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New Bismuth(III), Lanthanum(III), Praseodymium (III), and Heterodinuclear Bi–La and Bi–Pr Complexes with Polyaminocarboxylate Ligands

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New Bi(III), La(III) and Pr(III) complexes with a variety of high-denticity polyaminocarboxylic acids (H_4edta, H_5dtpa, H_6ttha, H_4Cydta, H_5hpdta, H_4egta) have been synthesized and characterized spectroscopically by FTIR. In the case of the decadentate ttha ligand, homodinuclear M_2(ttha) (M = Bi, La, Pr) and heterodinuclear MM'(ttha) complexes were isolated. Detailed investigations of their thermal degradation scheme were carried out in relationship with the possible use of these complexes as molecular precursors for the formation of mixed Bi–La and Bi–Pr oxides in which the crystal structure of the fluorite-like δ-Bi_2O_3 phase can be stabilized at room temperature. Decomposition proceeds in three successive stages, consisting of dehydration, ligand pyrolysis leading to monoxo-, dioxo- or simple carbonates, depending on the metal nature, and finally decarbonatation producing the corresponding oxide: α-Bi_2O_3, La_2O_3, Pr_6O_{11}, $BiLaO_3$ or $BiPrO_3$. © 2002 Elsevier Science (USA)

Key Words: **bismuth; lanthanides; polyaminocarboxylates; precursors; oxides.**

1. INTRODUCTION

The search for bismuth and lanthanide coordination complexes that could be used as molecular precursors to generate Bi- and/or *Ln*-based oxide-type materials displays a wide interest in the relationship with the numerous possible applications of such inorganic materials as ion conductors, high-T_c superconductors, ferroelectrics or inorganic pigments (1–4). When compared with the traditional ceramic route involving oxides or carbonates of the metal components, these precursor methods actually provide materials displaying a higher homogeneity. Furthermore, variations in composition and stoichiometry of the starting compounds often result in different morphological properties of the final oxide materials, not only from the point of view of particle shape and size distribution, specific surface area, porosity, but also of different levels of surface contamination. In that context, polyaminocarboxylate (PAC) complexes are demonstrated to be particularly interesting candidates, for the following reasons: (i) a wide variety of starting ligands is available which, in addition to oxygen, contain only carbon, hydrogen and nitrogen, i.e., elements that can be removed quite easily from the final solid residue upon adequate thermal treatment, leaving thereby no contamination of the final oxide by heteroelements like sulfur, phosphorus or halogens; (ii) when calcined in air, these complexes usually decompose at moderate temperatures that limit sintering effects, and finally (iii) depending on the functionality of the polyaminocarboxylic acid and the total number of N and O coordination sites, various geometrical arrangements and coordination numbers can be achieved to fit the size and geometry requirements of the cations involved.

Briand and Burford published recently an exhaustive review of Bi(III) coordination complexes involving organic ligands with pnictogen or chalcogen donors (5). Several Bi(III) complexes with nta, edta and dtpa were already obtained (6). Some years ago, we also described new Bi(III) complexes with ttha and Cydta (7, 8). In the particular case of the Bi(H_3ttha) complex, this previous report was the first one to describe a decadentate Bi(III) PAC complex, in which Bi(III) exhibits a tenfold coordination with bicapped square antiprismatic geometry (7). Because six acidic functions are present on the starting molecule, this ligand provides a unique opportunity to generate heterodinuclear complexes with two different tervalent elements, provided they are characterized by identical or similar size and geometrical preferences. With respect to that point, associations between Bi(III) and La(III) are particularly favored because these ions display identical ionic sizes

