SOLID-STATE COMPOUNDS OF 4-METHOXYBENZYLIDENEPYRUVATE AND CINNAMYLIDENEPYRUVATES WITH THORIUM (IV)
Preparation and thermal studies [*]

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Abstract

By close control of experimental variables affecting precipitation, solid-state compounds of the type $Th(OH)_mL_{4-m} \cdot nH_2O$, where L stands for 4-methoxy-benzylidenepyruvate, cinnamylidenepyruvate or 4-dimethylaminocinnamylidene-pyruvate; $m=0$ to 3 and $n=0.5$–3 were isolated. Chemical analysis, TG, DTG, DSC and X-ray powder diffractometry have been employed to characterize and to study the thermal behavior of these compounds in dynamic air atmosphere. In all cases, hydration water is slowly lost between 30 and 160°C; a continuous, slow rate, mass loss is observed thereafter and beyond 280–400°C the rate of decomposition/oxidation increased rapidly, to give ThO_2 as the final product, beginning at 412–510°C. The results associated with the hydroxo-compounds indicate that the loss of constitution water (OH ions) and the decomposition / oxidation of the organic moieties occur as simultaneous process.

Keywords: cinnamylidenepyruvates, 4-methoxybenzylidenepyruvate, thermal decomposition, Th(IV) compounds

Introduction

Complexes of 4-methoxybenzylidenepyruvate (4-MeO–BP) with several metal ions, including trivalent lanthanides and yttrium [1], alkaline-earth cations [2] and some bivalent transition metals [3] have been isolated and characterized. Complexation of cinnamylidenepyruvate (CP) itself and 4-dimethylaminocinnamylidenepyruvate (DMCP) by several metal ions was also investigated [4–6]. The formulae of the mentioned ligands are shown in Scheme I.

Scheme I
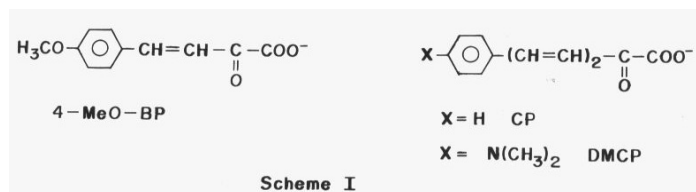
In all these studies, no major difficulties were faced in obtaining binary complexes of general formula $M^{m+}L_m \cdot nH_2O$, where M stands for the metal ion and L for the ligands under consideration. These complexes are very slightly soluble in aqueous media as well as in most organic solvents. Preliminary attempts directed towards the preparation of the analogous Th(IV) complexes from aqueous solutions by the already described procedures [1–6] presented difficulties: only solid materials with no definite stoichiometry were invariably obtained. It was soon depicted that the main drawback could be ascribed to the very pronounced tendency of Th(IV) to hydrolyse, especially for concentrations higher than 0.1 M and pH≥1.5, producing several mono- and polynuclear hydroxo-complexes [7–9] and thus competition between hydroxide ions and the above mentioned α-ketoacid anions for Th(IV) becomes quite significant at the usual working pH ranges (i.e., between 3.0 and 5.5).

As a result of a deep and extensive investigation involving rigidly controlled experimental variables affecting precipitation, such as pH ranges, ligand to Th(IV) concentration ratios, order and speed of reagents' additions, several hydrated compounds of definite stoichiometries, holding the general formula $Th(OH)_m L_{4-m} \cdot nH_2O$, with m ranging from 0 to 3 and n=0.5–3, could be isolated.

The present work deals mainly with the synthesis of the aforementioned compounds and their characterization via chemical analysis, TG, DTG, DSC and X-ray powder diffractometry. The results associated with the thermal behavior of these compounds are discussed particularly in connection with those found in previously reported studies on Th(IV) compounds comprising carboxylate-bearing ligands.

