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Thermal behaviour of metal complex with isoorotate and 2-thioisoorotate monoanions

F. Hueso-Ureña and M.N. Moreno-Carretero *

Departamento de Química Inorgánica, Facultad de Ciencias Experimentales, Universidad de Granada, 23071-Jaén (Spain)

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Abstract

The thermal behaviour of $M^{II}(H_2L)_2 \cdot 2H_2O$ complexes ($H_2L^- =$ isoorotate and 2-thioisoorotate monoanions; M = Mn, Fe, Co, Ni, Cu, Zn, Pd, Pt) has been studied by TG, DTG and DSC methods. The thermal decomposition of these compounds takes place in two steps: dehydration and pyrolytic decomposition. The TG and DSC data suggest that water molecules are structurally well defined, being coordinated to the metal ion, with the exception of the Pd(II) and Pt(II) complexes. When possible, the weight-loss effects have been assigned from the IR spectra of intermediate species.

INTRODUCTION

This paper describes a study of the thermal behaviour of eleven new complexes of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Pd(II) and Pt(II) of general formula $M^{II}(H_2L)_2 \cdot 2H_2O$ containing isoorotic (5-carboxyuracil, H_3CU) or 2-thioisoorotic (5-carboxy-2-thiouracil, H_3CTU) acids as organic ligands. This is part of a more extensive work whose major purpose is the study of metal complexes with 5-substituted uracil ligands from both the structural and biological points of view [1–11]. The study of the thermal behaviour of the isolated complexes forms a section of these investigations which provides useful information on the coordinative capacity and structural definition of the solvent molecules, as well as on the stability of the isolated compounds and the mechanisms of their pyrolysis [12–15]. In this way, the thermal behaviour of free isoorotic and 2-thioisoorotic acids and their NH_4^+, Na^+ and Ba^{2+} salts [16], as well as the thermal behaviour of several transition metal complexes with these uracil derivatives in both dianionic [17] and neutral form [18], have already been published. In order to complete the information obtained concerning this subject, this paper

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* Author to whom correspondence should be addressed.

presents the study of the thermal degradation of metal complexes with H_2CU^- and H_2CTU^- monoanions.

EXPERIMENTAL

Apparatus

Microanalyses of carbon, hydrogen and nitrogen were performed by the Technical Services of the University of Granada. Thermogravimetric (TG) and differential scanning calorimetry (DSC) curves were recorded on a Mettler TA-3000 system provided with a Mettler TG-50 thermobalance and a Mettler DSC-20 differential scanning calorimeter. TG diagrams were recorded in a dynamic atmosphere of pure air (100 ml $\min^{-1}$) and DSC curves were obtained in a static air atmosphere. The heating rate was 10 °C $\min^{-1}$ and the weight of samples was between 1.50 and 13.00 mg. IR spectra of isolated complexes and intermediate species obtained during pyrolytic processes were recorded as KBr pellets using a Perkin–Elmer 983-G apparatus in the 4000–250 cm^{-1} wavenumber range.

Preparation of complexes

The isoorotic and 2-thioisoorotic acids used in the present work were purchased from Sigma and used without further purification. All the chemicals used were analytical reagent grade.

The $M^{II}(H_2L)_2 \cdot 2H_2O$ complexes were synthesized as follows:

$Mn(H_2CTU)_2 \cdot 2H_2O$, $Zn(H_2CTU)_2 \cdot 2H_2O$ and $Fe(H_2CTU)_2 \cdot 2H_2O$

To 200 ml of hot solvent (ethanol for manganese and zinc complexes and water for the iron complex) containing 2 mmol of H_3CTU were added, slowly with stirring, 1 mmol of $MnCl_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$ of $FeSO_4 \cdot 7H_2O$ respectively, dissolved in the minimum amount of solvent. After half an hour for the first complex and instantaneously for the other two, a solid was precipitated.

$Co(H_2CU)_2 \cdot 2H_2O$ and $Ni(H_2CTU)_2 \cdot 2H_2O$

H_3CU (2 mmol) and H_3CTU (2 mmol) respectively were dissolved in 200 ml of hot water. To the solution obtained, 0.5 mmol of the corresponding carbonate was added. After stirring the resulting suspension for a few hours, the volume was reduced to around 50 ml. At this point, both complexes were precipitated.

