

Solid-state compounds of 2-methoxybenzylidenepyruvate and 2-methoxycinnamylidenepyruvate with thorium (IV)

Preparation and thermal studies

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Abstract Solid-state compounds of general formula $\text{ThL}_4 \cdot n\text{H}_2\text{O}$, where L represents 2-methoxybenzylidenepyruvate and 2-methoxycinnamylidenepyruvate, were synthesized. Complexometric titrations with EDTA, thermogravimetry (TG), differential thermal analysis (DTA), X-ray powder diffractometry, elemental analysis (EA), and infrared spectroscopy have been employed to characterize and to study the thermal behavior of these compounds in dynamic air atmosphere. The results led to informations about the composition, dehydration, crystallinity, and thermal decomposition of the isolated compounds. The performed molecular calculations in this study were done using the Gaussian 03 routine. Theoretical calculations help in interpretations of FT-IR spectra supplying structural and physicochemical parameters.

Keywords Thorium (IV) · Thermal behaviour · 2-methoxybenzylidenepyruvate · 2-methoxycinnamylidenepyruvate

Introduction

Synthesis of benzylidenepyruvic acid (HBP), as well as of phenyl-substituted derivatives of HBP, has been reported. These acids are of continuing interest as intermediates in pharmacological, industrial, and chemical synthesis, in the development of enzyme inhibitors and drugs, as model substrates of enzymes, and in other ways [1].

The preparation and investigation of several metal–ion complexes of phenyl-substituted derivatives of benzylidenepyruvate (BP), i.e., $\text{C}_6\text{H}_5\text{—CH=CH—COCOO}^-$ (BP), i.e., 4-dimethylamino (4-DM-BP), 4-methoxy (4-MeO-BP), 2-methoxy (2-MeO-BP), 4-chloro (4-Cl-BP), and 4-methyl (4-Me-BP) have been carried out in aqueous solutions [2]; these studies reported the thermodynamic stability (β_1) and spectroscopic parameters (ϵ_{max} , λ_{max}), associated with 1:1 complex species, analytical applications of the ligands, e.g., in gravimetric analysis and as metallochromic indicators, while in the solid-state, the establishment of the stoichiometry and detailed knowledge of the thermal behavior of the ligands and their metal ion compounds have been the main purposes of these studies [2].

In the solid-state, the studies reported the synthesis and investigation of the compounds by means of thermogravimetry, derivative thermogravimetry (TG/DTG), differential thermal analysis (DTA), X-ray powder diffractometry, and complexometry. Establishment of stoichiometry and the details of the thermal decomposition were the main purposes of these studies [1, 3–8].

In this study, the ligands 2-methoxybenzylidenepyruvate (2-MeOBP) and 2-methoxycinnamylidenepyruvate (2-MeOCP) and solid-state compounds of thorium (IV) were synthesized.

The compounds were investigated by means of chemical analysis, elemental analysis (EA), simultaneous thermogravimetry and differential thermal analysis (TG–DTA),

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X-ray powder diffractometry, and infrared spectroscopy (FT-IR).

The data obtained allowed us to acquire information concerning these compounds in the solid-state, including their thermal behavior and thermal decomposition.

Experimental

Sodium salts of 2-methoxybenzylidenepyruvic and 2-methoxycinnamylidenepyruvic and its corresponding acids were both synthesized following a procedure described in the literature [5, 6], respectively.

Aqueous solution of the ligands 0.1 mol L⁻¹ were prepared by direct weighing of the sodium salts of 2-methoxybenzylidenepyruvic and 2-methoxybenzylidenepyruvic acids, and the pH adjusted to 3.5 and 3.4 with NaOH 0.05 mol L⁻¹, respectively.

Aqueous Th(IV) nitrate solution (0.1 mol L⁻¹) was prepared by direct weighing of Th(NO₃)₄·4H₂O; its pH was adjusted to 2.0 by adding diluted nitric acid solution 0.01 mol L⁻¹.

The solid-state compounds were prepared by adding drop wise, with continuous stirring, of the Th(IV) solution to the ligand solutions. In all cases, precipitation took place immediately. Further adopted experimental conditions as well as some features of the obtained compounds are summarized in Table 1.

The precipitates were carefully washed by decantation with water until it becomes nitrate free. Next, they were filtered through Whatman n^o. 42 filter paper, left to dry at room temperature (12–24 h), and then stored in a desiccator over anhydrous calcium chloride to constant mass.