Experimental

Distilled, deionised water was used throughout and chemicals were of analytical reagent grade unless indicated otherwise. The sodium salts of 4-MeO–BP, CP and DMCP were synthesised and purified as detailed in references [10–12], respectively. Aqueous solutions of these ligands, whose pH(s) were adjusted to 3.50±0.10, 4.60±0.10, 5.00±0.05 and 5.25±0.05 by adding diluted nitric acid solutions, were prepared by direct weighing of the corresponding salts. Solutions were 0.10, 0.10 and 0.060 M, for 4-MeO–BP, CP and DMCP, respectively. For DMCP, the mentioned concentration corresponds to a nearly saturated solution, at 25°C. For all these solutions, precipitation takes place at pH≤3.3 as the corresponding protonated forms of the α-ketocarboxylates are sparingly soluble in aqueous media. Aqueous Th(IV) nitrate solution (0.20 M) was prepared by direct weighing of $Th(NO_3)_4 \cdot 4H_2O$; its pH was adjusted to 2.00 by adding diluted nitric acid solution.

Table 1 Thorium(IV) compounds of 4-methoxybenzylidenepyruvates and cinnamylidenepyruvates. Precipitation conditions[a]

pH of ligand solution	Ligand:Th(IV)/ molar ratio	Obtained compound[b]	Colour[c]	Film[d] pH
3.50	5	Th(4-MeO–BP)$_4\cdot$2H$_2$O	brownish-orange	2.98
3.60	6	Th(CP)$_4\cdot$2H$_2$O	golden-yellow	3.07
3.40	5	Th(DMCP)$_4\cdot$3H$_2$O	black	3.40
4.50	3	Th(OH)(4-MeO–BP)$_3\cdot$1.5H$_2$O	orange	2.73
4.50	4	Th(OH)(CP)$_3\cdot$H$_2$O	canary-yellow	2.84
4.70	3	Th(OH)(DMCP)$_3\cdot$2.5H$_2$O	bluish-black	2.87
5.00	3	Th(OH)$_2$(4-MeO–BP)$_2\cdot$H$_2$O	yellowish-orange	2.72
5.00	3	Th(OH)$_2$(CP)$_2\cdot$H$_2$O	yellow	2.71
5.00	2	Th(OH)$_2$(DMCP)$_2\cdot$H$_2$O	deep-blue	2.74
5.20	3	Th(OH)$_3$(4-MeO–BP)$\cdot$0.5H$_2$O	yellow	2.69
5.20	3	Th(OH)$_3$(CP)$\cdot$0.5H$_2$O	yellow	2.69
5.30	2	Th(OH)$_3$(DMCP)$\cdot$0.5H$_2$O	blue	2.74

[a]Added volume of 0.20 M Th(NO$_3$)$_4$ solution (pH=2.00) : 10.0 mL; 4-MeO–BP : 0.10 M; CP : 0.10 M; DMCP : 0.060 M
[b]See analytical results (Table 2)
[c]The colours of very dilute ThL^{3+} aqueous solutions (10^{-5}–10^{-6} M) are yellow (*L*=4-MeO–BP, λ_{max}=410 nm, ε_{max}=2.56$\cdot$10^4 M^{-1} cm^{-1}) [13], pale-yellow (*L*=CP, λ_{max}=380 nm, ε_{max}=1.83$\cdot$10^4 M^{-1} cm^{-1}) [14] and blue (*L*=DMCP, λ_{max}=620 nm, ε_{max}=6.18$\cdot$10^4 M^{-1} cm^{-1}) [12]
[d]Supernatant solution, after complete precipitation

The solid-state compounds were prepared by adding dropwise, with continuous stirring, the Th(IV) solution to the ligands' solutions. In all cases, precipitation took place immediately. Further adopted experimental conditions as well as some features of the obtained compounds are summarised in Table 1. The precipitates were carefully washed by decantation with water until nitrate free. Next, they were filtered through Whatman no. 42 paper, left to dry at room temperature (12–24 h), and then stored in a desiccator over anhydrous calcium chloride to constant mass.

After igniting the compounds to thorium(IV) oxide and dissolving it in a hot solution comprising a mixture of concentrated nitric acid and hydrogen peroxide, their Th(IV) contents were determined by complexometric titration with standard EDTA solution, using xylenol orange as indicator [15]. The Th(IV) contents of the compounds were also estimated from their corresponding TG curves. The dehydration of the complexes was firstly pointed out by their DTG curves and subsequently confirmed by the broad endothermic peaks centered at 90–140°C in the respective DSC curves. The water contents were then determined from the corresponding mass losses observed in the TG curves. Next, the ligands' contents (*L* or *L* plus OH$^-$, for the binary- or hydroxo-complexes, respectively) were also assessed from the TG curves.