$Pd(H_2CTU)_2 \cdot 2H_2O$, $Pt(H_2CTU)_2 \cdot 2H_2O$, $Co(H_2CTU)_2 \cdot 2H_2O$, $Cu(H_2CU)_2$ $2H_2O$ and $Zn(H_2CU)_2 \cdot 2H_2O$

The uracil ligand (1mmol) was dissolved in 100 ml of water with heating at around 70 °C; 1 mmol of the corresponding metal salt (K_2PdCl_4,

TABLE 1

Analytical data [a] and colour of isolated complexes

Compound	C (%)	H (%)	N (%)	M (%)	Colour
$Mn(H_2CU)_2\cdot 2H_2O$	30.19	2.51	14.90	10.64	White
	(29.94)	(2.52)	(13.97)	(13.69)	
$Co(H_2CU)_2\cdot 2H_2O$	29.78	2.18	14.48	14.77	Pink
	(29.64)	(2.49)	(13.83)	(14.54)	
$Cu(H_2CU)_2\cdot 2H_2O$	29.12	2.22	13.30	15.22	Light blue
	(29.31)	(2.46)	(13.68)	(15.51)	
$Zn(H_2CU)_2\cdot 2H_2O$	29.00	2.23	13.16	15.86	White
	(29.18)	(2.45)	(13.61)	(15.88)	
$Pd(H_2CU)_2\cdot 2H_2O$	25.27	2.15	13.14	26.59	Grey
	(26.53)	(2.23)	(12.38)	(23.51)	
$Fe(H_2CTU)_2\cdot 2H_2O$	28.05	2.29	13.32	13.37	Orange
	(27.66)	(2.33)	(12.91)	(12.86)	
$Co(H_2CTU)_2\cdot 2H_2O$	27.47	2.25	13.06	15.73	Pink
	(27.46)	(2.31)	(12.82)	(13.48)	
$Ni(H_2CTU)_2\cdot 2H_2O$	28.07	2.22	12.60	12.29	Light green
	(27.48)	(2.31)	(12.82)	(13.43)	
$Zn(H_2CTU)_2\cdot 2H_2O$	27.39	1.98	12.60	14.43	White
	(27.07)	(2.28)	(12.63)	(14.73)	
$Pd(H_2CTU)_2\cdot 2H_2O$	24.33	1.65	11.42	21.65	Brown
	(24.78)	(2.08)	(11.56)	(21.95)	
$Pt(H_2CTU)_2\cdot 2H_2O$	20.68	1.54	10.06	36.07	Green
	(20.94)	(1.76)	(9.77)	(34.02)	

[a] Calculated values in parentheses.

K_2PtCl_4, $CoCl_2\cdot 6H_2O$, $CuCl_2\cdot 2H_2O$ or $Zn(NO_3)_2\cdot 6H_2O$), dissolved in the minimum amount of water, was then added. The resulting solution was stirred for a few hours and the volume was reduced to 50 ml. When the solution was cool the complexes were isolated.

$Pd(H_2CU)_2\cdot 2H_2O$

The synthesis of this compound was carried out using the same method as that described above for its analogous complex with the H_2CTU^- monoanion, the only difference being that 2 mmol of NaN_3 were added to the solution containing H_3CU ligand and K_2PdCl_4 in the molar ratio 2:1. When the solution was allowed to stand at room temperature, the complex appears as a grey powder. It must be pointed out that if sodium azide is not added, the $PdCl_2(H_3CU)_2$ complex is obtained.

All isolated complexes were filtered by suction, washed consecutively with ethanol and diethyl ether, and air dried. The analytical data and colour of the complexes are given in Table 1.

RESULTS AND DISCUSSION

Spectral (IR, NMR, visible) and magnetic measurements [19] indicate that, with the exception of Pd(II) and Pt(II) compounds with H_2CTU^-, all complexes seem to have octahedral structures in which the monoanionic ligands, H_2L^-, are bound to the metal ion through the O-4 atom and an oxygen atom of the carboxylate group, both water molecules being directly coordinated to the metallic centre. For Pd(II) and Pt(II) compounds with the 2-thioisoorotate monoanion, two square-planar structures can be proposed: in the first, a monomer $M^{II}S_2(H_2O)_2$ may be suggested; the other possibility is the formation of a dimeric structure with two metal ions bound through four carboxylate-bridging H_2CTU^- monoanions.