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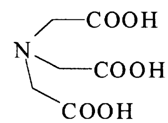
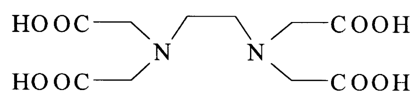
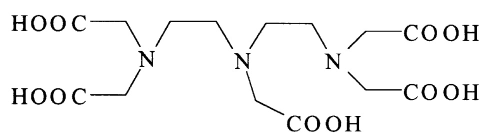
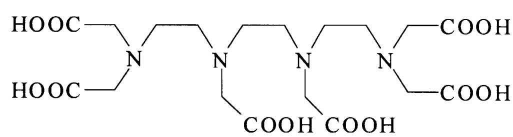
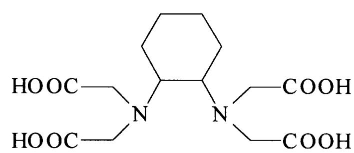
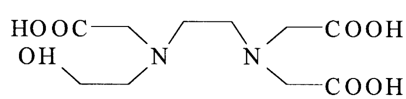
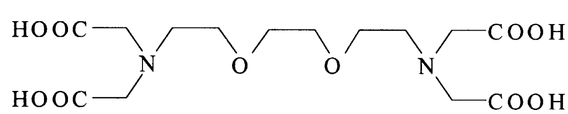
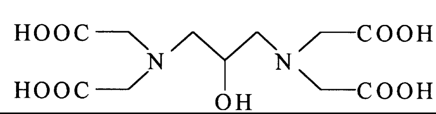
when they are involved in the same coordination polyhedra (in sixfold coordination: $r_{Bi(III)} = 117$ pm, $r_{La(III)} = 117.2$ pm; in eightfold coordination: $r_{Bi(III)} = 131$ pm, $r_{La(III)} = 130$ pm) (9). The ionic size of Pr(III) is just somewhat smaller ($r_{Pr(III)} = 113$ pm for C.N = 6 and 126.6 pm for C.N. = 8). For these reasons, precursor routes based on Bi and *Ln* PAC compounds are particularly useful to prepare homogeneous ternary oxides corresponding to the general formula $Bi_{2-x}Ln_xO_3$, as recently shown in a paper dealing with the synthesis of $Bi_{2-x}La_xO_3$ and $Bi_{2-x}Pr_xO_3$ phases (10).

The ligands used in this work are listed in Table 1. The Bi(III) PAC complexes whose molecular and crystal structures were already described in the literature can be divided into two groups: neutral complexes in which one or several carboxylic groups are not deprotonated (except in the case of nta, where all three groups are ionized), and anionic bismuthate complexes associated with various counter-ions like ammonium, guanidinium (gu) or alkali metals. For the reasons mentioned earlier, our interest is focused on precursor compounds which do not contain heteroelements or other metals in addition to the main one. The following Bi(III), La(III) and Pr(III) PAC complexes described previously in the literature and based on the various ligands used in this work fulfill this requirement:

For Bi(III): Bi(nta)·$(H_2O)_2$ (6), $(NH_4)_3$[Bi(nta)$_2$] (11), Bi(Hedta) (12), Bi(Hedta)·$(H_2O)_2$ (6), (NH_4)[Bi(edta)·(H_2O)] (12), (gu)[Bi(edta)·(H_2O)] (13) and its aminoguanidinium (14) and *β*-alaninium (15) analogs, Bi(H_2dtpa)·

TABLE 1
List and Abbreviations of Polyaminocarboxylic Acids Used in This Work

H_3nta Nitrilotriacetic acid	
H_4edta Ethylenediamine-tetraacetic acid	
H_5dtpa Diethylenetriamine-pentaacetic acid	
H_6ttha Triethylenetetraamine-hexaacetic acid	
H_4Cydta 1,2-*trans*-cyclohexane- diaminetetraacetic acid	
H_4hedta *N*-(2-hydroxyethyl)-ethylene-diaminotriacetic acid	
H_4egta Ethyleneglycol-O,O′-bis-(2-aminoethyl)-tetraacetic acid	
H_5hpdta 2-hydroxy-1,3-diaminopropane-tetraacetic acid	

$(H_2O)_2$ (16), $(gu)_2[Bi(dtpa)]\cdot(H_2O)_4$ (6), $Bi(H_3ttha)\cdot 3H_2O$ (7), $(gu)_2Bi(Httha)\cdot 4H_2O$ (8), $Bi(HCydta)\cdot 5H_2O$ (7).