Simultaneous TG–DTA curves were obtained with thermal analysis system, model SDT 2960, from TA Instruments. The purge gas was an air flow of 100.0 mL min⁻¹. A heating rate of 20 °C min⁻¹ was adopted, with samples weighing about 5.0 mg. Alumina crucibles were used for recording the TG–DTA curves.

The metal ions were also determined by complexometric titrations with standard EDTA solutions, using xylenol orange as indicator [9].

X-ray powder patterns were obtained using a Siemens D-5000 X-ray diffractometer, employing CuK α radiations ($\lambda = 1.541 \text{ \AA}$) and setting of 40 kV and 20 mA.

Infrared spectra for Th(2-MeO-BP)₄·3.5H₂O and Th(2-MeOCP)₄·2.5H₂O compounds were run on a Nicolet mod. Impact 400 FT-IR instruments, within 4000–400 cm⁻¹ range. The solid samples were pressed into KBr pellets.

Carbon and hydrogen contents were determined by micro-analytical procedures, with an EA 1110 CHNSO Elemental Analyzer (CE Instruments).

Computational strategy

In this study, the employed quantum chemical approach to determine the molecular structures was Becke three-parameter hybrid theory [10] using the Lee–Yang–Par (LYP) correlation functional [11], and the basis sets used for calculations were: 4s for H (²S) [12], [5s4p] for C (³P) and O (³P), and [20s17p12d6f] for Th (³F). Basis set for Th (³F) atom. The 33s22p16d9f [discretization parameters: $\Omega_{(s)} = -0.622$, $\Delta\Omega_{(s)} = 0.112$, $N_{(s)} = 6.0$; $\Omega_{(p)} = -0.296$, $\Delta\Omega_{(p)} = 0.109$, $N_{(p)} = 6.0$; $\Omega_{(d)} = -0.324$, $\Delta\Omega_{(d)} = 0.117$, $N_{(d)} = 6.0$; $\Omega_{(f)} = -0.102$, $\Delta\Omega_{(f)} = 0.122$, $N_{(f)} = 6.0$]/20s17p12d6f (9,2,2,2,1,1,1,1,1,1,1,2,1,2,1,1,1,1,1/6,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1/5,1,1,1,1,1,1,1,1,1,1/4,1,1,1,1) basis set were built with the add of the Generator Coordinate Hartree-Fock method. The polarization function is $\alpha_g = 3.83435027$. The diffuse functions are: $\alpha_s = 0.00197245$, $\alpha_p = 0.084657025$, $\alpha_d = 0.05156514$, and $\alpha_f = 0.12205797$. Full details about the wave function developed in this study for thorium are available upon request to the e-mail address: oswatreu@iq.unesp.br. In order to better describe the properties of the compound in the implementation of the calculations, it was necessary to include polarization functions for all atoms of the compounds. The polarization functions are: $\alpha_p = 0.33353749$ for H (²S), $\alpha_d = 0.72760279$ and $\alpha_d = 0.36059494$ for C (³P) and O (³P), respectively, and $\alpha_g = 3.83435027$ for Th (³F) atoms. The role of a basis set is a crucial point in theoretical studies of metal complexes, since the description of the configuration of the metal in the complex differs from the neutral state. For the Th (³F) atom, the diffuse functions are: $\alpha_s = 0.00197245$, $\alpha_p = 0.084657025$, $\alpha_d = 0.05156514$, and $\alpha_f = 0.12205797$. The performed molecular calculations in this study were done using the Gaussian 03 routine [13]. The computational strategy used in this study has

Table 1 Thorium(IV) compounds of 2-methoxybenzylidenepyruvate and 2-methoxycinnamylidenepyruvate

pH of ligand solution	Ligand: Th(IV) molar ratio	Obtained compound	Final pH ^a
3.5	5:1	Th(2-MeO-BP) ₄ ·3.5H ₂ O	3.02
3.4	5:1	Th(2-MeO-CP) ₄ ·2.5H ₂ O	3.08

Precipitation conditions: added volume of 0.1 mol L⁻¹ of Th(NO₃)₄ up to 0.1 mol L⁻¹ of each ligand

^a Supernatant solution, after complete precipitation

already been successfully applied in previous articles in coordination compounds and organic molecules [1, 12].