TG, DTG and DSC diagrams for these complexes are shown in Figs. 1–3. From these plots, it can easily be observed that, in all cases, the thermal decomposition starts with the loss of water molecules. The thermoanalytical data referring to the dehydration processes have been collected in Table 2. The data obtained indicate that the water molecules are structurally well defined, with the exception of the Pd(II) and Pt(II) compounds (Fig. 3), as may be inferred from the form of the associated endothermic effects, the

TABLE 2

Thermoanalytical data for dehydration processes

Compound	Process	Weight loss [a] (%)	ΔT, TG (°C)	T_{peak}, DSC (°C)	ΔH (kJ mol^{-1})
$Mn(H_2CU)_2 \cdot 2H_2O$	$-2H_2O$	9.1 (8.98)	200–260	225	101
$Co(H_2CU)_2 \cdot 2H_2O$	$-2H_2O$	9.5 (8.89)	180–260	228	84
$Cu(H_2CU)_2 \cdot 2H_2O$	$-2H_2O$	9.3 (8.79)	100–175	156	77
$Zn(H_2CU)_2 \cdot 2H_2O$	$-2H_2O$	9.8 (8.75)	150–250	230	67
$Pd(H_2CU)_2 \cdot 2H_2O$	$-2H_2O$	8.1 (7.96)	50–200	140	45
$Fe(H_2CTU)_2 \cdot 2H_2O$	$-2H_2O$	8.7 (8.30)	150–260	223	46
$Co(H_2CTU)_2 \cdot 2H_2O$	Overlapping with pyrolysis				
$Ni(H_2CTU)_2 \cdot 2H_2O$	Overlapping with pyrolysis				
$Zn(H_2CTU)_2 \cdot 2H_2O$	$-H_2O$	5.0 (4.06)	75–200	137	30
$Pd(H_2CTU)_2 \cdot 2H_2O$	$-2H_2O$	7.3 (7.43)	40–200	73	32
$Pt(H_2CTU)_2 \cdot 2H_2O$	$-2H_2O$	6.7 (6.28)	40–160	72	29

[a] Calculated values in parentheses.

