Thermochimica Acta, 230 (1993) 225–233
Elsevier Science Publishers B.V., Amsterdam
SSDI 0040-6031(93)01197-B

The thermal study of Zn(II), Cd(II), Hg(II), Pd(II), Pt(II) and Au(III) complexes of 4,6-dimethyl-2-thiopyrimidine

Mª Luz Godino-Salido [a], M.D. Gutierrez-Valero [a], R. López-Garzón [a,*] and A. Bernalte-García [b]

[a] *Departamento de Química Inorgánica, Facultad de Ciencias Experimentales, 23071-Jaén (Spain)*
[b] *Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Extremadura, Badajoz (Spain)*

(Received 25 February 1993; accepted 31 March 1993)

Abstract

The thermal decompositions of the 4,6-dimethyl-2-thiopyrimidine complexes $Zn(DMTP)_2Cl_2$, $Cd(DMTP)_2Cl_2$, $HgDMTPCl_2$, $Pt(DMTP)_2Cl_2$, $Pd(DMTP)_2Cl_2$, and $AuDMTPCl_3$ have been studied in air atmosphere by thermogravimetric and differential scanning calorimetric techniques. IR spectroscopy was used for the characterization of the intermediate and final products of the pyrolysis.

The complexes show different thermal behaviours depending on the coordination mode of the DMTP ligands to the metal ions in the series of complexes studied. The enthalpies of several of the decomposition processes were calculated.

INTRODUCTION

It is well known that many derivatives of the pyrimidine base are constituents of molecules existing in living systems. Likewise, there is strong evidence for the important roles played by certain metal ions in many of the biological processes in which these molecules are involved [1]. Therefore, the study of the interactions between pyrimidine derivatives and metal ions has become a research area that has grown considerably in recent years [1–4]. Moreover, many thiopyrimidine derivatives as well as some of their metal complexes, e.g. the platinum pyrimidine blues [3], have been used as chemotherapeutic agents [5–8].

In the present paper, we describe the thermal characterization of the following metal complexes obtained by the reaction of 4,6-dimethyl-2-thiopyrimidine (DMTP) with metal ions: $Zn(DMTP)_2Cl_2$, $Cd(DMTP)_2Cl_2$,

---

* Corresponding author.

$HgDMTPCl_2$, $Pd(DMTP)_2Cl_2$, $Pt(DMTP)_2Cl_2$, and $AuDMTPCl_3$, which were synthesized and characterized as reported in a previous paper [9].

EXPERIMENTAL

The pyrimidine derivative used, DMTP, was of reagent grade quality and was obtained from commercial sources. It was used without further purification.

The preparative methods for the isolated complexes have been described in a previous paper [9]. The chemical analyses are summarized in Table 1.

The TG and DTG curves of DMTP and the six complexes under study were obtained on a Mettler TG50 thermobalance, and the DSC curves were recorded using a Mettler DS20 differential scanning calorimeter, with a 10°C min^{-1} heating rate and sample weights of between 8.428 and 15.195 mg, for the TG and DSC curves, and between 1.930 and 2.423 mg, for the DSC curves. TG curves were obtained with an oxygen flow rate of 100 ml $min.^{-1}$ and DSC curves were measured in a static air atmosphere. The IR spectra of the residues obtained from the pyrolytic processes were recorded on a Perkin-Elmer 983G spectrophotometer using KBr pellets in the 4000–600 cm^{-1} range, and polyethylene pellets in the 600–180 cm^{-1} range.

TABLE 1

Colour and analytical data (theoretical values in parentheses)

Compound	Colour	C%	H%	N%
$Zn(DMTP)_2Cl_2$	Pale yellow	34.46 (34.58)	3.84 (3.84)	13.62 (13.45)
$Cd(DMTP)_2Cl_2$	Pale yellow	30.79 (31.07)	3.44 (3.45)	12.22 (12.08)
$Hg(DMTP)Cl_2$	White	18.53 (17.49)	1.80 (1.94)	7.34 (6.80)
$Pd(DMTP)_2Cl_2$	Dark brown	29.50 (31.48)	2.90 (3.50)	11.33 (12.24)
$Pt(DMTP)_2Cl_2$	Orange	25.07 (26.36)	2.24 (2.93)	9.77 (10.25)
$Au(DMTP)Cl_3$	Dark brown	16.07 (16.23)	1.71 (1.80)	6.27 (6.31)

RESULTS AND DISCUSSION

The ^{13}C- and ^{1}H-NMR spectral data of DMTP suggest that this compound is in the dimeric form shown in Fig. 1. This is due to the existence of two N–H···S hydrogen bonds [10].