As the molecular structure of the compounds could not be determined by the single crystal X-ray diffraction technique, a geometry optimization was computed using the optimized algorithm of Berny [14].

The theoretical infrared spectrum, it was calculated using a harmonic field [15] based on C_1 symmetry (electronic state 1A). Frequency values (not scaled), relative intensities, assignments, and description of vibrational modes are presented. The calculations of vibrational frequencies were also implemented to determine an optimized geometry constitutes minimum or saddle points. The principal infrared-active fundamental modes assignments and descriptions were done by the GaussView 5.0.2 W graphics routine [16].

Results and discussion

The analytical and thermoanalytical results of the synthesized compounds are shown in Table 2. These results permitted to establish the stoichiometry of the compounds, which is in agreement with the formula $\text{Th}(2\text{-MeO-BP})_4 \cdot 3.5\text{H}_2\text{O}$ and $\text{Th}(2\text{-MeO-CP})_4 \cdot 2.5\text{H}_2\text{O}$, where 2-MeO-BP and 2-MeO-CP represent 2-methoxybenzylidenepyruvate and 2-methoxycinnamylidenepyruvate, respectively.

The TG/DTG and DTA curves of the compounds are shown in Fig. 1. These curves show mass losses in consecutive and/or overlapping steps and thermal events corresponding to these losses. For both compounds, the first mass loss up to 100 °C, corresponding to an endothermic peak at 90 °C, is attributed to dehydration with loss of 3.5 H_2O (Th-2MeO-BP) and 2.5 H_2O (Th-2MeO-CP).

Once dehydrated, the TG and DTA curves of $\text{Th}(2\text{MeO-BP})_4$, show mass losses in two steps between 190–400 °C and 400–490 °C with losses of 34.37 and 39.12%, corresponding to the small exothermic peak at 260 °C and a large exothermic are attributed to thermal decomposition/oxidation of the organic matter.

For the anhydrous $\text{Th}(2\text{-MeO-CP})_4$, the TG and DTA curves show mass losses in three steps between 180–310,

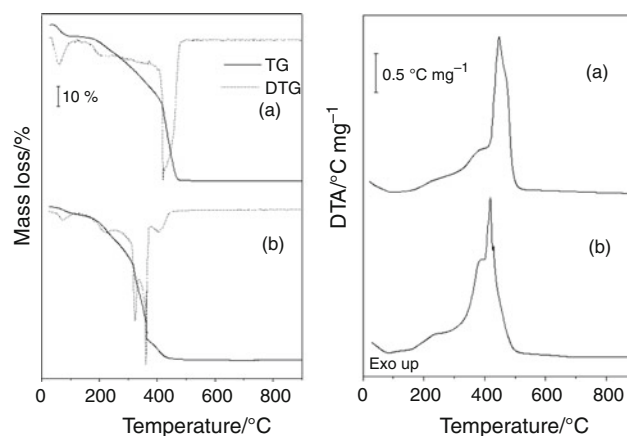


Fig. 1 TG/DTG and DTA curves of (a) $\text{Th}(2\text{-MeOBP})_4 \cdot 3.5\text{H}_2\text{O}$ and (b) $\text{Th}(2\text{-MeOCP})_4 \cdot 2.5\text{H}_2\text{O}$

Table 3 Spectroscopic data of sodium salt 2-methoxybenzylidenepyruvate and 2-methoxycinnamylidenepyruvate and for its compounds with thorium (IV)

Compound	$\nu_{\text{O-H}}$ H_2O	$\nu_{\text{as.}(\text{COO}^-)}$	$\nu_{\text{sym}(\text{COO}^-)}$	$\nu_{\text{C=O}}$
Na(2MeOBP)	3420	1679	1479	1713
Th(2MeOBP) ₄	3154 and 3132	1597	1402	1657
Na(CP)	3418	1600	1400	1629
Th(2MeOCP) ₄	3430	1560	1400	1618

310–360, and 360–450 °C with losses of 23.04, 40.97, and 12.80%, respectively, corresponding to the exothermic peaks at 245 and 415 °C with shoulder at 390 °C, attributed to the thermal decomposition/oxidation of the organic matter. For both compounds, the final residue was ThO_2 .

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, the Th(IV) contents were determined by complexometric titration with standard EDTA (0.01 mol L^{-1}) solution, using xylenol orange as indicator [9]. The Th(IV) contents were also estimated from their corresponding TG curves, and the results shown in Table 2.