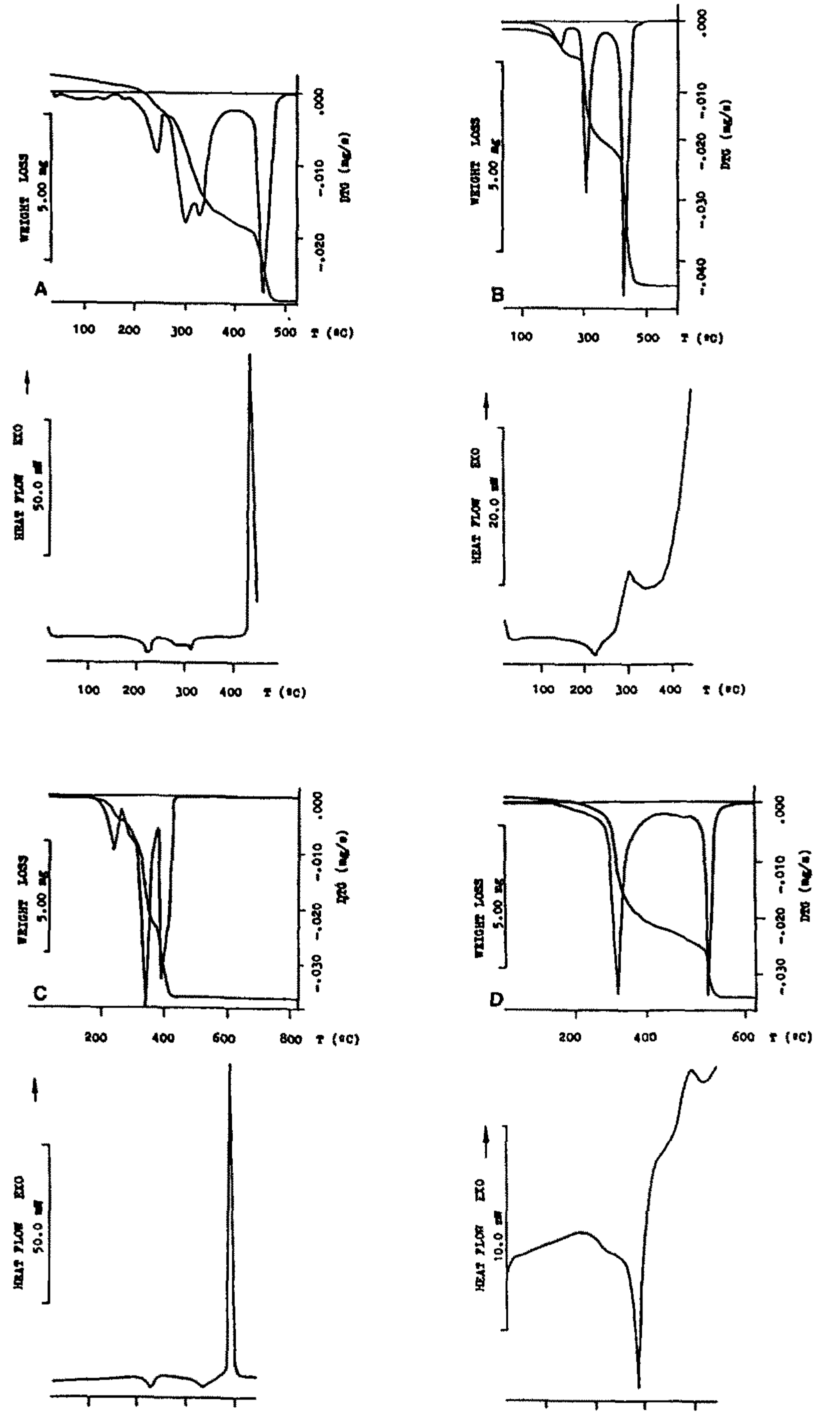

Fig. 1. TG and DSC curves of: A, $Mn(H_2CU)_2 \cdot 2H_2O$; B, $Fe(H_2CTU)_2 \cdot 2H_2O$; C, $Co(H_2CU)_2 \cdot 2H_2O$; D, $Co(H_2CTU)_2 \cdot 2H_2O$.