The analytical data and formulae of the complexes are also collected in Table 1. It can be seen that all the complexes are anhydrous and contain the organic ligand, DMTP, in the neutral molecular form.

The IR, ^{13}C- and ^{1}H-NMR data of the six complexes indicate the existence of three different coordination patterns of DMTP to the six metal ions studied. Monodentate S-coordination was established for the Zn(II)

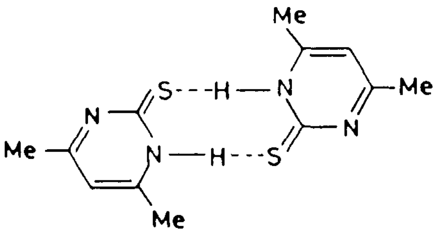

Fig. 1. Dimeric structure of DMTP.

and Cd(II) complexes. This was demonstrated by the X-ray diffraction data obtained from suitable monocrystals of these two complexes, whose tetrahedral molecular structures are showed in Fig. 2.

Because of the similarity between the IR and NMR spectral data of $AuDMTPCl_3$ and those of the Zn(II) and Cd(II) complexes, it has been established that DMTP is also S-coordinated in the Au(III) complex.

The spectral data of both $Pd(DMTP)_2Cl_2$ and $Pt(DMTP)_2Cl_2$ clearly show that DMTP acts as a monodentate ligand through one of the N cyclic atoms, whereas in the case of $HgDMTPCl_2$, DMTP acts as an S—N_{cyclic} chelating ligand. In all of the complexes, the Cl ions are also coordinated to the corresponding metal ions. The proposed structures for the complexes are tetrahedral for the Zn(II), Cd(II) and Hg(II) complexes, and square-planar for the Pd(II), Pt(II) and Au(III) diamagnetic complexes.

The TG and DSC curves of DMTP and of the metal complexes are shown in Figs. 3 and 4 respectively, and the corresponding thermal data of the complexes obtained from these curves are summarized in Table 2.

The TG curve of DMTP shows an abrupt weight loss which starts at about 120°C and finishes at 320°C; this is accompanied by a sharp endothermic effect at 219°C in the DSC curve. The accumulated weight loss for this effect is 91.8% and it corresponds to sublimation of part of the DMTP sample, as demonstrated by IR spectroscopy of the sublimated sample. The remaining unsublimated DMTP simultaneously starts the pyrolytic decomposition which takes place in the 320–700°C temperature range, with complete combustion of the sample. The energy of the sublimation process is $72.4\,kJ\,mol^{-1}$, which suggests the breaking of the above-cited hydrogen bonds in the $(DMTP)_2$ dimers and also suggests an approximate value for each of these bonds of $35\,kJ\,mol^{-1}$.

The TG and DSC curves of $Zn(DMTP)_2Cl_2$ and $Cd(DMTP)_2Cl_2$ complexes are very similar (see Figs. 3 and 4) which, because they have similar molecular structures, suggests that they also have similar thermal decomposition mechanisms. These TG curves show a first step which consists of an abrupt weight loss whose value is 35.0% in the case of $Zn(DMTP)_2Cl_2$. This is in good agreement with the theoretical weight loss corresponding to the sublimation of one of the two DMTP molecules attached to the Zn(II) ion. Moreover, gentle heating of the Zn(II) and