The TG, DTG and DSC curves were obtained by employing a Mettler TA-4000 thermal analysis system with air flow of 150 mL min^{-1}, heating rate of 10°C min^{-1} and

with the sample weighing about 7–8 mg. Platinum and aluminium crucibles, the latter with a perforated cover, were used for recording the TG/DTG and DSC curves, respectively. Diffraction patterns were recorded on a Siemens mod. D–500 X-ray diffractometer, using CuK_α radiation (λ=1.542 Å) and settings of 40 kV and 30 mA.

Acidities of aqueous solutions were measured with a Tecnal, mod. TEC-2 pH/ion meter equipped with a combination pH electrode (Metrohm, mod. 6.0234.100). Before each measurement the assembly was standardized by using a NBS phthalate buffer (pH=4.01, at 25°C).

Results and discussion

Analytical and thermoanalytical (TG) results for the prepared compounds are presented in Table 2. Comparison of the results comprised in that Table shows very good agreement between calculated and experimental contents, thereby supporting the proposed general formulae. The X-ray powder patterns showed that all the compounds were obtained in amorphous state.

Table 2 Analytical and thermoanalytical (TG) results

Compounds	Th(IV)/%			ΔL^a/%		Water/%	
	Calcd.	TG	EDTA	Calcd.	TG	Calcd.	TG
$Th(L_1)_4 \cdot 2H_2O$	21.31	21.28	21.25	75.39	75.31	3.30	3.36
$Th(OH)(L_1)_3 \cdot 1.5H_2O$	26.02	25.99	26.08	70.95	70.90	3.03	3.02
$Th(OH)_2(L_1)_2 \cdot H_2O$	33.41	33.44	33.34	64.00	63.92	2.59	2.56
$Th(OH)_3(L_1) \cdot 0.5H_2O$	46.66	46.62	46.69	51.53	51.56	1.81	1.82
$Th(L_2)_4 \cdot 2H_2O$	21.62	21.59	21.55	75.02	75.00	3.36	3.31
$Th(OH)(L_2)_3 \cdot H_2O$	26.64	26.72	26.61	71.29	71.23	2.07	2.05
$Th(OH)_2(L_2)_2 \cdot H_2O$	33.80	33.84	33.87	63.58	63.49	2.62	2.59
$Th(OH)_3(L_2) \cdot 0.5H_2O$	47.04	46.93	46.90	51.54	51.13	1.82	1.80
$Th(L_3)_4 \cdot 3H_2O$	18.36	18.37	18.45	77.36	77.38	4.28	4.33
$Th(OH)(L_3)_3 \cdot 2.5H_2O$	22.59	22.57	22.60	77.03	77.01	4.38	4.39
$Th(OH)_2(L_3)_2 \cdot H_2O$	30.03	30.00	29.98	67.64	67.69	2.33	2.29
$Th(OH)_3(L_3) \cdot 0.5H_2O$	41.70	41.65	41.62	56.62	56.58	1.68	1.71

$^a\Delta L$, ligands' loss (L or L+OH$^-$, for binary and hydroxo-complexes, respectively);
L_1, 4-methoxy-benzylidenepyruvate; L_2, cinnamylidenepyruvate;
L_3, 4-dimethylaminocinnamylidenepyruvate