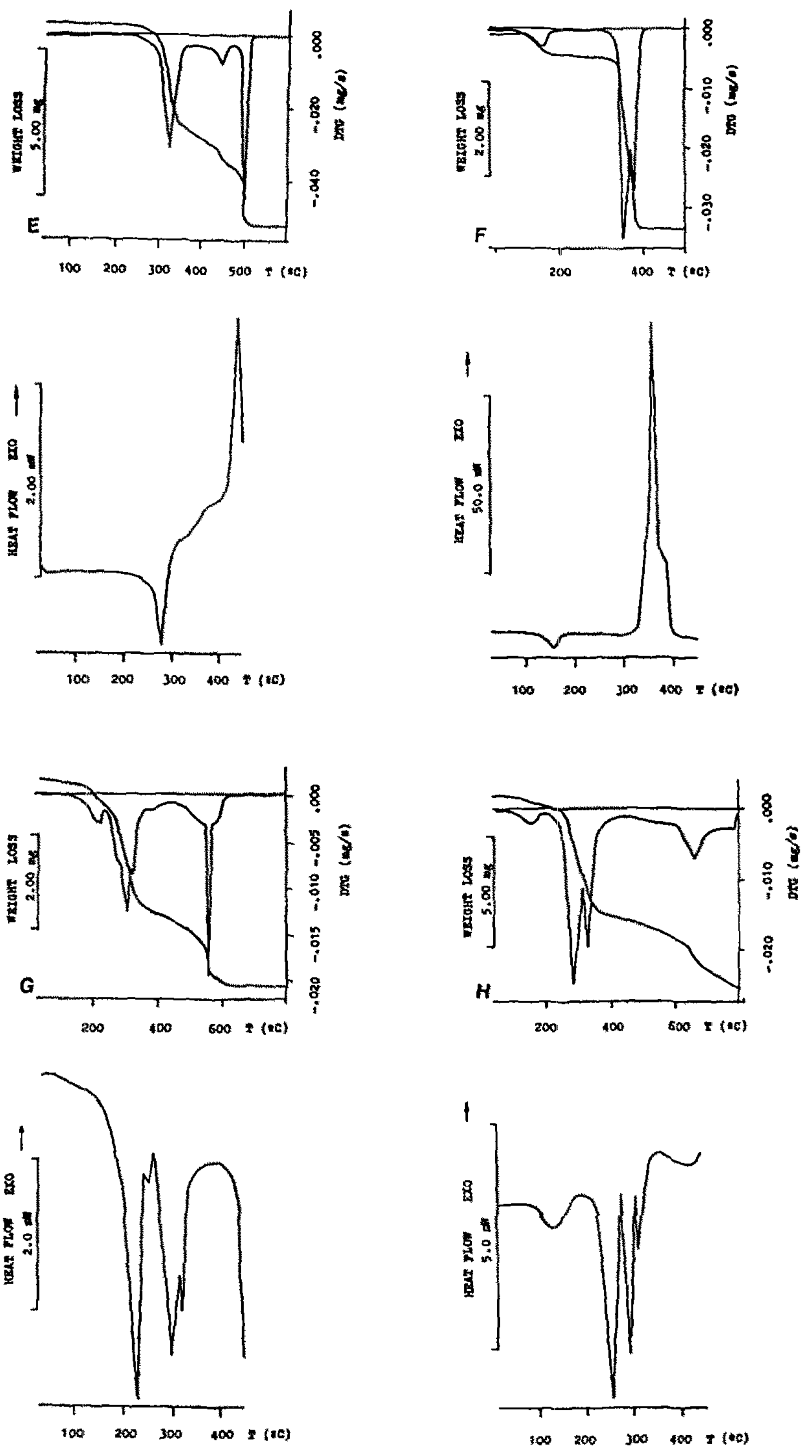

Fig. 2. TG and DSC curves of: E, $Ni(H_2CTU)_2 \cdot 2H_2O$; F, $Cu(H_2CU)_2 \cdot 2H_2O$; G, $Zn(H_2CU)_2 \cdot 2H_2O$; H, $Zn(H_2CTU)_2 \cdot 2H_2O$.

