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Thermal analysis applied to the study of metal complexes: thermal behaviour of 6-amino-2-thiouracil and its complexes with several transition metal ions

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Abstract

The thermal decomposition processes of 6-amino-2-thiouracil and its Co(II), Ni(II), Cu(I), Ag(I), Zn(II), Cd(II) and Hg(II) complexes have been studied by TG and DSC techniques. Heats of dehydration have been calculated from the DSC curves. Infrared spectroscopy applied to some of these complexes heated in air has elucidated the decomposition steps and the nature of the intermediate products. The pyrolysis of these compounds ends between 600 and 800°C with different products as final residues.

INTRODUCTION

The study of the metal complexes of heterocyclic thio derivatives is an area of great interest, as indicated recently by Raper [1]. Among this type of compounds, thiopyrimidines are important owing to their multiple potential sites for binding metal ions [2–9]. However, it is known that thiopyrimidine derivatives act as potent inhibitors [10] and antimetabolites [11], and pyrimidine-2-thione shows pronounced in vitro bacteriostatic activity [12]. Likewise, 2-thiouracil is known as a basic constituent of some t-RNAs [13], and it exhibits antitumour and antithyroid activity because it readily incorporates into nucleic acids [14].

Thermal studies on metal complexes of pyrimidines and, in particular, of thiopyrimidine derivatives are scarce [8,15]. These studies are of interest because in most cases they permit coordinated and uncoordinated solvate molecules, such as water or ammonia, to be distinguished. Also, dehalo-

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genation and decarboxylation processes may be detected and their enthalpies calculated. Likewise, if relatively stable intermediates in the pyrolytic process can be isolated, their chemical nature and the mechanism of the thermal degradation of the compound, may be inferred by means of other techniques, such as IR and UV–visible–near-IR spectroscopies and magnetic measurements. Finally, the nature of the final product of pyrolysis as a function of the atmosphere used can help to suggest metal–ligand binding sites, especially when sulphur-containing ligands are used.

For this reason, and following our systematic investigation on the coordination chemistry of pyrimidine and purine derivatives [16–25], we report here the preparation and thermal behaviour of some metal complexes with 6-amino-2-thiouracil (H_2ATU).

EXPERIMENTAL

Preparation of the compounds

The ligand H_2ATU used in this work was obtained from thiourea and ethyl cyanoacetate using a previously described method [26].

$[Co(HATU)_2(H_2O)]\cdot 2H_2O$ (**I**), $[Ni(HATU)_2(H_2O)_2]$ (**II**), $[Zn(HATU)_2(H_2O)]\cdot 2H_2O$ (**III**), $Cu(HATU)\cdot H_2O$ (**V**), $Ag(HATU)\cdot 0.5\,H_2O$ (**VI**) and $Ni(HATU)_2$ (**VII**) were all synthesized by the following procedure: 0.64 g of H_2ATU (4 mmol) were dissolved in 50 ml of hot water and added to an aqueous solution of the corresponding metallic acetate (4 mmol), except for the copper and silver complexes where perchlorate and nitrate were used as the inorganic salts respectively. The resulting solutions were kept at 60°C. After several hours, microcrystalline powders of **I**, **III**, **V**, **VI** and **VII** were obtained. Compound **II** was obtained from the mother liquor of **VII**. Likewise, crystals suitable for X-ray diffraction analysis were obtained from the mother liquor of **III**.

The complex $[Cd(HATU)_2(H_2O)]\cdot H_2O$ (**IV**) was prepared by reacting hydrated cadmium chloride (0.23 g, 1.2 mmol) and sodium acetate (3 mmol) with 6-amino-2-thiouracil (0.16 g, 1 mmol) in aqueous solution. After standing for several hours, a white solid was isolated from the reaction mixture.

$Hg(HATU)_2$ (**VIII**) was prepared by mixing an aqueous solution of $HgCl_2$ (0.54 g, 2 mmol) with another containing 0.32 g (2 mmol) of H_2ATU in 200 ml of water. A white precipitate of **VIII** was immediately obtained.

$Zn(ATU)\cdot 1.5H_2O$ (**IX**) and $Cd(ATU)\cdot H_2O$ (**X**) were prepared in a similar way: 2 mmol of zinc acetate or cadmium chloride were dissolved with stirring in concentrated ammonia. To these solutions was added H_2ATU (0.32 g, 2 mmol) dissolved in 20 ml of ammonia. Precipitation of the cadmium complex was immediate and the zinc complex was isolated after standing for several hours.