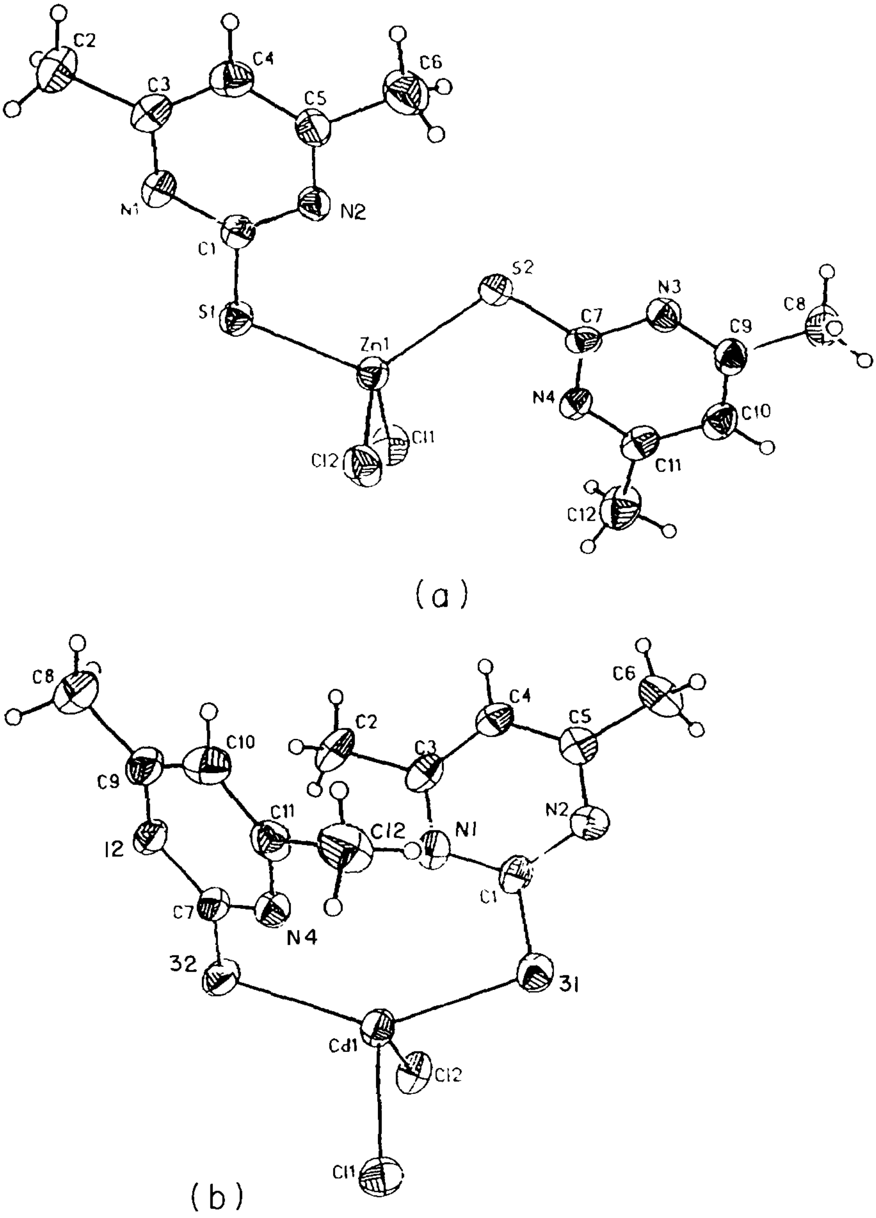

Fig. 2. Tetrahedral structures of (a) $Zn(DMTP)_2Cl_2$, and (b) $Cd(DMTP)_2Cl_2$.