For La(III): $La(Hedta)\cdot 7H_2O$ (17), $La(Hhedta)(H_2O)_2]\cdot 3H_2O$ (18), $(gu)_2La(Httha)\cdot 3.5H_2O$ (19).

For Pr(III): $[Pr(nta)\cdot(H_2O)_2]\cdot H_2O$ (20).

This paper reports the preparation and characterization by FTIR and TGA of new complexes of Bi(III), La(III) and Pr(III) with edta, dtpa, ttha and egta ligands. Elemental analyses are provided for each of them. The various complexes are characterized by thermogravimetry under air in order to determine the water content, to validate the assumed stoichiometry on the basis of the total weight loss up to the oxide stage, to determine their final decomposition temperature and to investigate their thermal degradation scheme.

2. EXPERIMENTAL

2.1. General Procedure for the Synthesis of the Mononuclear Bi(III) Complexes

In general, the complexes were synthesized according to a preparation procedure described by Summers *et al.* (6) for the synthesis of nta, edta or dtpa complexes of Bi(III). The main principles are as follows: the ligand is introduced in its non-ionized form in boiling water (1 g in 100 mL). All PAC acids were purchased from Fluka, except H_6ttha (Aldrich) and H_4edta (Merck), and used as received. After complete dissolution, the insoluble Bi(III) oxocarbonate ($Bi_2O_2CO_3$, Fluka, p.a.) is added to the aqueous solution with a slight excess with respect to the Bi:L stoichiometry of 1:1. The white suspension obtained is heated under stirring until progressive disappearance of the solid due to the formation of a soluble Bi–L complex. At this point, the solution is filtered off to remove the excess Bi(III) oxocarbonate. Guanidinium carbonate (Aldrich, 99.99%) or aminoguanidinium hydrogenocarbonate (Fluka, p.a.) is added to the filtrate when needed. The resulting filtrate is concentrated upon slow evaporation and leaves either a precipitate, or sometimes, crystals.

2.2. General Procedure for the Synthesis of the Homobinuclear ttha Complexes

As already mentioned above, the decadentate nature of the ttha ligand allowed us to synthesize homodinuclear Bi(III) complexes of Bi(III), La(III) or Pr(III), but also heterodinuclear Bi–La and Bi–Pr complexes. In this case, the synthesis follows initially the general procedure described above, resulting in the formation of soluble $Bi(H_3ttha)$ complex, into which the second cation is introduced according to the molar ratio Bi:*M*:ttha of 1:1:1. Reagents used are the (oxo)carbonate BiO_2CO_3 (Fluka, p.a.), $Pr_2(CO_3)_3$ (Strem Chemicals, 99.9%) or the oxide La_2O_3 (Aldrich, 99.99%). The dinuclear complexes of ttha being insoluble, the obtained slurry is filtered off and the collected solid is washed with water and dried in air.

2.3. General Procedure for the Synthesis of the Mononuclear La(III) and Pr(III) Complexes

The La and Pr complexes are obtained according to the same general procedure, starting from La_2O_3 continuously stored under argon, or praseodymium carbonate, $Pr_2(CO_3)_3$. In the case of the edta complex, pH was increased up to 8–9 with a 5 mol/L solution of ammonia.

2.4. Analytics

The complexes were characterized by infrared (IR) spectroscopy, thermogravimetric analysis (TGA) and chemical analysis.

The metal content is determined by complexometric titration using edta in the presence of xylenol orange, Bi at a pH value of 1, and La and Pr at a pH between 5 and 6, adjusted by hexamethylenetetramine. In the case of the heterometallic complex, Bi is analyzed first at pH = 1, then La or Pr at pH = 6 after the addition of hexamethylenetetramine. The direct implementation of this technique to determine the Bi concentration in the presence of strong chelating agents like PAC ligands is not possible because of the competitive complexation by the initial ligands and the titrating agent, the stability constants being of comparable magnitude. Therefore, the PAC complexes were previously degraded thermally upon calcination in air, at a temperature where the resulting product is either the oxide, the carbonate or the oxocarbonate.

