmosphere

Compound	Residue	T (°C)	% residue weight	
			Exp.	Calc.
$Ni(Acm)_2(NH_3)_4$	NiO	680	13.1	13.3
$Co(Acm)_2(NH_3)_2$	CoO	980	13.8	14.0
$Zn(Acm)_2(NH_3)_2$	ZnO	850	11.8	12.1
$Cd(Acm)\cdot 1.5H_2O$	CdO	900	36.2	35.8
$K_2Ni_2(Acm)_3\cdot 5H_2O$	K_2SO_4 + NiO	750	33.7	34.2
$Ag_2(Acm)(NH_3)$	Ag	1000	46.7	47.6
$Ag_2(Acm)$	Ag	740	48.4	49.5

The TG and DTA curves indicate that the evolution of these intermediate products is different in air and in nitrogen atmospheres. In air the loss of weight stabilizes from ca. 550–600 °C, with the TG curves being nearly horizontal, while in nitrogen the TG curves continue to drop until the end. On the other hand, in air the DTA curves show several overlapping exothermic events (between 400 and 600 °C for the Ni(II) and Co(II) compounds and between 600 and 700 °C for the Zn(II) compound), while in nitrogen no change is observed. All of this suggests that oxidation processes take place in the presence of oxygen.

With regard to the Co(II) complex, in air the IR spectra of samples collected at around 550–600 °C show the presence of sulphate, which must originate from partial oxidation of the S thiadiazole ring atom, as happens during the pyrolysis of Cu(II)–Acm complexes. Within this temperature range and up to approximately 850 °C the TG curve shows only a weak increase in weight. This observation, together with the weight percentage (experimental result: 16.8%), indicates that the $CoSO_4$ is produced in a very small proportion. (If all the Co(II) had been transformed into $CoSO_4$, the percentage of the residual weight would have been 28.9%, a value far bigger than the experimental result obtained.) From the experimental result it could be supposed that the $CoSO_4$ detected by IR spectroscopy is only an impurity, but its formation is supported by a comparative study of the DTA curves in air and nitrogen atmospheres, as indicated above. Furthermore, formation of the sulphate from the sulphide by reaction with oxygen at 700 °C has already been described for several metals [8].

For the Cu(II)–Acm complexes the process observed was similar, although the oxidation of sulphides to sulphate produced a more obvious increase in weight.

For the Ni(II) and Zn(II) complexes the curves suggested a behaviour similar to that of the Co(II) complex, but spectra IR of samples taken at different temperatures always showed the absence of the typical sulphate bands.

Finally, the sulphates decompose to give the metal oxide in air and the metal sulphide in nitrogen.

Schemes (1)–(3) summarize the thermal degradation of these three complexes *.

$$Ni(Acm)_2(NH_3)_4 \rightarrow Ni(Acm)_2 \rightarrow \text{“}Ni\text{–}(tdz)_2\text{”} \rightarrow NiO \tag{1}$$

$$Zn(Acm)_2(NH_3)_2 \rightarrow \text{“}Zn\text{–}(tdz)_2\text{”} \rightarrow ZnO \tag{2}$$

$$Co(Acm)_2(NH_3)_2 \rightarrow \text{“}Co\text{–}(tdz)_2\text{”} \rightarrow (-)CoSO_4 + CoO \rightarrow CoO \tag{3}$$

The ligand degradation of the Cd(II) complex starts with a very sharp decrease in weight (15.7%) between 230 and 247 °C. Thereafter, decomposi-

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* Key: (−), in small proportion.

tion occurs more slowly. This large weight loss is accompanied in the DTA curve by an exothermic peak at around 230 °C. The IR spectra of a sample collected at 250 °C indicates a reduction in the intensity of the carbonyl band. Assuming that the sharp loss of weight is due to elimination of the acetamido group, the experimental percentage of weight loss (15.7%) and the calculated value (15.9%) agree quite well. (Nevertheless, the IR spectra at this temperature indicate that the st(CO) band does not disappear completely.)