Cd(II) complexes led to sublimation of DMTP, as demonstrated by IR spectroscopy; the endothermic effects corresponding to this process are clearly differentiated in the DSC plots of the complexes and the relative values of their energies suggest that the S—Cd bond is stronger than the S—Zn bond in the corresponding complexes. The DTG curve of $Zn(DMTP)_2Cl_2$ shows a second minimum, peaking at 386°C, which

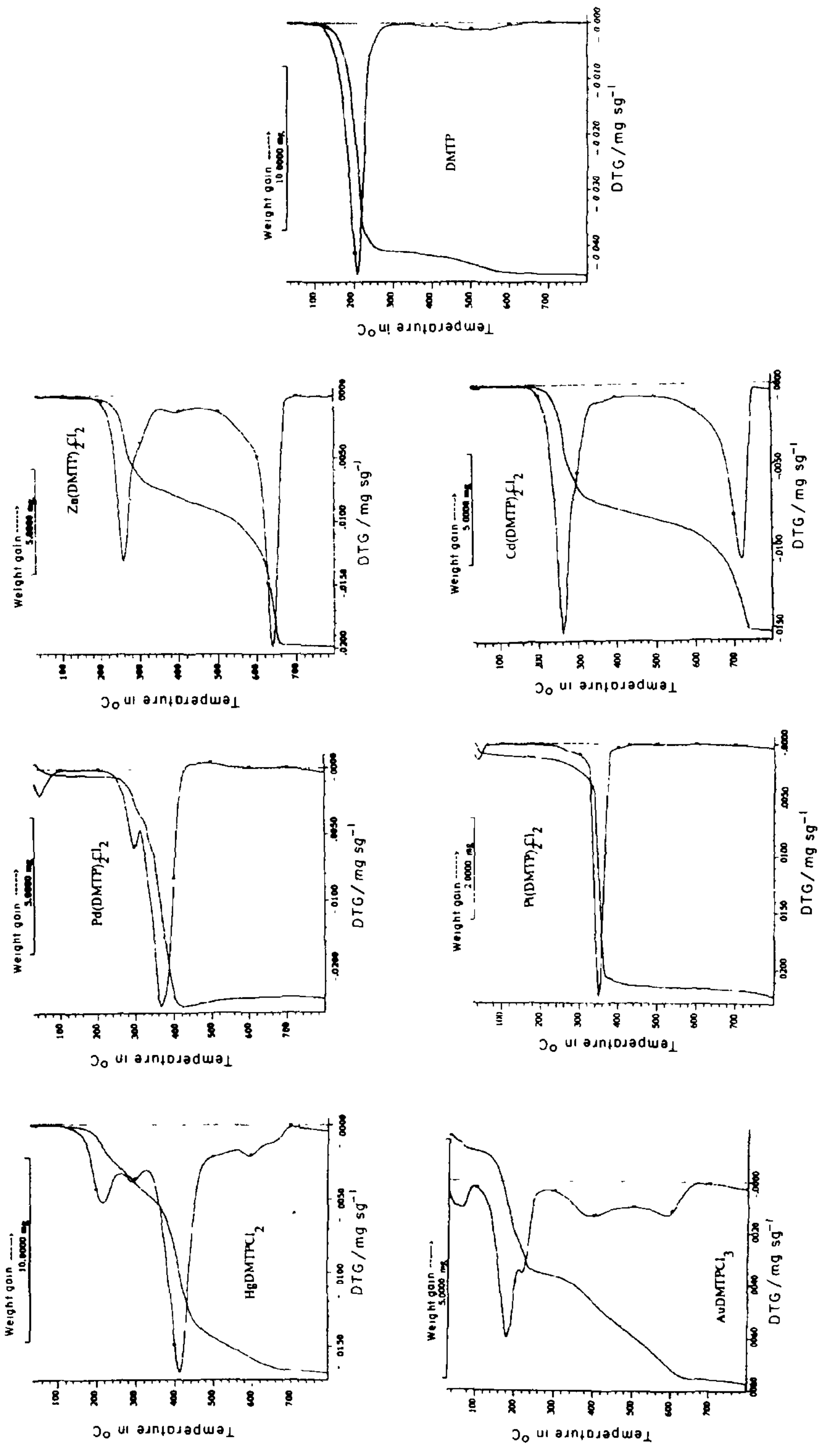

Fig. 3. TG and DTG plots of DMTP and the metal complexes.