The water content was determined by TGA. C–H–N elemental analysis was carried out at the University College, London.

IR spectra were registered in the form of KBr pellets on a BioRad FTS-135 Fourier transform spectrometer operating in the range 400–4000 cm^{-1}. TGA was performed in air with a Setaram TGC85 analyser at a heating rate of 10°C/min.

3. RESULTS AND DISCUSSION

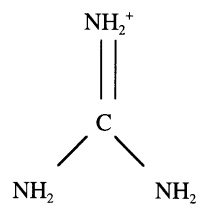
3.1. Synthesis and Characterization

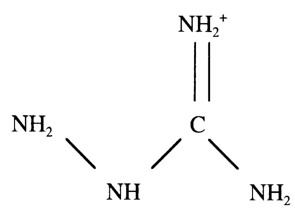
Table 2 summarizes the different Bi(III), La(III), Pr(III) and mixed Bi–La and Bi–Pr complexes which are synthesized for the first time in this work, together with some directly related complexes reported previously. In some cases, ammonium, guanidinium (gu) or

TABLE 2
List of Polyaminocarboxylate Complexes of Bi(III), La(III) and Pr(III) Synthesized in This Work (Water Molecules Are Not Specified)

Ligand	Bi	La	Pr
nta	Bi(nta) (6)	—	Pr(nta) (20) $Pr_2(Hnta)_3$
edta	Bi(Hedta) (6)	$(NH_4)La(edta)$	$(NH_4)Pr(edta)$
dtpa	$(gu)_2Bi(dtpa)$ (6)	$La(H_2dtpa)$	$Pr(H_2dtpa)$
ttha	$Bi(H_3ttha)$ (7) $Bi_2(ttha)$ $(gu)_2Bi(Httha)$ (8)	$La(H_3ttha)$ $La_2(ttha)$ $(gu)_2La(Httha)$ (19) BiLa(ttha)	$(gu)_2Pr(Httha)$ (21a) $(agu)_2Pr(Httha)$ (21b) $Pr_2(ttha)$ BiPr(ttha)
egta	Bi(Hegta)	$La_4(egta)_3$	$Pr_4(egta)_3$
hedta	Bi(Hhedta)	—	—
hpdta	$Bi(H_2hpdta)$	$La(H_2hpdta)$	—
Cydta	Bi(HCydta) (7)	La(HCydta) (gu)La(Cydta)	—

Note.

gu =


agu =


aminoguanidinium (agu) cations were used as counter-ions. For simplification purposes, crystallization water molecules are not specified in this table.

The results of the chemical analyses carried out on the various complexes synthesized in this work are presented in Tables 3–5 for Bi, La and Pr, respectively. Theoretical and experimental values for the C–H–N, metal and water contents are compared. Because the results of the elemental analyses are rather insensitive to the water content, the corresponding values have been determined essentially from the first decomposition step of the TGA analysis. In some cases, the limited accuracy of this value results from the fact that the thermograms do not exhibit a true horizontal stage between the end of the dehydration step and the subsequent pyrolysis of the ligand framework. The proposed stoichiometry therefore corresponds to the best compromise between the elemental C–H–N and metal analyses, on one side, and the TGA results, on the other side.

3.1.1. *Bi(III) PAC Complexes*

The following new compounds were obtained.

With the ttha ligand: the homodinuclear complex $Bi_2(ttha) \cdot 3.5H_2O$, (triethylenetetraaminehexaacetato) dibismuth(III) hemiheptahydrate.

With the egta ligand: (hydrogenethyleneglycol-O,O’-bis-(2-aminoethyl) tetraacetato) bismuth(III) dihydrate, $Bi(Hegta) \cdot 2H_2O$.

With the hedta ligand: (hydrogen-N-(2-hydroxyethyl) ethylenediaminetetraacetato) bismuth(III) hemitrihydrate, $Bi(Hhedta) \cdot 1.5H_2O$.