The IR spectra of samples taken at around 500 °C are typical of the tdz derivatives. The exothermic peak of this second ligand degradation stage appears between 430 and 500 °C, but this is not observed in nitrogen (see Table 2). Later, in the range 600–635 °C, it appears as weak–medium bands at 2000–2100 cm^{-1}, as observed for the three compounds discussed above. The partial oxidation of these intermediate products leads to the formation of $CdSO_4$, in a process similar to that observed for the Co(II) complex. The presence of $CdSO_4$ is clearly shown in the IR spectra of a sample taken at 600–700 °C. However, the weight of the residue at this temperature (36.2%) corresponds to CdO (calculated value: 35.8%) rather than $CdSO_4$ (calculated value: 58.0%), indicating that one of these intermediate products must have suffered oxidation to $CdSO_4$, but in very small yield. The oxidation process is supported by an exothermic event at around 550–650 °C in the DTA curve in air. The DTA curve in nitrogen does not show any exothermic peak. The $CdSO_4$ isolated finally gives CdO (weight percentages and indicated in Table 3). In nitrogen, the final product is CdS.

This study of the ligand degradation by means of IR spectra of samples taken at different temperatures allows us to propose scheme (4). *

$$\begin{aligned} &\mathrm{Cd(Acm)} \cdot 1.5\mathrm{H_2O} \rightarrow \mathrm{Cd(Acm)} \rightarrow \text{“Cd–(tdz)”} \rightarrow (-)\mathrm{CdSO_4} + \mathrm{CdO} \\ &\qquad \rightarrow \mathrm{CdO} \end{aligned} \tag{4}$$

The formula of the compound $K_2Ni_2(Acm)_3 \cdot 5H_2O$ suggests many possible explanations for the process of pyrolytic decomposition.

The IR spectrum of the residue at 360 °C shows sulphate bands already present. At temperatures close to 360 °C, the degradation of the other complexes gave a $M(II)–(tdz)_2$ derivative characterized by a strong band at 1400 cm^{-1}. The formation of the sulphate, when it happened, took place later, at higher temperatures. With the present complex, at 360 °C the band at 1400 cm^{-1} is still very weak. At 590 °C the IR spectrum shows the sulphate bands, the broad band at 1400 cm^{-1} and a third weak band at 2100–2200 cm^{-1}. At 650 °C the sulphate bands have become stronger, the band at 1400 cm^{-1} has disappeared, and a band characteristic of the oxide has begun to appear. Finally, above 750 °C the IR spectrum only shows

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* Key: (−), in small proportion.

sulphate and oxide bands (and this time, the oxide band is stronger than at 650 °C).

These results suggest that as a first step K_2SO_4 is formed from the sulphonamido moiety, while the other portion of the ligand, the tdz ring, probably bonded to the Ni(II) ion, follows the usual degradation scheme to give a "Ni(II)–(tdz)$_2$" derivative. The product is then transformed into a species such as $Ni(S\underset{..}{-}C\underset{..}{-}N)_2$, which would explain the band at around 2100–2200 cm^{-1}. Finally, this last compound could lead to the formation of NiO (see percentages in Table 3).

In air, the first stage of the pyrolytic degradation could be ascribed to an exothermic peak between 260 and 340 °C. After this, the DTA curve exhibits a series of multiple weak exothermic peaks, which is in agreement with oxidative processes occurring in the presence of oxygen.

In nitrogen, the final residue is a mixture of potassium sulphate and nickel sulphide.