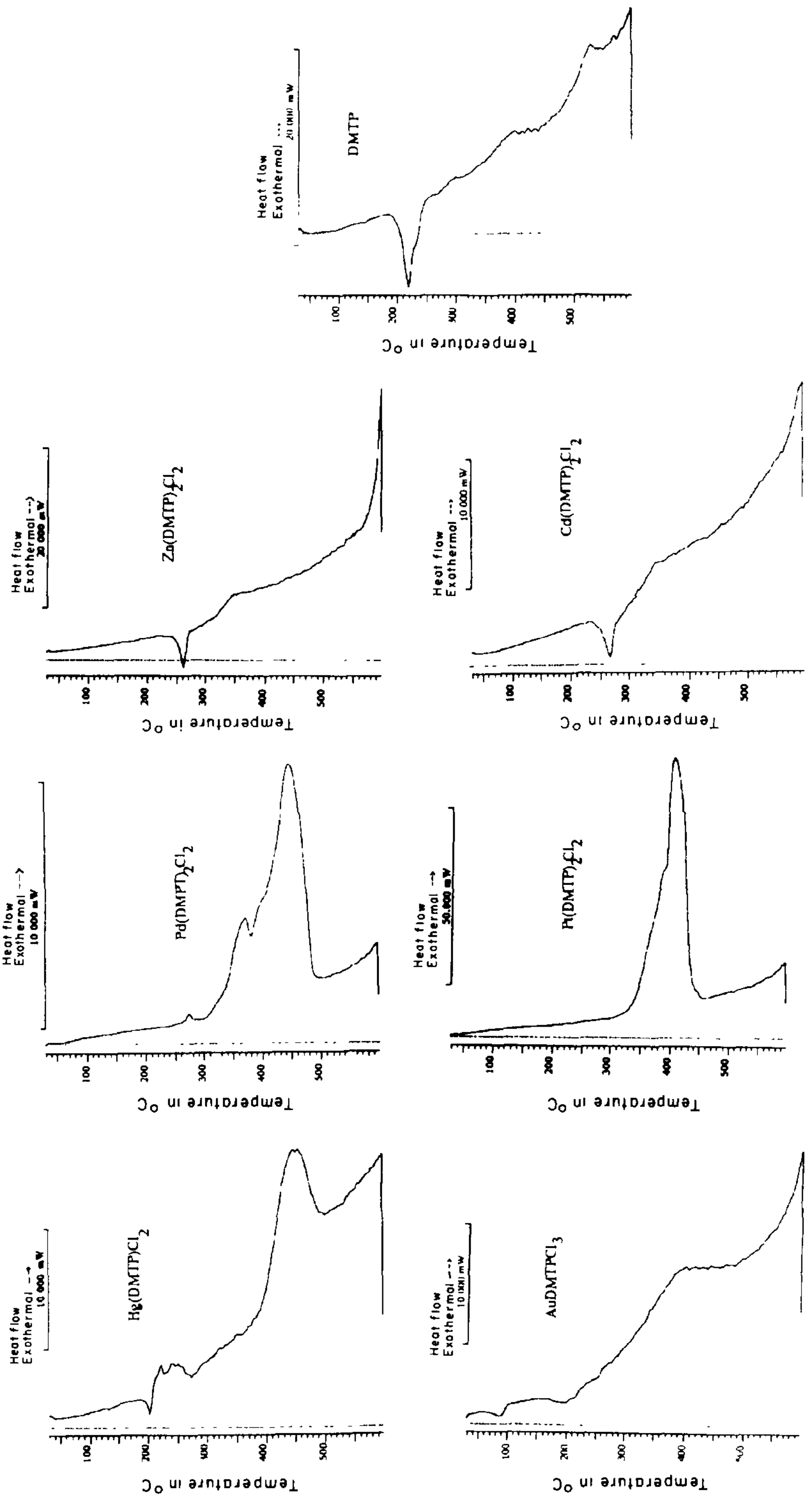

Fig. 4. DSC plots of DMTP and the metal complexes.