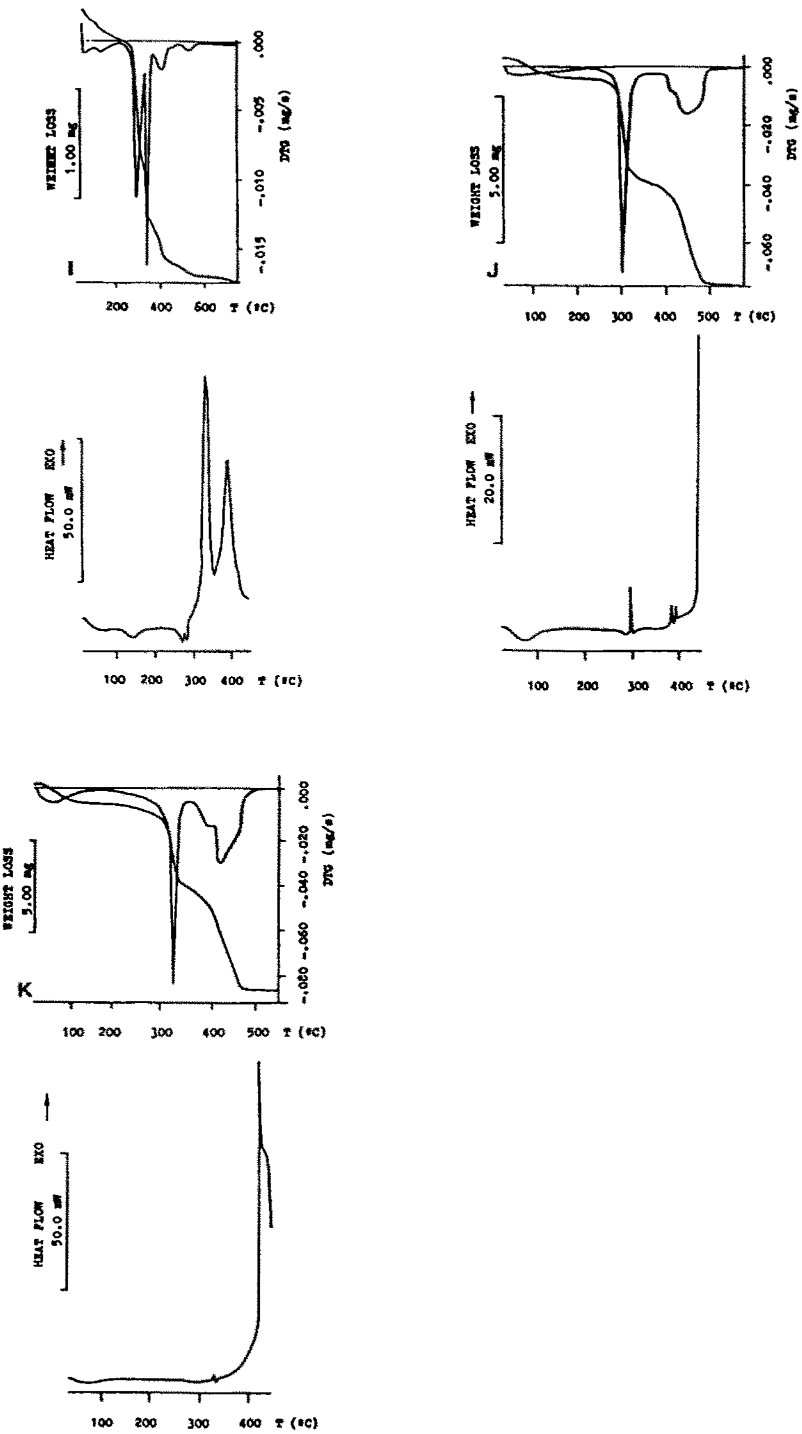

Fig. 3. TG and DSC curves of: I, $Pd(H_2CU)_2 \cdot 2H_2O$; J, $Pd(H_2CTU)_2 \cdot 2H_2O$; K, $Pt(H_2CTU)_2 \cdot 2H_2O$.

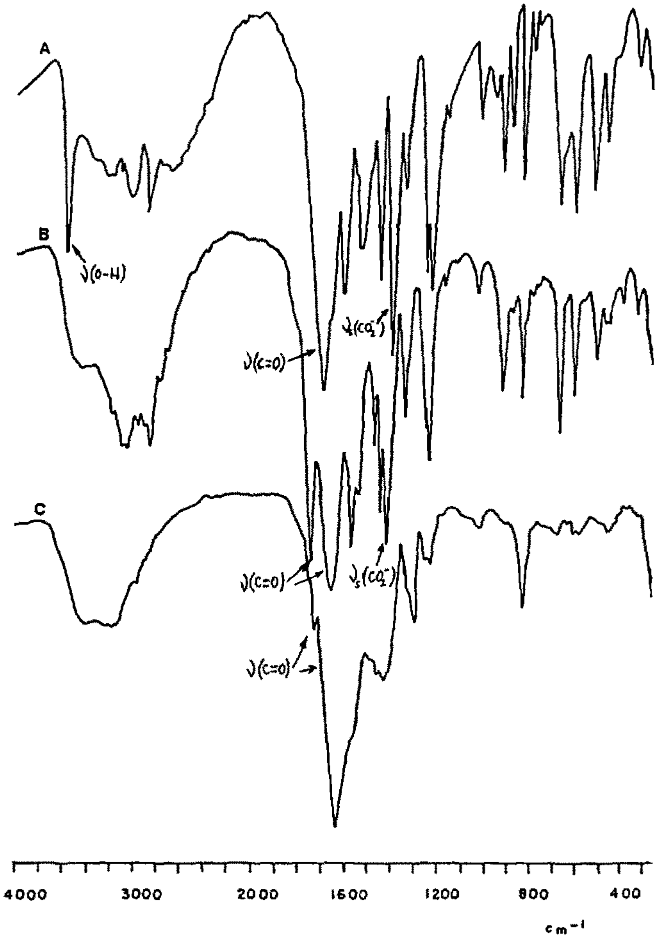

Fig. 4. IR spectra of $Co(H_2CU)_2 \cdot 2H_2O$: curve A, before heating; curve B, heated at 260 °C; curve C, heated at 370 °C.

enthalpy values being in good accordance with those expected for the loss of coordinated water [12,20–22]. In the case of the $Zn(H_2CTU)_2 \cdot 2H_2O$ complex (Fig. 2H), the water molecules are not both lost at the same time, the elimination of the second molecule overlapping with the pyrolytic process. This also takes place in the Co(II) and Ni(II) complexes with 2-thioisoorotate monoanion (Figs. 1D and 2E).