Table 2 Data of analysis: theoretical, complexometric titrations with EDTA, and thermogravimetric experiments of the $\text{Th}(2\text{-MeOBP})_4 \cdot 3.5\text{H}_2\text{O}$ and $\text{Th}(2\text{-MeOCP})_4 \cdot 2.5 \text{H}_2\text{O}$

Compound	Water/%		L. lost/%		Metal/%		$\Delta m/\%$	$\Delta m/\%$		Carbon/%		Hydrogen/%	
	Theor.	TG	Theor.	TG	Theor.	TG		Theor.	TG	Theor.	EA	Theor.	EA
Th(BP) ₄ ·3.5H ₂ O	5.66	5.61	73.55	73.49	20.79	20.83	20.92	79.21	79.10	47.50	46.64	3.79	4.30
Th(CP) ₄ ·2.5H ₂ O	3.75	3.81	76.95	76.81	19.30	19.38	19.32	80.70	80.62	46.96	45.94	3.99	4.17

L ligand (BP 2-methoxybenzylidenepyruvate and CP 2-methoxycinnamylidenepyruvate)

Infrared spectroscopic data on 2-methoxybenzylidene pyruvate (2-MeO-BP) and 2-methoxycinnamylidenepyruvate (2-MeO-CP) sodium salt and its compounds with thorium (IV) are shown in Table 3. The bands found for 2-MeO-BP or 2-MeO-CP, centered at 1713 and 1629 cm^{-1} , respectively (ketonic carbonyl stretching) and 1679 and 1600 cm^{-1} (anti-symmetrical carboxylate vibration) are both shifted to lower frequencies in the complexes, suggesting thorium coordination by the α -ketonic carbonyl and carboxylate groups of the ligands [17].

The bands found for 2-methoxybenzylidenepyruvate and 2-methoxycinnamylidenepyruvate (sodium salts) centered at 1713, 1629 cm^{-1} (ketonic carbonyl stretching), 1679,

1600 cm^{-1} (anti-symmetrical carboxylate vibration), and 1479, 1400 cm^{-1} (symmetrical carboxylate vibration), respectively. The vibration stretching both shifted to lower frequencies in the compounds, namely, 1657, 1618 cm^{-1} (ketonic carbonyl stretching), 1597, 1560 cm^{-1} (anti-symmetrical carboxylate vibration), and 1402, 1400 cm^{-1} (symmetrical carboxylate vibration), respectively. These data suggest thorium coordinated by the α -ketonic carbonyl and carboxylate groups of the ligands.

Based on the theoretical calculus and spectroscopic infrared, it was possible to suggest structural model for the $\text{Th}(2\text{-MeOBP})_4$ compound. The theoretical structure and parameters are shown in Fig. 2 and Table 4.

Fig. 2 Theoretical 2D and 3D structure of $\text{Th}(2\text{-MeOBP})_4$ compound. The 3D structure was optimized using Becke three-parameter hybrid theory, the Lee–Yang–Par (LYP) correlation functional and the basis sets used for calculations were: [4s] for H (^2S) [10], [5s4p] for C (^3P) and O (^3P), and [20s17p12d6f] for Th (^3F)