corresponds to an accumulated weight loss in the TG curve of 41.9%, which is in agreement with that corresponding to the loss of an HCl molecule. The same happens with the $Cd(DMTP)_2Cl_2$ complex. In confirmation, samples of Zn(II) and Cd(II) complexes were heated up to the theoretical temperatures at which the HCl molecules are lost and their IR spectra were then obtained in the 600–180 cm^1 range. These spectra clearly show the absence of the Zn—Cl stretching vibration band of $Zn(DMTP)_2Cl_2$ at 269 cm^{-1}, and that of the Cd—Cl stretching vibration of $Cd(DMTP)_2Cl_2$ at 206 cm^{-1}, and the appearance of new M–Cl stretching vibration bands corresponding to the formation of $ZnCl_2$ (298 cm^{-1}) and $CdCl_2$ (249 cm^{-1}) [11, 12]. All these data suggest that the following processes occur during the onset of the pyrolytic decomposition of the Zn(II) and Cd(II) complexes: $M(DMTP)_2Cl_2 \rightarrow HCl + 0.5MCl_2 + DMTP\ (sublim.) + 0.5M(DMTP)_2$. The resulting residues decompose in the 440–680°C temperature range in the case of the Zn(II) complex, and in the 400–760°C temperature range in that of the Cd(II) complex. At the final temperatures, the residues were ZnO, and a mixture of CdO and unsublimated $CdCl_2$ [13], respectively.

The TG curve of the compound $AuDMTPCl_3$ shows a first slight weight loss which corresponds to the loss of 2.5% of non-stoichiometric water; the energy of the corresponding endothermic process, which is centred at 88.1°C is equal to 17.2 kJ mol^{-1}. The dehydrated compound begins its pyrolytic decomposition at 130°C (see the TG plot) with the partial sublimation of DMTP (this was demonstrated by IR spectroscopy of the sublimated sample). The energy calculated for this process in the DSC plot by integrating the corresponding endothermic effect was $\Delta = -68.5$ kJ mol^{-1}. The pyrolysis of the unsublimated DMTP is completed at the end of a second weight loss step which appears on the TG curve in the 280–500 cm^{-1} range, with an accumulated weight loss of 34.2% in very good agreement with the theoretical value (34.22%). The similarity in the thermal behaviours of the Zn(II), Cd(II) and Au(III) complexes is obviously related to the lability of the metal–S bonds characteristic of these compounds. The lower sublimation temperature and energy of the Au(III) complex than those of the Zn(II) and Cd(II) complexes, for the DMTP sublimation, suggest that the weakest M–S bonds are the Au–S bonds. The final product of the pyrolysis of the Au(III) complex at 640°C was Au_2O_3 which is reduced to Au(0) at this temperature.

In contrast, the complexes $Pd(DMTP)_2Cl_2$ and $Pt(DMTP)_2Cl_2$ are stable up to an approximate temperature of 240°C, when pyrolysis of the CH_3 substituents on the DMTP molecules takes place, as was demonstrated by the IR spectrum of a sample of the Pd(II) complex which had been previously heated up to the final temperature of the first step of the pyrolysis (315°C); the found and calculated weight losses for this process are in good agreement in both complexes (see Table 2). The structural similarity between the Pd(II) and Pt(II) complexes explains the similarity

TABLE 2

Thermoanalytical data of the metal complexes

Complex	Process	Temperature/°C	ΔH/ kJ mol^{-1}	Accumulated weight loss in %		Residue		
				Found	Calculated	Compound[a]	Weight loss in %	
							Found	Calculated
Zn(DMTP)$_2$Cl$_2$	DMTP sublimation	261.9(endo)	−75.65	35.00	33.80	ZnO	9.10	9.67
	HCl loss	≈380	–	41.90	42.51			
	Pyrolysis	440–680(exo)	–	–	–			
Cd(DMTP)$_2$Cl$_2$	DMTP sublimation	269.0(endo)	−84.62	–[b]	–	CdO	20.20[c]	13.79
	HCl loss	≈380	–	39.90	38.20			
	Pyrolysis	400–760(exo)	–	–	–			
Au(DMTP)Cl$_3$	DMTP sublimation	199.2(endo)[d]	−68.50	–	–	Au$_2$O$_3$	48.10	49.83
	Pyrolysis	280–700(exo)	–	–	–			
Pd(DMTP)$_2$Cl$_2$	Pyrolysis of CH$_3$ substituents	250–300(exo)	31.67	12.60	13.06	PdO	31.52[c]	26.53
	Pyrolysis of the rest	365.3(exo) 448.2(exo)	5119.50	–	–			
Pt(DMTP)$_2$Cl$_2$	Pyrolysis	409 (exo)	5564.80	–	–	PtO	43.55[c]	38.38
Hg(DMTP)Cl$_2$	Melting	204.1(endo)	−13.70	–	–		Non-existent	
	HgCl$_2$ sublimation	273.2(endo)	–	–	–			
	Pyrolysis	445(exo)	664.00	–	–			