TABLE 1

Analytical data for isolated complexes of 6-amino-2-thiouracil [a]

Compound	Colour	C (%)	H (%)	N (%)
$[Co(HATU)_2(H_2O)]\cdot 2H_2O$ (I)	Violet	24.28 (24.19)	3.56 (3.53)	22.02 (21.16)
$[Ni(HATU)_2(H_2O)_2]$ (II)	Green	25.11 (25.35)	3.20 (3.20)	22.61 (22.16)
$[Zn(HATU)_2(H_2O)]\cdot 2H_2O$ (III)	White	24.28 (23.80)	3.53 (3.47)	21.75 (20.82)
$[Cd(HATU)_2(H_2O)]\cdot H_2O$ (IV)	White	22.14 (22.18)	2.32 (2.77)	19.27 (19.41)
$Cu(HATU)\cdot H_2O$ (V)	White	22.04 (21.46)	2.86 (2.68)	19.27 (18.77)
$Ag(HATU)\cdot 0.5H_2O$ (VI)	White	18.90 (18.53)	1.71 (1.93)	15.31 (16.21)
$Ni(HATU)_2$ (VII)	Yellow-green	27.85 (28.01)	2.36 (2.33)	25.35 (24.51)
$Hg(HATU)_2$ (VIII)	White	19.06 (19.79)	1.66 (1.64)	17.13 (17.32)
$Zn(ATU)\cdot 1.5H_2O$ (IX)	White	20.39 (20.55)	2.40 (2.57)	17.55 (17.98)
$Cd(ATU)\cdot H_2O$ (X)	White	17.43 (17.68)	1.79 (1.84)	15.75 (15.46)

[a] Calculated values in parentheses.

All products were filtered by suction, washed with water, ethanol and diethyl ether, and air-dried at room temperature. Their colour and analytical data are given in Table 1.

Experimental methods

Microanalysis of C, H and N was performed by the Technical Services of the University of Granada using a Perkin–Elmer 240C microanalyser. IR spectra of the compounds (4000–180 cm^{-1}) were recorded from KBr pellets using a Perkin–Elmer 983-G spectrophotometer.

TG studies were carried out under a pure air atmosphere on a Mettler TG-50 thermobalance, using samples varying in weight from 1.785 to 15.125 mg and a heating rate of 10°C min^{-1}. DSC plots were obtained under the same conditions on a Mettler DSC-20 differential scanning calorimeter. The sample weights were between 1.394 and 7.427 mg.

RESULTS AND DISCUSSION

Spectral studies on the isolated complexes have suggested that the coordination mode of H_2ATU to these metal ions can occur in (i) a monoanionic and chelating bidentate form through the N1 and S2 atoms,

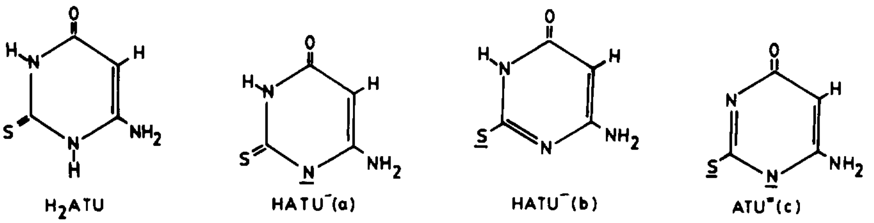

Fig. 1. Molecular structures of neutral, monoanionic and dianionic 6-amino-2-thiouracil (H_2ATU).

and (ii) a dianionic form, the N1, N3, O4 and S2 atoms being involved, and the ATU^{2-} dianion acting as a bridging ligand. Figure 1 shows the molecular structures of the neutral H_2ATU ligand, $HATU^-$ monoanion (a) and (b) and ATU^{2-} dianion (c).