When possible, the dehydration effects were verified by IR spectroscopy, the IR spectra of anhydrous species showing the characteristic disappearance of the sharp band at about 3500 cm^{-1} assigned to the stretching vibration of water O–H bonds in the IR spectra of the hydrated compounds. As an example, the IR spectra of $Co(H_2CU)_2 \cdot 2H_2O$ and $Co(H_2CU)_2$ (obtained by heating the hydrated complex at 260 °C) are shown in Figs. 4A and 4B. A comparison of these spectra reveals that both water molecules, in

TABLE 3

TG and DSC data for pyrolytic processes

Compound	T_{final} (°C)	Weight loss [a] (%)	Residue	T_{peak}, DSC (°C)
$Mn(H_2CU)_2 \cdot 2H_2O$	480	81.0 (80.99)	Mn_3O_4	312 endo 420 exo
$Co(H_2CU)_2 \cdot 2H_2O$	420	79.9 (80.19)	Co_3O_4	337 endo 390 exo
$Cu(H_2CU)_2 \cdot 2H_2O$	400	80.9 (80.59)	CuO	360 exo
$Zn(H_2CU)_2 \cdot 2H_2O$	625	80.6 (80.21)	ZnO	288 endo
$Pd(H_2CU)_2 \cdot 2H_2O$	> 750	69.9 (72.95)	PdO	271, 282 endo 340, 390 exo
$Fe(H_2CTU)_2 \cdot 2H_2O$	480	81.6 (82.22)	Fe_3O_4	305, > 440 exo
$Co(H_2CTU)_2 \cdot 2H_2O$	530	79.7 (81.64)	Co_3O_4 [b]	287 endo 410 exo
$Ni(H_2CTU)_2 \cdot 2H_2O$	510	81.4 (82.90)	NiO [b]	276 endo
$Zn(H_2CTU)_2 \cdot 2H_2O$	800	82.0 (81.65)	ZnO [b]	259, 297, 315 endo 360 exo
$Pd(H_2CTU)_2 \cdot 2H_2O$	490	75.1 (74.73)	PdO [b]	295 exo > 450 exo
$Pt(H_2CTU)_2 \cdot 2H_2O$	480	63.9 (65.95)	Pt	430 exo

[a] Calculated values in parentheses.

[b] Residue contaminated with the corresponding sulphate.

addition to being bound to the metal ion, are involved in hydrogen bonds, probably with the oxygen atoms of carbonyl groups, because on dehydration the band corresponding to the stretching vibration of C=O bonds is shifted to higher wavenumbers. Moreover, the 1550–1750 cm^{-1} range appears to be better resolved as a consequence of the disappearance of the δ(O–H) vibration bands.

Once dehydrated, all the complexes undergo a pyrolytic process that is reflected in their DSC diagrams by several heat-change effects. Data corresponding to these processes are given in Table 3. From these data, it may be observed that most complexes show an endothermic effect at about 300 °C that can be assigned to the decarboxylation of the compounds [23]. However, the observed weight losses are higher than those expected for CO_2 elimination alone. This has also been observed in the thermal study of the free ligands and their sodium and ammonium salts [16]. Therefore, this effect must include other decomposition processes. The IR spectra of compounds heated just to the end of this weight loss (around 300–350 °C) (see Fig. 4C as an example) show no evidence of carboxylate bands (symmetric stretching appears at about 1380 cm^{-1}) and the absence of the band at about 1700 cm^{-1} that can be assigned to the stretching vibration of a carbonyl group (probably the substituent in the 2-position of the uracil ring). Figure 4C indicates that on heating these compounds to about 350 °C the resulting IR spectrum shows a lower number of bands than expected for the corresponding uracilato complex (only CO_2 loss), this IR spectrum being very similar to the one obtained when free ligands are heated at 415 °C [16]. All these conclusions can be verified, as an example, by comparison of the spectra shown in Figs. 4B and 4C.

The exothermic effects (Table 3) can be assigned to the combustion of the residual organic matter. This process leaves the corresponding metallic oxide as a residue, with the exception of the Pt(II) compound which leaves metallic platinum. In 2-thioisoorotate complexes, the residue is contaminated by the presence of a small amount of the corresponding sulphate. In all cases, the nature of the residues was investigated by IR spectroscopy. Thermoanalytical data are given in Table 3.

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