Scheme (5) summarizes the thermal decomposition process proposed.

$$\begin{aligned} &K_2Ni_2(Acm)_3 \cdot 5H_2O \rightarrow K_2Ni_2(Acm)_3 \rightarrow K_2SO_4 + \text{"Ni–(tdz)}_2\text{"} \\ &\qquad \rightarrow K_2SO_4 + NiO \end{aligned} \qquad (5)$$

The ligand degradation of $Ag_2(Acm)(NH_3)$ begins above 180 °C. Between 250 and 270 °C a sharp slope is observed, but identification of the product formed or the portion of the ligand lost is very difficult. In the IR spectra of a sample taken at 280 °C, the st(CO), st(N–H) and δ(N–H) bands are absent. This suggests that the intermediate product could be a tdz derivative, although a different one to that produced in the ligand pyrolysis of the other Acm complexes, as the SO_2 group remains (see percentages in Table 2). In the DTA curve the process is characterized by an exothermic peak in the range 240–280 °C. Subsequent stages of the decomposition lead finally to Ag in an air atmosphere (see Table 3) and Ag_2S in nitrogen, probably because the degradation is slower in nitrogen than in air.

It is interesting to note that during the second step of the decomposition in air, a large exothermic peak appears between 570 and 735 °C. In nitrogen, however, the DTA curve only exhibits a weak endothermic event between 550 and 650 °C. The exothermic peak in air cannot be due to an oxidation process of sulphide to sulphate, as was the case with other Acm compounds: firstly, because the IR spectra of samples taken at different temperatures show that Ag_2SO_4 is not formed at any time; and secondly, because the silver sulphate melts at lower temperatures (m.p. 652 °C). Our hypothesis to explain this energetic event can be represented by the following scheme.

$$Ag_2S(s) \rightarrow 2Ag(s) + S(s) \begin{cases} \xrightarrow{Air} 2Ag(s) + SO_2(g) & \text{Exothermic} \\ \xrightarrow[N_2]{} 2Ag(s) + S(g) & \text{Endothermic} \end{cases}$$

The pyrolytic decomposition of the compound $Ag_2(Acm)$ (Fig. 8) is similar to the corresponding process for the complex with ammonia. Since $Ag_2(Acm)$ does not contain ammonia, it can be considered stable up to