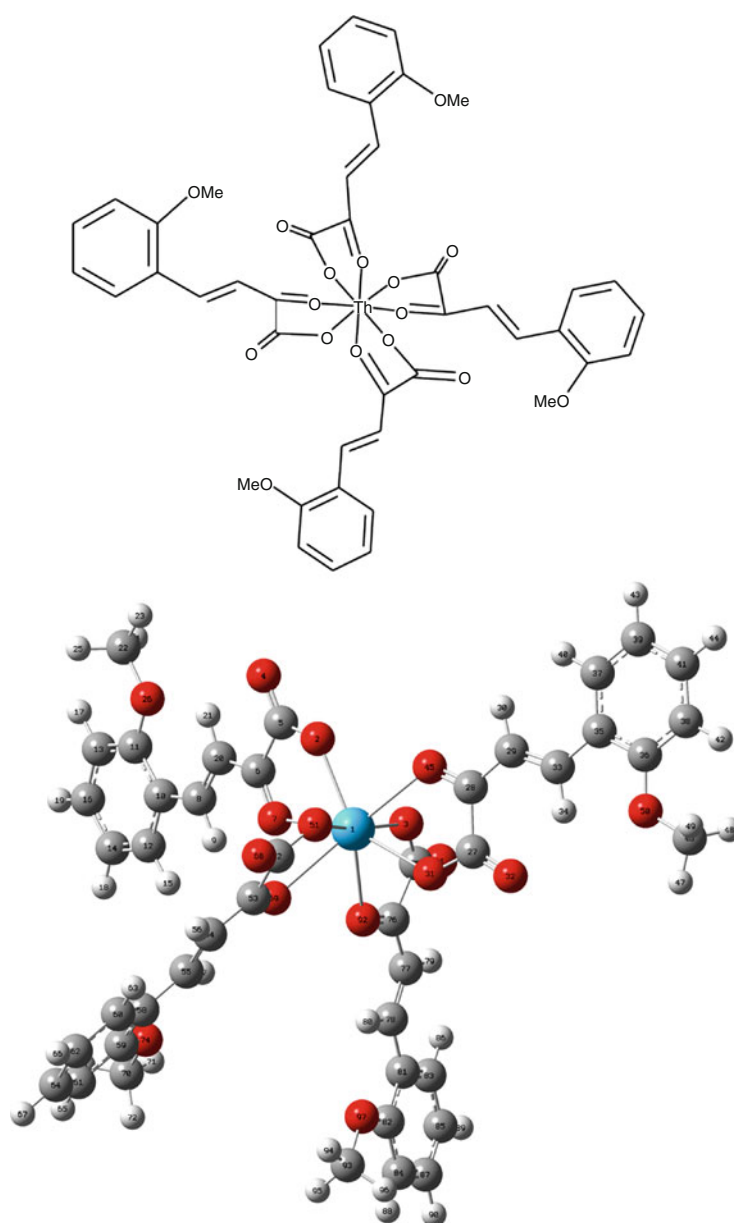


Table 4 Theoretical data of geometry 3D of Th(2-MeOBP)₄ compound

Atom No	Atom symbol	NA	NB	NC	Bond/Å	Angle/°	Dihedral/°	X/Å	Y/Å	Z/Å
1	Th							0.92853	0.77182	0.32116
2	O	1			2.37155			0.82356	3.11742	0.65493
3	O	1	2		2.41533	90.34772		1.02152	1.10139	-2.06978
4	O	2	1	3	2.26723	154.19999	72.22075	-0.1933	5.14315	0.60274
5	C	4	2	1	1.22175	26.90849	1.3512	-0.16575	3.93331	0.43485
6	C	5	4	2	1.54762	119.59307	179.27341	-1.42776	3.20519	-0.08697
7	O	6	5	4	1.24908	117.42955	-176.17137	-1.37892	1.96012	-0.17432
8	C	6	5	4	2.42785	146.68409	5.25267	-3.6938	3.42489	-0.93034
9	H	8	6	5	1.08725	84.8788	177.26745	-3.65489	2.3436	-1.03718
10	C	8	6	5	1.4455	161.19998	-1.04274	-4.94387	4.01131	-1.35799
11	C	10	8	6	1.42115	125.33896	-2.11095	-5.2576	5.39687	-1.31944
12	C	10	8	6	1.40736	117.25595	177.65121	-5.92795	3.13797	-1.85753
13	C	11	10	8	1.39474	120.13104	179.73761	-6.50013	5.84607	-1.76624
14	C	12	10	8	1.38436	122.47079	-179.76841	-7.16137	3.58366	-2.30082
15	H	12	10	8	1.0841	117.82549	0	-5.69447	2.07992	-1.89339
16	C	13	11	10	1.3905	120.44954	0.0192	-7.4419	4.94579	-2.25209
17	H	13	11	10	1.08034	120.22566	-179.90997	-6.73969	6.89916	-1.73898
18	H	14	12	10	1.08251	120.44521	179.83045	-7.89342	2.88293	-2.68148
19	H	16	13	11	1.08374	119.15976	-179.92471	-8.40027	5.31782	-2.59503
20	C	8	6	5	1.35423	30.75198	-3.20696	-2.57655	4.00475	-0.43086
21	H	20	8	6	1.07582	123.37866	179.0675	-2.47717	5.06522	-0.27954
22	C	11	10	8	2.41935	147.74091	0.29417	-4.53998	7.64273	-0.7769
23	H	22	11	10	1.08664	134.38662	-0.37745	-3.63027	8.07143	-0.36528