[a] The composition of the residues corresponds to the final temperature of the pyrolysis. [b] This step overlaps with that corresponding to the HCl loss. [c] See text. [d] This step overlaps with the start of the pyrolytic decomposition.

of their TG and DSC plots and also suggests their similar thermal behaviours. However, the fact that DMTP molecules do not sublime during the heating of these compounds, suggests that the metal–N bonds are stronger in these two compounds than the metal–S bonds in the Zn(II), Cd(II) and Au(III) complexes.

After the pyrolysis of the CH_3 substituents, the remainder of the DMTP molecules attached to the Pd(II) and Pt(II) ions decomposes steadily. The processes are complete at 420°C (Pd(II) complex) and at 380°C (Pt(II) complex) when PdO and PtO residues, contaminated by the corresponding sulphates, were determined by IR spectroscopy.

In the case of the $HgDMTPCl_2$ complex, the TG and DSC plots show a thermal behaviour that is different from those of the two series of complexes cited above. This accords with the different coordination pattern (N···S chelation) of DMTP to the Hg(II) ion in this complex. The complex melts at 201.1°C ($\Delta H = -13.7$ kJ mol^{-1}), at which temperature the pyrolytic decomposition of the compound also starts without DMTP sublimation. This decomposition consists of the oxidation of the organic part of the compound together with the sublimation of $HgCl_2$ (endothermic effect at 273.2°C) which are completed at 660°C when there is no residue left in the crucible.

ACKNOWLEDGEMENT

The authors thank the CICYT for financial support (FAR 89/414) of this work.

REFERENCES

1 T.D. Tullius (Ed.), ACS Symposium Series: Metal DNA Chemistry, Johns Hopkins Univ., Washington, 1989.
2 H. Sigel, Metal Ions in Biological Systems, Vol. 8, M. Dekker, New York, 1979.
3 H. Sigel, Metal Ions in Biological Systems, Vol. 11, M. Dekker, New York, 1980.
4 H. Sigel, Metal Ions in Biological Systems, Vol. 25, M. Dekker, New York, 1989.
5 V.N. Krishna Murthy, K.V. Nagaswara Rao, P.L. Narasimha Rao and B. Praphulla, Br. J. Pharmacol. Chemother., 31 (1967) 1.
6 R.H. Lyndsay, H. Nakagawa and P. Philipcohen, Endocrinology, 76 (1965) 728.
7 I. Votruba, A. Holy and K. Jost, FEBS Lett., 22 (1972) 287.
8 M.Y.W. Yu, J. Seddlack and R.H. Lyndsay, Arch. Biochem. Biophys., 135 (1973) 111.
9 R. Lopez-Garzón, M. Gutierrez-Valero, M.L. Godino-Salido, B.K. Keppler and B. Nuber, submitted.
10 B.G. Olby and S.D. Robinson, Inorg. Chim. Acta, 165 (1989) 153.
11 J.N. Ferraro, Low Frequency Vibrations of Inorganic and Coordination Compounds, Plenum, New York, 1971.
12 M. Romero-Molina, M. Gutierrez-Valero, R. López-Garzón, J.M. Salas, M. Arriortúa and F.J. Zúñiga, Inorg. Chim. Acta, 136 (1987) 87.
13 F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 5th edn., Wiley, New York, 1988.