$[Co(HATU)_2(H_2O)] \cdot 2H_2O$ (I), $[Ni(HATU)_2(H_2O)_2]$ (II), $[Zn(HATU)_2(H_2O)] \cdot 2H_2O$ (III), $[Cd(HATU)_2(H_2O)] \cdot H_2O$ (IV), $Cu(HATU) \cdot H_2O$ (V) and $Ag(HATU) \cdot 0.5\ H_2O$(VI) complexes can be included in the first group because in these six cases the coordination of the $HATU^-$ ligand to these metal ions takes place in its monoanionic thione form (see (a) in Fig. 1). $Ni(HATU)_2$ (VII) and $Hg(HATU)_2$ (VIII) might also be expected to fall in this group, but in these cases the negative charge of the ligand seems to be located on the sulphur atom ((b) in Fig. 1), and therefore IR spectra of both complexes show features similar to those of the analogous 2-methylthio derivative. Finally, $Zn(ATU) \cdot 1.5H_2O$ (IX) and $Cd(ATU) \cdot H_2O$ (X) complexes show a polymeric structure in which the dianionic ATU^{2-} ligand ((c) in Fig. 1) acts as a bridging ligand.

The thermal behaviour of the H_2ATU ligand and of its metal complexes described above has been deduced from their corresponding TG and DSC curves.

The TG curve of $H_2ATU \cdot H_2O$ (Fig. 2) shows two weight-loss effects in the 100–750°C temperature range, assigned to the dehydration and decomposition of the ligand respectively. The dehydration process can be observed in the 100–140°C temperature range and the observed weight loss (11.6%) is in good agreement with the theoretical one (see Table 2). The expected endothermic behaviour for this dehydration process has been observed from its DSC curve, the calculated enthalpy value being 59 kJ mol^{-1}. This suggests that there are strong hydrogen-bond interactions between the water molecule and the pyrimidine ligand. However, the IR spectrum of a sample heated at 250°C (just above the end of the first endothermic effect) and cooled rapidly to room temperature revealed modifications in the 3500–3000 and 1700–1600 cm^{-1} ranges, in which the main water vibration modes appear. Bands corresponding to the vibration

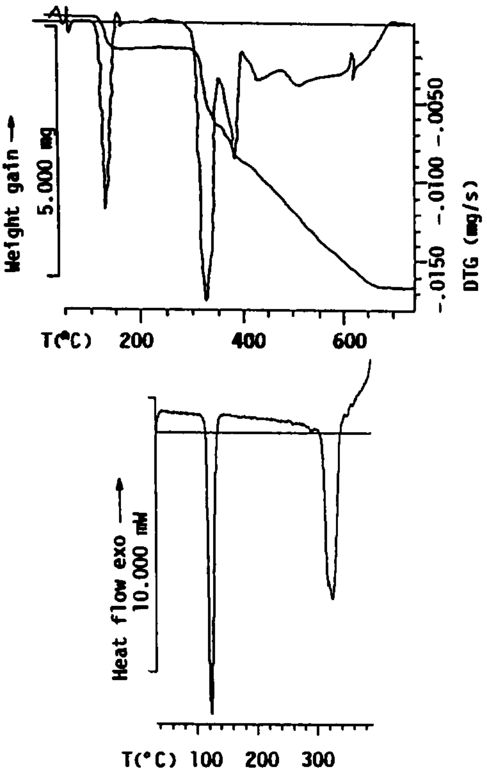

Fig. 2. TG and DSC curves for $H_2ATU \cdot H_2O$.

TABLE 2

Thermoanalytical data for dehydration processes

Compound	Process	Weight loss			DSC data	
		Temp. range (°C)	Found (%)	Calc. (%)	T_{peak} (°C)	ΔH (kJ mol^{-1} H_2O)
$H_2ATU \cdot H_2O$	$-H_2O$	100–140	11.6	11.18	123	59
$[Co(HATU)_2(H_2O)] \cdot 2H_2O$	$-3H_2O$	75–250	13.9	13.59	155	53
$[Ni(HATU)_2(H_2O)_2]$	$-2H_2O$	150–275	10.2	9.50	236	63
$[Zn(HATU)_2(H_2O)] \cdot 2H_2O$	$-H_2O$	100–250	9.8	8.92	126	56
	$-H_2O$				165	
	$-H_2O$		13.8	13.39	216	20
$[Cd(HATU)_2(H_2O)] \cdot H_2O$	$-H_2O$	35–200	3.5	4.16	60	–[a]
	$-H_2O$		7.7	8.32	120	–[a]
$Cu(HATU) \cdot H_2O$	$-H_2O$	35–150	8.7	8.05	95	28
$Ag(HATU) \cdot 0.5H_2O$	$-0.5H_2O$	75–200	3.3	3.47	165	11
$Zn(ATU) \cdot 1.5H_2O$	$-1.5H_2O$	35–150	8.9	11.56	60	–[a]
$Cd(ATU) \cdot H_2O$	$-H_2O$	35–150	8.7	8.05	100	–[a]

[a] Not calculated owing to the broadness of the endothermic effect.