The TG and DTG curves of the compounds are shown in Figs 1–4. These curves show mass losses between 30 and 510°C, without evidence concerning the formation of stable, anhydrous compounds. As previously stressed, the temperatures corresponding to the mass losses due to dehydration were depicted from the DTG curves. The mass losses beginning at 30°C, observed in all the TG and DTG curves, were un-
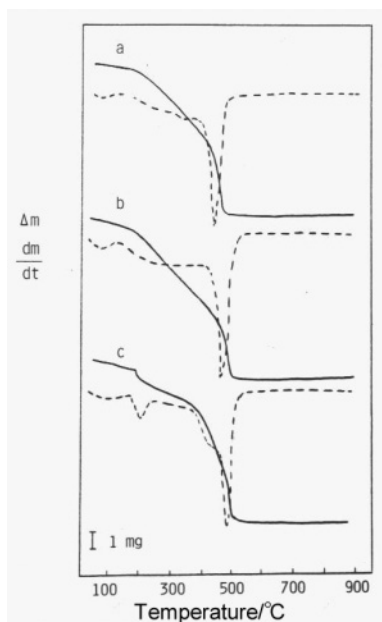
Fig. 1 TG and DTG curves of the compounds: a – Th(4-MeO-BP)$_4$·2H$_2$O (7.187 mg);
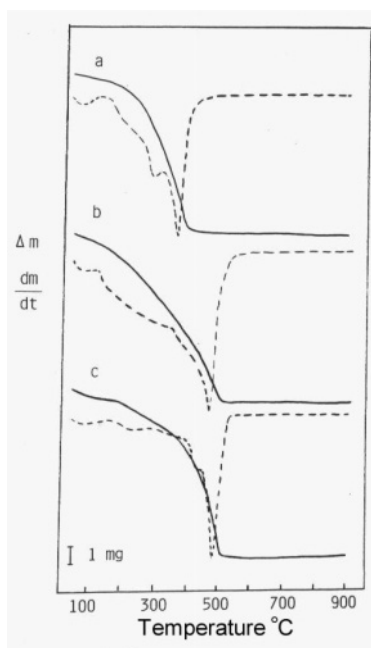b – Th(CP)$_4$·2H$_2$O (7.439 mg) and c – Th(DMCP)$_4$·3H$_2$O (7.658 mg)

Fig. 2 TG and DTG curves of: a – Th(OH)(4-MeO-BP)$_3$·1.5H$_2$O (7.643 mg);
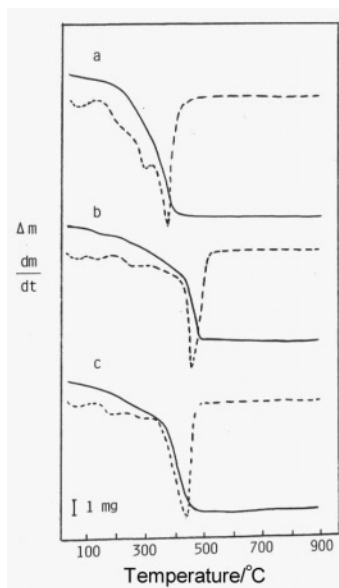b – Th(OH)(CP)$_3$·H$_2$O (7.534 mg) and c – Th(OH)(DMCP)$_3$·2.5H$_2$O (7.657 mg)

Fig. 3 TG and DTG curves of: a – Th(OH)$_2$(4-MeO-BP)$_2$·H$_2$O (7.806 mg);
   b – Th(OH)$_2$(CP)$_2$·2H$_2$O (6.998 mg) and c – Th(OH)$_2$(DMCP)$_2$·H$_2$O (8.112 mg).
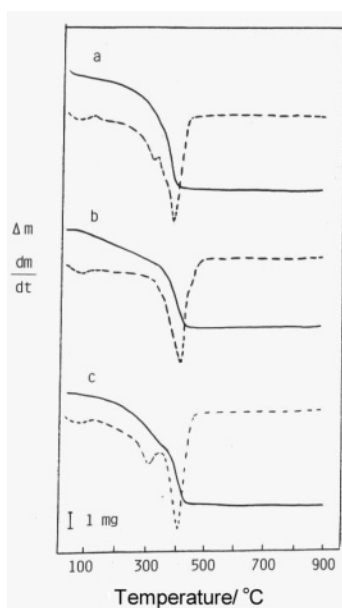
Fig. 4 TG and DTG curves of: a – Th(OH)$_3$(4-MeO-BP)·0.5H$_2$O (8.744 mg);
   b – Th(OH)$_3$(CP)·0.5H$_2$O (8.041 mg) and c – Th(OH)$_3$(DMCP)·0.5H$_2$O
   (8.737 mg)

doubtedly provoked by the purge gas (air) flowing at a rate of 150 mL min^{-1}, as already observed for other amorphous compounds [1, 5, 6, 17]. The final residue in all cases was ThO$_2$, as evidenced by the location and relative intensity of its X-ray diffraction peaks in comparison with those provided by the ASTM files [16]. After the last step of thermal decomposition the minimum oxide level temperatures (MOLT) for ThO$_2$ were observed within the 412–510°C range (Table 3).