24	H	22	11	10	1.09271	95.29822	123.99949	-4.72068	8.05018	-1.77457
25	H	22	11	10	1.0928	95.6541	-125.21008	-5.38407	7.87001	-0.12112
26	O	11	10	8	1.35636	116.95199	-0.2565	-4.30281	6.23016	-0.83602
27	C	1	2	5	3.35805	122.50609	160.8303	3.83758	-0.88935	0.08794
28	C	27	1	2	1.55929	77.81087	-3.90179	4.31209	0.59215	0.1946
29	C	28	27	1	1.43445	124.91902	178.93654	5.68223	1.01669	0.20633
30	H	29	28	27	1.08433	112.90804	179.69967	5.78998	2.09298	0.28218
31	O	27	1	2	1.29934	33.47467	179.16733	2.5407	-0.96921	0.08564
32	O	27	1	2	1.22203	160.44514	171.63483	4.63294	-1.81443	0.01725
33	C	29	28	27	1.35616	125.30347	-0.56116	6.75822	0.19409	0.13754
34	H	33	29	28	1.08112	117.33794	-0.08715	6.56771	-0.86795	0.06969
35	C	33	29	28	1.4477	126.06484	-179.9685	8.14658	0.60414	0.14871
36	C	35	33	29	1.41986	119.05614	178.84404	9.15949	-0.38935	0.09417
37	C	35	33	29	1.40495	123.21249	-1.28621	8.55161	1.94811	0.20867
38	C	36	35	33	1.39566	120.41039	179.89255	10.50691	-0.02564	0.10109
39	C	37	35	33	1.3837	121.91093	-179.86264	9.88714	2.30996	0.21509
40	H	37	35	33	1.08241	119.01344	0.01463	7.79658	2.72266	0.24904
41	C	38	36	35	1.38933	119.93973	-0.02453	10.86266	1.31603	0.16114
42	H	38	36	35	1.08054	120.49027	179.9841	11.27881	-0.78065	0.05988
43	H	39	37	35	1.0824	120.29505	179.95674	10.16982	3.35378	0.2612
44	H	41	38	36	1.08384	119.20256	-179.98317	11.91258	1.58502	0.16558
45	O	28	27	1	1.25305	115.92348	-1.239	3.40535	1.45361	0.2712
46	C	36	35	33	2.41639	147.23062	-0.4383	9.69257	-2.74375	-0.01335
47	H	46	36	35	1.08673	134.61463	0.14246	9.10646	-3.65823	-0.0478