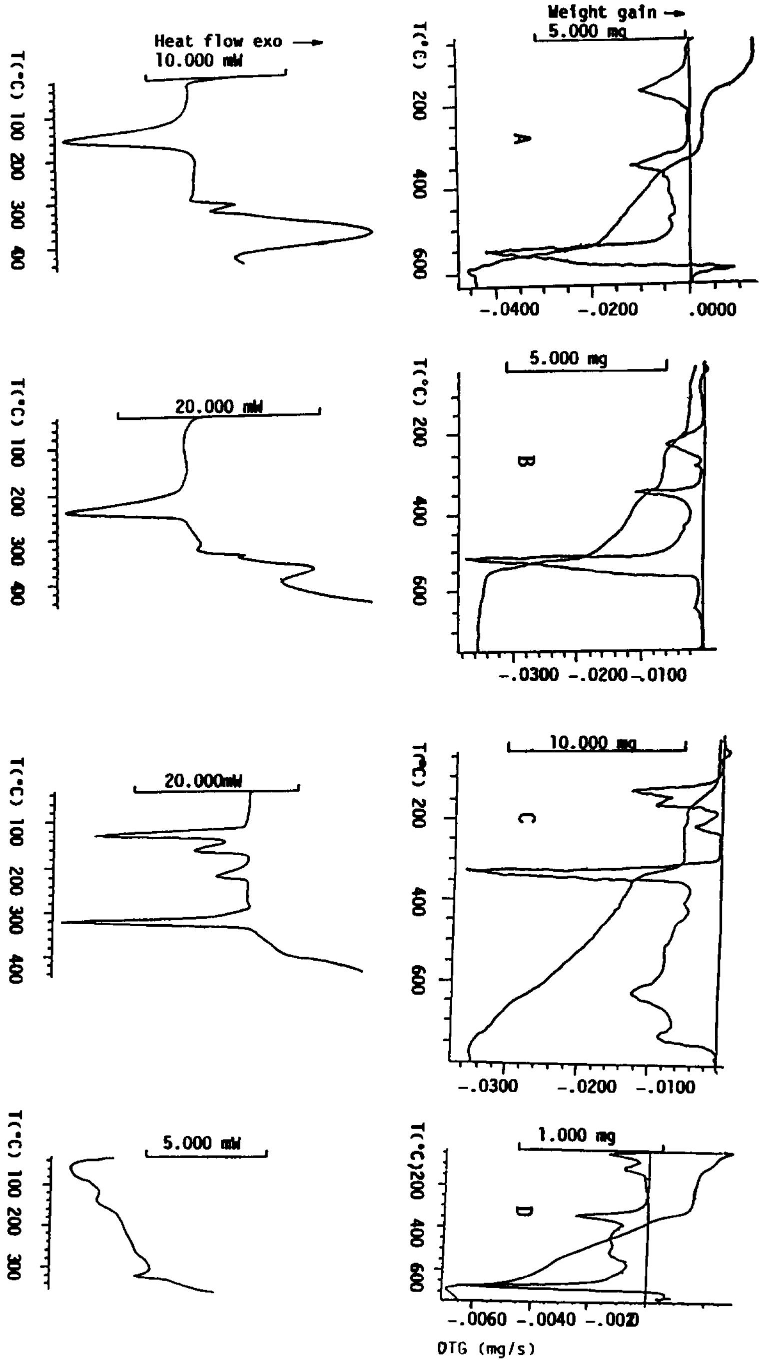

Fig. 3. TG and DSC curves for (A) $[Co(HATU)_2(H_2O)]\cdot 2H_2O$, (B) $[Ni(HATU)_2(H_2O)_2]$, (C) $[Zn(HATU)_2(H_2O)]\cdot 2H_2O$, (D) $[Cd(HATU)_2(H_2O)]\cdot H_2O$.

modes of the organic ligand remain in the same position as in the IR spectrum of the hydrated product.