Table 3 Dehydration processes and MOLT values for the prepared compounds

Process	Peak temperature[a]/°C	MOLT[b] for ThO$_2$/°C
Th(4-MeO–BP)$_4$·2H$_2$O →Th(4-MeO–BP)$_4$	140	451
Th(OH)(4-MeO–BP)$_3$·1.5H$_2$O →Th(OH)(4-MeO–BP)$_3$	140	430
Th(OH)$_2$(4-MeO–BP)$_2$·H$_2$O →Th(OH)$_2$(4-MeO–BP)$_2$	120	420
Th(OH)$_3$(4-MeO–BP)·0.5H$_2$O →Th(OH)$_3$(4-MeO–BP)	100	412
Th(CP)$_4$·2H$_2$O →Th(CP)$_4$	90	490
Th(OH)(CP)$_3$·H$_2$O →Th(OH)(CP)$_3$	90	480
Th(OH)$_2$(CP)$_2$·H$_2$O →Th(OH)$_2$(CP)$_2$	100	474
Th(OH)$_3$(CP)·0.5H$_2$O →Th(OH)$_3$(CP)	90	452
Th(DMCP)$_4$·3H$_2$O →Th(DMCP)$_4$	140	510
Th(OH)(DMCP)$_3$·2.5H$_2$O →Th(OH)(DMCP)$_3$	120	502
Th(OH)$_2$(DMCP)$_2$·H$_2$O →Th(OH)$_2$(DMCP)$_2$	110	441
Th(OH)$_3$(DMCP)·0.5H$_2$O →Th(OH)$_3$(DMCP)	90	432

[a]From DSC curves
[b]Minimum oxide level temperature [18]

A close similarity is observed in all TG and DTG curves, both for binary and hydroxo-compounds. Although the TG curves suggest mass losses in one step, the DTG curves show mass losses in several overlapping consecutive or simultaneous steps through a rather complex pathway.

For all the binary and hydroxo-compounds, the first mass loss indicated by DTG curves is due to dehydration. After the dehydration, the thermal decomposition of
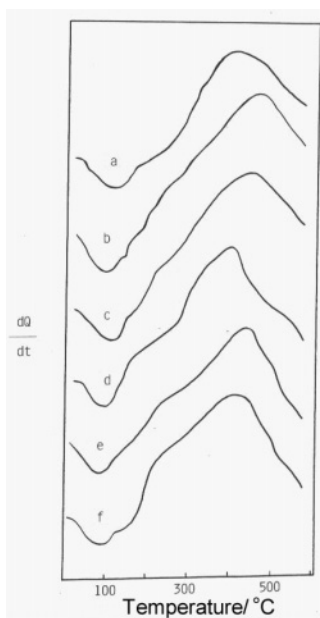
Fig. 5 DSC curves of: a – Th(4-MeO-BP)$_4$·2H$_2$O; b – Th(CP)$_4$·2H$_2$O;
c – Th(DMCP)4·3H$_2$O; d – Th(OH)(4-MeO-BP)$_3$·1.5H$_2$O;
e – Th(OH)(CP)$_3$·H$_2$O and f – Th(OH)(DMCP)$_3$·2.5H$_2$O
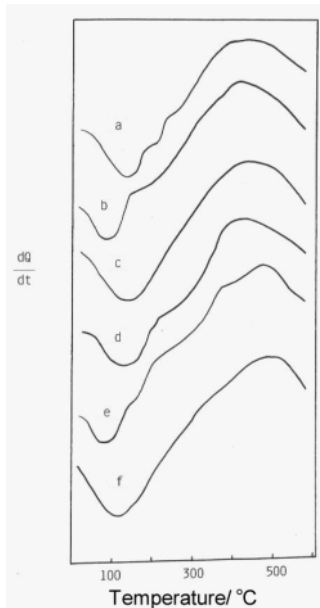
Fig. 6 DSC curves of: a – Th(OH)(4-MeO-BP)$_2$·H$_2$O; b – Th(OH)$_2$(CP)$_2$·H$_2$O;
c – Th(OH)$_2$(DMCP)$_2$·H$_2$O; d – Th(OH)$_3$(4-MeO-BP)·0.5H$_2$O;
e – Th(OH)$_3$(CP)·0.5H$_2$O and f – Th(OH)$_3$(DMCP)·0.5H$_2$O

these compounds begins as a slow process, followed by a fast one giving MOLT values for ThO_2 which depend on the identity of each compound.