Table 4 continued

Atom No	Atom symbol	NA	NB	NC	Bond/Å	Angle/°	Dihedral/°	X/Å	Y/Å	Z/Å
48	H	46	36	35	1.09322	95.58713	124.9574	10.31368	-2.67141	-0.91007
49	H	46	36	35	1.09318	95.3582	-124.39016	10.32511	-2.74602	0.87825
50	O	36	35	33	1.3587	116.39429	-0.14949	8.73756	-1.67963	0.03742
51	O	1	2	5	2.41887	88.40886	-118.10376	1.29805	0.51803	2.69812
52	C	51	1	2	1.29394	128.17129	117.55629	0.55285	-0.09151	3.56266
53	C	52	51	1	1.54846	111.89436	-3.46264	-0.75101	-0.62947	2.9237
54	C	53	52	51	1.43845	118.29049	-177.91061	-1.70359	-1.2924	3.77355
55	C	54	53	52	1.35327	121.46795	178.61763	-2.87606	-1.76263	3.28824
56	H	54	53	52	1.08104	114.80017	-0.78616	-1.40925	-1.36941	4.81089
57	H	55	54	53	1.08347	117.00627	0.1944	-3.06328	-1.62017	2.23062
58	C	55	54	53	1.44682	126.95727	-179.53904	-3.91832	-2.43552	4.0327
59	C	58	55	54	1.4188	119.5514	178.24332	-5.10771	-2.8324	3.36874
60	C	58	55	54	1.40508	122.64689	-1.66299	-3.80826	-2.71786	5.40471
61	C	59	58	55	1.39482	120.41328	-179.81955	-6.12561	-3.47889	4.06976
62	C	60	58	55	1.38372	121.83195	179.89099	-4.81681	-3.36053	6.10076
63	H	60	58	55	1.08238	118.87227	-0.18133	-2.90759	-2.42402	5.92816
64	C	61	59	58	1.38996	119.93844	-0.08764	-5.97623	-3.73907	5.42696
65	H	61	59	58	1.0805	120.57394	179.82952	-7.03362	-3.77982	3.56732
66	H	62	60	58	1.08239	120.25135	179.98673	-4.7049	-3.56554	7.15765
67	H	64	61	59	1.08373	119.19426	179.97792	-6.77486	-4.24172	5.95988
68	O	52	51	1	1.22419	128.9997	176.74238	0.75078	-0.27539	4.75667
69	O	53	52	51	1.25104	117.53239	1.9854	-0.90733	-0.45545	1.69473
70	C	59	58	55	2.41657	147.35686	-0.64477	-6.35976	-2.89851	1.30289
71	H	70	59	58	1.08691	134.90799	1.03236	-6.17786	-2.56543	0.28438
72	H	70	59	58	1.09322	95.49322	125.84162	-6.51876	-3.98007	1.31145
73	H	70	59	58	1.09307	95.28766	-123.61259	-7.24136	-2.39116	1.70312
74	O	59	58	55	1.36264	116.42594	0.08347	-5.18481	-2.54474	2.03905
75	C	3	1	2	1.29532	127.52326	-142.95216	0.47011	0.37361	-2.98855
76	C	75	3	1	1.54837	112.20018	-3.87873	-0.23613	-0.87319	-2.40189
77	C	76	75	3	1.43998	118.22705	-172.7429	-0.75545	-1.8557	-3.31761
78	C	77	76	75	1.35273	121.21585	173.96303	-1.27473	-3.02302	-2.8731
79	H	77	76	75	1.0811	114.98651	-3.60807	-0.65713	-1.60182	-4.36386
80	H	78	77	76	1.08336	116.96241	0.63892	-1.29046	-3.17694	-1.80084
81	C	78	77	76	1.44729	127.05559	-178.29568	-1.79675	-4.10751	-3.67685
82	C	81	78	77	1.41874	119.47785	174.98315	-2.2071	-5.30979	-3.04524
83	C	81	78	77	1.4047	122.70275	-4.71309	-1.91296	-4.02854	-5.07451
84	C	82	81	78	1.39497	120.40027	-179.48029	-2.70297	-6.37129	-3.80238
85	C	83	81	78	1.38397	121.83119	179.63685	-2.408	-5.07974	-5.82636
86	H	83	81	78	1.08248	118.84918	-0.50604	-1.60787	-3.11757	-5.57334
87	C	84	82	81	1.38995	119.94314	-0.2105	-2.80098	-6.25197	-5.18373
88	H	84	82	81	1.08054	120.54174	179.64999	-3.01089	-7.29007	-3.32426
89	H	85	83	81	1.08244	120.2598	-179.99707	-2.48649	-4.99136	-6.90232
90	H	87	84	82	1.08377	119.19719	179.9723	-3.18751	-7.08434	-5.76018
91	O	75	3	1	1.22438	128.6843	175.67854	0.44287	0.55956	-4.19842
92	O	76	75	3	1.24872	117.67327	7.02661	-0.31487	-0.96397	-1.15896
93	C	82	81	78	2.41709	147.24883	-2.6006	-2.41263	-6.55573	-0.98424
94	H	93	82	81	1.08684	134.83629	2.75913	-2.20179	-6.34745	0.06141

Table 4 continued

Atom No	Atom symbol	NA	NB	NC	Bond/Å	Angle/°	Dihedral/°	X/Å	Y/Å	Z/Å
95	H	93	82	81	1.09336	96.11272	128.42833	-3.47074	-6.80405	-1.10333
96	H	93	82	81	1.09289	94.68925	-120.99964	-1.795	-7.3913	-1.32299
97	O	82	81	78	1.36201	116.40872	0.30056	-2.08227	-5.35513	-1.68973

Atom No + NA = Bond; Atom No + NA + NB = Angle; Atom No + NA + NB + NC = Dihedral; X, Y, Z Cartesian coordinate

Conclusions

Based on the TG curves, EA, and the results of complexometric titration, a general formula could be established for the synthesized compounds. TG-DTA experiments provided previously unreported information concerning the thermal behavior and thermal decomposition of these compounds. The spectroscopic infrared data theoretical calculus suggests that thorium coordinated by the α -ketonic carbonyl and carboxylate groups of the ligands.