At 326°C, the DSC plot of H_2ATU shows a strong endothermic effect which is assigned to the fusion of the sample. This effect overlaps with a partial vaporization of the liquid. Finally, the pyrolytic decomposition of the pyrimidine ligand occurs in the 350–675°C temperature range.

The TG and DSC curves of some of the isolated complexes are collected in Fig. 3. Complexes **I** and **II** display similar thermal behaviour. The TG and DSC curves of these complexes indicate that under the experimental conditions used in the present work, the dehydration processes take place in one step. The experimental enthalpy values suggest that the water molecules are more weakly bound in the cobalt complex (**I**) than in the nickel complex (**II**). This is compatible with the spectral data because trigonal bipyramidal and tetragonally distorted octahedral geometries for the cobalt and nickel complexes, respectively, have been assigned from the UV–visible–near-IR diffuse reflectance spectra [26]. Thus we suggest that only one water molecule is coordinated to the Co(II) ion, whereas in the Ni(II) complex, both water molecules are bound to the metal centre.

The zinc (**III**) and cadmium (**IV**) complexes show different thermal behaviour (Fig. 3). The dehydration process of **III** takes place in three steps (endothermic effects centred at 126, 165 and 216°C), whereas the dehydration of **IV** occurs in two steps (endothermic effects at 60 and 120°C) which suggests that the water molecules in these complexes are not equivalent. In the zinc complex (**III**), the weight losses and dehydration enthalpies for the first two water of crystallization molecules cannot be calculated because these processes overlap. The high value of the DSC peak temperature corresponding to the loss of the third water molecule suggests that this molecule is directly linked to the metal ion.

In order to demonstrate this dehydration sequence, the IR spectrum of a sample of $[Zn(HATU)_2(H_2O)] \cdot 2H_2O$ heated at 180°C (just to the end of the first two endothermic effects on the DSC curve) and immediately cooled to room temperature was recorded. In this IR spectrum, the presence of the vibration modes corresponding to coordinated water molecules can be clearly observed. To verify the total dehydration processes in the complexes **I**–**IV** and to identify the nature of the intermediate products, IR spectra of samples heated at 250°C have been recorded (Fig. 4). All these spectra are similar and in accordance with the 6-amino-2-thiouracilato tautomeric form of the ligand $HATU^-$ (see Fig. 1(a)).

In copper (**V**) and silver (**VI**) complexes the dehydration processes occur in a single step, the dehydration enthalpy values being fairly low. This suggests a weak interaction between water molecules and 6-amino-2-thiouracil.

Once dehydrated, the complexes undergo pyrolytic decomposition. Thermogravimetric data for these processes are given in Table 3.