The DSC curves of the compounds are shown in Figs 5 and 6. These curves comprise broad endothermic peaks, followed by exotherms that are all in accord with the mass losses given in the DTG curves. The broad endothermic peaks located at 90–140°C, observed in all DSC curves, are due to the dehydration process. The exotherms observed after the dehydration step are attributed to the thermal decomposition of the anhydrous compounds, where the oxidation of the organic matter takes place in consecutive or simultaneous steps; this is in agreement with the DTG curves. The temperatures associated with the dehydration process, along with the MOLT values for ThO_2 are displayed in Table 3.

A close similarity is also observed in the DSC curves, both for binary and hydroxo-compounds and in agreement with the TG and DTG curves.

No endothermic peak due to the loss of constitution water from the hydroxo-compounds is observed in the DSC curves. This is an indication that the constitution water and the organic ligands are lost simultaneously, prevailing the heat due to oxidation of the organic matter (exothermic reaction).

The DSC curves also show that the thermal decomposition are still being observed up to 600°C, while the TG and DTG curves display temperatures that do not exceed 510°C. This difference is undoubtedly provoked by the crucible with perforated cover used to obtain the DSC curves, while a crucible without perforated cover is used for recording the TG and DTG curves.

A literature search comprising dated [8, 19–21] and updated [22] reviews points out that thermal analysis investigations on Th(IV) carboxylates received scant attention, particularly concerning compounds of monocarboxylates and hydroxo-monocarboxylates. The complex formulated as $Th(DMBP)_4 \cdot 2H_2O$, where DMBP stands for 4-dimethylaminobenzylidenepyruvate, was investigated through TG, DTG and DSC [17]; TG and DTA were employed in the study of compounds of general formula $Th(OH)_m(CH_3COO)_{4-m} \cdot nH_2O$, where m is within 1 and 3 [20, 23]; only TG curves were recorded for $Th(CH_3COO)_4$ [20] and $Th(OH)_m(A)_{4-m}$ [18] with m ranging from 0 to 3 and A represents benzoate, phenylacetate, 3-hydroxybenzoate, 2-aminobenzoate, 3-methyl-phenoxyacetate, 2,4-dichlorophenoxyacetate, cinnamate or stearate. Differential thermal analysis results are available for $Th(OHCH_2COO)_4 \cdot 2H_2O$ [24], $Th(OH)_{0.5}(2\text{-NB})_{3.5}$ and $Th(OH)_2(4\text{-NB})_2 \cdot H_2O$, where 2-NB and 4-NB stand for 2-nitrobenzoate and 4-nitrobenzoate, respectively [25].

Except for the study on $Th(DMBP)_4 \cdot 2H_2O$ [17], the investigations highlighted above concerning the thermal behaviour of the Th(IV) carboxylates are rather incomplete. Furthermore, most of these studies are quite deficient in terms of data interpretation. Additionally, important experimental information such as sample mass [20, 23–27], sample support [20, 23–25], kind of atmosphere adopted in static dynamic fashion [18, 20, 23–25] and heating rates [20] is missing or not clearly stated. Thus, the results gathered in the aforementioned studies are best regarded as exploratory and/or preliminary ones. Nevertheless, some tentative comparisons of these results with those obtained in the present work seem possible, a) as previously stated,