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References

- Bannach G, Schnitzler E, Treu-Filho O, Utuni VHS, Ionashiro M. Synthesis, characterization and thermal studies on solid compounds of 2-chlorobenzylidenepyruvate of heavier trivalent lanthanides and yttrium (III). *J Therm Anal Calorim.* 2006;83:233–40.
- Pereira NCS, Melios CB, Marques RN, Siqueira OS, Moraes M, Molina M, Ionashiro M. 4-dimethylaminocinnamylidenepyruvic acid: synthesis, characterization and complexation with trivalent lanthanides, yttrium (III), scandium (III), thorium (IV) and uranium (VI) in aqueous solution. *J Alloys Compd.* 1997;249:94–8. References there in.
- Schnitzler E, Melios CB, Ionashiro M. Solid-state compounds of 4-methoxybenzylidenepyruvate and cinnamylidenepyruvates with thorium (IV) - Preparation and thermal studies. benzylidenepyruvate of heavier trivalent lanthanides and yttrium (III). *J Therm Anal Calorim.* 2002;70:581–92.
- Bannach G, Mendes RA, Ionashiro EY, Mauro AE, Schnitzler E, Ionashiro M. Thermal studies on solid 2-chlorobenzylidenepyruvate of lighter trivalent lanthanides. *J Therm Anal Calorim.* 2005;79:329–34.
- Ionashiro EY, Bannach G, Siqueira AB, Carvalho CT, Rodrigues EC. Ionashiro M 2-methoxybenzylidenepyruvate with heavier trivalent lanthanides and yttrium (III) synthesis and characterization. *J Therm Anal Calorim.* 2008;92:953–9.
- Carvalho CT, Siqueira AB, Treu-Filho O, Ionashiro EY, Ionashiro M. Synthesis, characterization and thermal behaviour of solid 2-methoxycinnamylidenepyruvate of light trivalent lanthanides. *J Braz Chem Soc.* 2009;20:1313–9.
- Dametto PR, Ambrozini B, Siqueira AB, Carvalho CT, Ionashiro M. Synthesis, characterization and thermal behaviour of solid-state 3-methoxybenzoates of heavy trivalent lanthanides and yttrium(III). *J Therm Anal Calorim.* 2009;101:933–9.
- Siqueira AB, Carvalho CT, Rodrigues EC, Ionashiro EY, Bannach G, Ionashiro M. Synthesis, characterization and thermal behaviour of heavy lanthanide and yttrium pyruvates in the solid state. *J Therm Anal Calorim.* 2010;100:95–100.
- Ionashiro M, Graner CAF, Zuanon-Netto J. Titulação complexométrica de lantanídeos e Ítrio. *Ecl Quim.* 1983;8:29–32.
- Becke AD. Density-functional thermochemistry. 3. The role of exact exchange. *J Chem Phys.* 1993;98:5648–52.
- Lee C, Yang W, Parr RG. Development of the colle-salvetti correlation-energy formula into a functional of the electron-density. *Phys Rev B.* 1988;37:785–9.
- Treu-Filho O, Pinheiro JC, da Costa EB, Ferreira JEV, de Figueiredo AF, Kondo RT, de Lucca Neto VA, de Souza RA, Legendre AO, Mauro AE. Experimental and theoretical study of the compound [Pd(dmba)(NCO)(imz)]. *J Mol Struct.* 2007;829:195–201.
- Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA, Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Rega N, Salvador P, Dannenberg JJ, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Baboul AG, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Andres JL, Gonzalez C, Head-Gordon M, Replogle ES, Pople JA. *Gaussian 03, Revision B.04.* Pittsburgh: Gaussian, Inc; 2003.
- Schelegel HB. In: Bertran J, editor. *New theoretical concepts for understanding organic reactions.* The Netherlands: Academic; 1989. p. 33–53.
- Goodson DZ, Sarpal SK, Bopp P, Wolfsberg M. Influence on isotope effect calculations of the method of obtaining force constants from vibrational data. *J Phys Chem.* 1982;86:659–63.
- Roy Dennington II, Keith Todd, Millam John, Ken Eppinnett W, Hovell Lee, Gilliland Ray. *Gaussview, version 3.0.* Shawnee Mission: Semichem, Inc.; 2003.
- Deacon GB, Phillips RJ. Relationships between the carbon-oxygen stretching frequencies of carboxylate complexes and the type of carboxylate coordination. *J Coord Chem.* 1980;33:227–50.