With the hpdta ligand: (dihydrogen(2-hydroxy)-1, 3-diaminopropanetetraacetato) bismuth(III) dihydrate, $Bi(H_2hpdta) \cdot 2H_2O$.

3.1.2. *La(III) PAC Complexes*

The following new La(III) compounds were obtained.

With the edta ligand: ammonium (ethylenediaminetetraacetato) lanthanate(III) dihydrate, $(NH_4)La(edta) \cdot 2H_2O$.

With the dtpa ligand: (dihydrogendiethylenetriaminepentaacetato) lanthanum(III) hemipentahydrate, $La(H_2dtpa) \cdot 2.5H_2O$.

With the ttha ligand: (trihydrogentriethylenetetraaminehexaacetato) lanthanum(III) tetrahydrate ($La(H_3ttha) \cdot 4H_2O$), and the homodinuclear complex $La_2(ttha) \cdot 4.5H_2O$, (triethylenetetraaminehexaacetato) dilanthanum(III) heminonahydrate.

TABLE 3
Chemical Analysis of Bi(III) PAC Complexes: Experimental vs Calculated Contents (%) of C, H, N, Bi and H_2O

		C[a]	H[a]	N[a]	Bi[b]	H_2O[c]
$Bi(nta) \cdot 2H_2O$	Exp.	16.58	2.19	3.01	48.42	8.3
	Calc.	16.64	2.33	3.23	48.25	8.32
$Bi(Hedta) \cdot 2H_2O$	Exp.	22.47	3.19	5.03	38.84	6.8
	Calc.	22.48	3.21	5.24	39.12	6.74
$(gu)_2Bi(dtpa) \cdot 2H_2O$	Exp.	25.77	4.62	16.48	27.43	5.4
	Calc.	25.51	4.55	16.73	27.74	4.78
$Bi(H_3ttha) \cdot 2.5H_2O$	Exp.	28.69	4.43	7.37	—	6.3
	Calc.	29.00	4.33	7.52	28.03	6.04
$Bi_2(ttha) \cdot 3.5H_2O$	Exp.	22.09	3.11	5.83	43.26	6.5
	Calc.	22.30	3.22	5.78	43.11	6.50
$(gu)_2Bi(Httha) \cdot 4H_2O$	Exp.	26.90	5.08	15.58	23.29	—
	Calc.	26.97	5.09	15.73	23.46	8.09
$Bi(Hegta) \cdot 2H_2O$	Exp.	26.88	3.94	4.48	30.20	4.6
	Calc.	27.02	4.05	4.50	33.58	5.79
$Bi(Hhedta) \cdot 1.5H_2O$	Exp.	23.15	3.55	5.27	40.40	5.4
	Calc.	23.49	3.55	5.48	40.88	5.29
$Bi(H_2hpdta) \cdot 2H_2O$	Exp.	22.48	3.05	4.67	—	6.9
	Calc.	23.41	3.39	4.96	37.04	6.39
$Bi(HCydta) \cdot H_2O$	Exp.	29.16	3.70	4.71	—	3.4
	Calc.	29.48	3.71	4.91	36.64	3.46

[a] Elemental analysis.
[b] Complexometric titrations.
[c] TGA analysis.

With the egta ligand: tris(ethyleneglycol-O,O′-bis-(2-aminoethyl)tetraacetato) tetralanthanum(III) decahydrate, $La_4(egta)_3 \cdot 10H_2O$.

With the Cydta ligand: (hydrogen-*trans*-1,2-cyclohexanediaminetetraacetato) lanthanum(III) tetrahydrate, $La(HCydta) \cdot 4H_2O$ and guanidinium (*trans*-1,2-cyclohexanediaminetetraacetato) lanthanate(III) trihydrate, $(gu)La(Cydta) \cdot 3H_2O$.

With the hpdta ligand: (dihydrogen(2-hydroxy)-1,3-diaminopropanetetraacetato) lanthanum(III) trihydrate, $La(H_2hpdta) \cdot 3H_2O$.

3.1.3. *Pr(III) PAC Complexes*

The following new Pr(III) compounds were obtained.