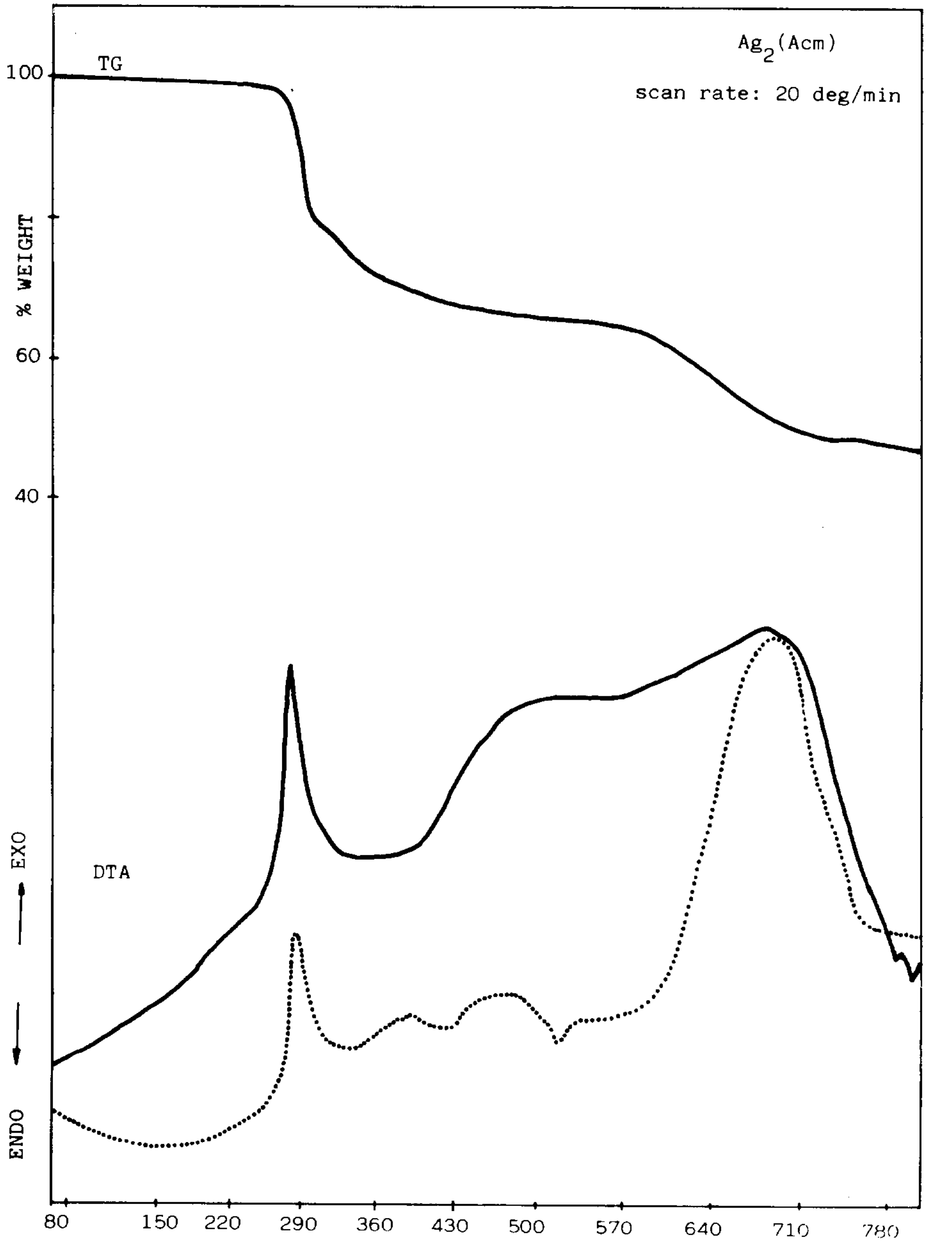

Fig. 8. $Ag_2(Acm)$: TG curves in nitrogen and in air (———); and DTA curves in nitrogen (———) and in air (· · · · · ·).

240–250 ° C. The final residues in air and nitrogen are both Ag (see Scheme (6).

$$Ag_2(Acm)(NH_3) \rightarrow Ag_2(Acm) \rightarrow \text{“}Ag_2\text{–}(tdz\text{–}SO_2)\text{”} \rightarrow Ag_2S \rightarrow Ag \qquad (6)$$

The pyrolytic degradation of $Hg(Acm) \cdot 0.5H_2O$ takes place in a single step. The TG curve exhibits a strong loss of weight (see Table 2) associated with an exothermic event in the range 212–325 ° C. We have no information about the nature of the species formed at 278 ° C, when this process finishes. IR spectra of the residue at this temperature show a broad undefined band at around 1400 cm^{-1}, but the percentage of weight remaining is too low for a Hg–tdz derivative. At 300 ° C no peak is observed in the IR spectra. From this temperature, the weight decreases more slowly.

The percentage of the final residue at 600 ° C is 5.6%, which implies that even Hg has been lost (the total percentage of Hg in the complex is 47.7%). In fact, the volatilization point of Hg is 357 ° C, and exactly at this temperature a weak change is observed in the TG curve. However, between 450 and 570 ° C the DTA curve shows three overlapping endothermic events, which suggests that the species which sublimates may be HgS (HgS sublimation point: 580–585 ° C). This hypothesis would explain why there is no endothermic peak at around 357 ° C in the DTA curve, as would be expected for sublimation of Hg; and why there are no bands in the IR spectra of samples taken at these temperatures. It is also consistent with the experimental weight percentage at 300 ° C (experimental result: 55.2%, calculated value for HgS: 54.1%).

$$Hg(Acm) \cdot 0.5H_2O \rightarrow Hg(Acm) \rightarrow ? \rightarrow HgS\uparrow \qquad (7)$$

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