the decomposition profile of all compounds investigated in this work, as displayed by their TG and DTG curves (Figs 1–4) shows slow mass loss beginning at 30°C; beyond 280–400°C, the rate of decomposition increased rapidly to give MOLT values for ThO$_2$ within 412–510°C. Similar decomposition profiles are followed for both hydrated and anhydrous compounds involving DMBP [17], 3-hydroxy-, 2-amino-benzoate and stearate [18], for which the first mass loss is observed at 50–85°C and the vigorous decomposition process begins within the 205–360°C range; b) the anhydrous compounds involving acetate [20], benzoate [18] and cinnamate [18] present a different behavior as these are thermally stable up to 300, 285 and 180°C, respectively; c) previously reported MOLT values for ThO$_2$ [17, 18, 24] as well as those determined in the present work (Table 3) are in good agreement: all are comprised in the 412–550°C range; d) the DSC curves for the hydroxo-compounds prepared in this work (Figs 5 and 6) indicate that the loss of constitution water and the organic moiety decomposition/oxidation are simultaneous processes. A similar pattern of behaviour is suggested for Th(OH)$_2$(4-NB)$_2$·H$_2$O through its DTA data [25]. On the other hand, for the hydroxo-acetate complexes, the TG [20] and DTA [23] data point out that the two mentioned processes can be distinguished, proceeding stepwise. A two-stage process is also suggested by the DTA data associated with the compound formulated as Th(OH)$_{0.5}$ (2-NB)$_{3.5}$ [25]. It is worth noting that the DTA plots for the hydroxo-acetate [23] and hydroxo-2-NB [25] complexes are quite distinct from the DSC ones associated with the presently prepared hydroxo-compounds (Figs 5 and 6); e) the data given in Table 1 show that different complexes have often been obtained by changing the experimental conditions only slightly. This kind of behaviour, observed also for many reported Th(IV) systems [18, 20, 23, 25], stresses, once again, the uncertainty concerning the composition of the precipitates proposed for the gravimetric determination of thorium. Mainly for this reason, the majority of the well-established gravimetric methods available for Th(IV) are usually completed by igniting the precipitate to ThO$_2$ [18].

Except for the compounds isolated in this work and for the binary ones comprising acetate [20], glycolate [24] and DMBP [17], no information is given concerning the crystallinity of the remaining Th(IV) carboxylates considered herein. Moreover, for all but some acetate complexes [20] nothing is mentioned about the compounds' nuclearity.

It is difficult to establish the nuclearity of the presently investigated complexes. The difficulty stems mainly from their very low solubility, both in aqueous media and in organic solvents. So, the most common techniques employed for the detection of polymeric species in solution, such as molecular mass determinations, equilibrium centrifugation and measurement of light scattering power cannot be applied. On the other hand, magnetic susceptibility measurements on solids, which proved to be very useful in indicating bridged polymeric arrangements and/or metal–metal interactions in paramagnetic complexes [26] are not applicable to Th(IV) compounds as all these are diamagnetic [8]. It is known that for Th(IV) concentrations equal to or higher than 0.1 M, in aqueous nitrate media, at 25°C, within the pH values encompassed during the precipitation step, i.e., 5.30–2.69 (Table 1), both mono- and polynuclear soluble

Th(IV) hydroxo-complexes exist in solution. For the above mentioned pH range, the following species, in addition to the hydrated Th(IV) ion, have been identified in labile equilibrium: $Th(OH)^{3+}$, $Th_2(OH)_2^{6+}$, $Th_4(OH)_8^{8+}$ and $Th_6(OH)_{15}^{9+}$ [7–9]. Even for the hydrated basic nitrate, $Th(OH)(NO_3)_3 \cdot 4H_2O$, a discrete dimeric structure has been pointed out from single crystal X-ray diffraction [7]. Moreover, most Th(IV) carboxylates whose structural analyses have been completed on crystals exhibit polymeric structures [8, 20, 21].

All attempts at growing good single crystals of the presently investigated compounds or at obtaining them, as polycrystalline powders were unsuccessful. Their amorphous state, absence of definite melting points and insolubility in a wide variety of solvents suggest that these compounds might be polymeric in nature. It is known that high molecular mass metal coordination polymers bearing oxygen or sulphur as donor atoms are generally hard, fiber- or film-like materials, stable at relatively elevated temperatures (i.e., up to ca 400°C) [27, 28]. The presently prepared compounds do not display these features. So, if polymeric, they should be, almost certainly, of low nuclearity.

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