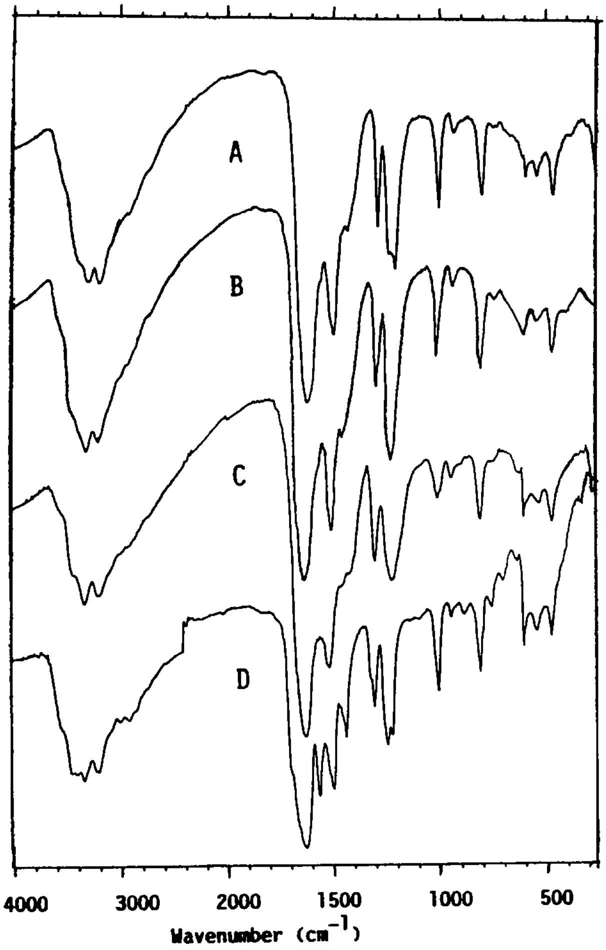

Fig. 4. IR spectra of intermediate compounds obtained by heating at 250°C: curve A, $[Co(HATU)_2(H_2O)]\cdot 2H_2O$, curve B, $[Ni(HATU)_2(H_2O)_2]$; curve C, $Zn(HATU)_2(H_2O)]\cdot 2H_2O$; curve D, $[Cd(HATU)_2(H_2O)]\cdot H_2O$.

This pyrolytic decomposition is reflected in the corresponding DSC curves by the presence of several exothermic effects. A marked difference is shown in the DSC curve of **III**, where a new strong endothermic effect appears (DSC peak temperature, 320°C), which is due to the fusion and partial vaporization of the anhydrous $Zn(HATU)_2$ sample, the associated enthalpy value being 120 kJ mol^{-1}. This effect was also observed in the free ligand. The pyrolytic processes were completed in the 600–800°C range. The percentage and nature of the remaining residues are indicated in Table 3. The resulting oxides and sulphates were identified by IR spectroscopy.

Thermal studies on $Ni(HATU)_2$ (**VII**) and $Hg(HATU)_2$ (**VIII**) have shown that these complexes are thermally stable up to 350°C and 300°C

TABLE 3

TG and DSC data for pyrolytic processes

Compound	Process	Residue			DSC peak temp. range (°C)
		Found (%)	Calc. (%)	Nature	
Ligand	Fusion [a]	–	–	–	326 endo
	Pyrolysis	–	–	–	350–675
$[Co(HATU)_2(H_2O)]\cdot 2H_2O$	Pyrolysis	23.1	20.20	Co_3O_4 [b]	300–650
$[Ni(HATU)_2(H_2O)_2]$	Pyrolysis	22.3	19.71	NiO [b]	325–650
$[Zn(HATU)_2(H_2O)]\cdot 2H_2O$	Fusion [a]	–	–	–	320 endo
	Pyrolysis	13.6	17.80	ZnO	300–775
$[Cd(HATU)_2(H_2O)]\cdot H_2O$	Pyrolysis	38.4	29.68	CdO [b]	300–750
$Cu(HATU)\cdot H_2O$	Pyrolysis	26.7	28.39	CuO [c]	300–500
$Ag(HATU)\cdot 0.5H_2O$	Pyrolysis	43.0	41.64	Ag	300–800
$Ni(HATU)_2$	Pyrolysis	23.0	21.80	NiO [b]	350–700
$Hg(HATU)_2$	Pyrolysis	–	–	–	300–700
$Zn(ATU)\cdot 1.5H_2O$	Pyrolysis	36.9	34.84	ZnO [b]	300–800
$Cd(ATU)\cdot H_2O$	Pyrolysis	46.9	47.28	CdO	300–700

[a] With partial sublimation.
[b] Contaminated with sulphate.
[c] Contaminated with $Cu_3(OH)_4(SO_4)$.

respectively. Then the pyrolytic decomposition of both compounds begins and is completed at about 700°C, with the total elimination of the sample in the case of the mercury complex (**VIII**). The IR spectrum of the residue remaining after the pyrolysis of **VII** indicates the presence of a mixture of $NiSO_4$ and NiO as final product.

The polymeric $Zn(ATU)\cdot 1.5H_2O$ (**IX**) and $Cd(ATU)\cdot H_2O$ (**X**) complexes undergo dehydration in the 35–150°C temperature range and their DSC curves suggest that water molecules are weakly retained in the crystal lattices. Once dehydrated, the complexes decompose pyrolytically. The weight loss continues without interruption up to 800°C (**IX**) and 700°C (**X**) respectively, at which temperatures the weight of the residues remaining in the crucible were in accordance with those calculated for the corresponding oxides. However, the IR spectrum of the residue from the zinc complex (**IX**) shows that it is contaminated with zinc sulphate, which accords with the slightly higher value found for the percentage of residue if it is compared with the theoretical value for pure zinc oxide residue.

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