With the nta ligand: tris(hydrogennitrilotriacetato) dipraseodymium(III), $Pr_2(Hnta)_3$.

With the edta ligand: ammonium (ethylenediaminetetraacetato) praseodymate(III) pentahydrate, $(NH_4)Pr(edta) \cdot 5H_2O$.

With the dtpa ligand: (dihydrogendiethylenetriaminepentaacetato) praseodymium(III) hemitrihydrate, $Pr(H_2dtpa) \cdot 1.5H_2O$.

With the ttha ligand: bis(guanidinium)(hydrogentriethylenetetraaminehexaacetato) praseodymate(III) hemiheptahydrate $(gu)_2Pr(Httha) \cdot 3.5H_2O)$, bis(aminoguanidinium) (hydrogentriethylenetetraaminehexaacetato) praseodymate(III) trihydrate $(agu)_2Pr(Httha).3H_2O)$, and the homodinuclear complex $Pr_2(ttha) \cdot 3.5H_2O$, (triethylenetetra-aminehexaacetato) dipraseodymium(III) hemiheptahydrate.

With the egta ligand: tris(ethyleneglycol-O,O′-bis-(2-aminoethyl)tetraacetato) tetrapraseodymium(III) trihydrate, $Pr_4(egta)_3 \cdot 3H_2O$.

The crystal structures of $(gu)_2Pr(H_3ttha) \cdot 3.5H_2O$ and $(agu)_2Pr(H_3ttha).3H_2O$ are detailed elsewhere (21).

TABLE 4
Chemical Analysis of La(III) PAC Complexes: Experimental vs Calculated Contents (%) of C, H, N, La, Bi and H_2O

		C[a]	H[a]	N[a]	La[b]	Bi[b]	H_2O[c]
$(NH_4)La(edta) \cdot 3H_2O$	Exp.	23.26	4.62	7.79	—	—	10.5
	Calc.	24.06	4.44	8.42	27.83	—	10.83
$La(H_2dtpa) \cdot 2.5H_2O$	Exp.	29.09	3.60	5.70	—	—	7.5
	Calc.	29.28	4.04	7.32	24.19	—	7.84
$La(H_3ttha) \cdot 4H_2O$	Exp.	30.37	4.90	7.77	19.75	—	10.0
	Calc.	30.78	5.02	7.98	19.78	—	10.26
$La_2(ttha) \cdot 4.5H_2O$	Exp.	24.77	4.05	6.30	32.36	—	10.0
	Calc.	25.52	3.93	6.61	32.78	—	9.57
$(gu)_2La(Httha) \cdot 3.5H_2O$	Exp.	29.48	5.46	17.12	—	—	7.3
	Calc.	29.60	5.46	17.26	17.12	—	7.77
$BiLa(ttha) \cdot 4H_2O$	Exp.	23.31	3.51	5.85	14.94	23.61	7.8
	Calc.	23.80	3.55	6.17	15.29	23.01	7.93
$La_4(egta)_3 \cdot 10H_2O$	Exp.	27.39	4.57	4.47	27.72	—	8.6
	Calc.	27.05	4.32	4.51	29.80	—	9.66
$La(H_2hpdta) \cdot 3H_2O$	Exp.	25.57	3.95	5.21	—	—	10.0
	Calc.	25.79	4.13	5.47	27.12	—	10.55
$La(HCydta) \cdot 4H_2O$	Exp.	30.49	5.08	4.87	23.59	—	14.7
	Calc.	29.85	5.01	4.97	24.66	—	14.39
$(gu)La(Cydta) \cdot 3H_2O$	Exp.	—	—	—	23.30	—	8.7
	Calc.	30.26	5.08	11.76	23.33	—	9.08

[a] Elemental analysis.
[b] Complexometric titrations.
[c] TGA analysis.

TABLE 5
Chemical Analysis of Pr(III) PAC Complexes : Experimental vs Calculated Contents (%) of C, H, N, Pr, Bi, and H_2O

		C[a]	H[a]	N[a]	Pr[b]	Bi[b]	H_2O[c]
Pr(nta)·H_2O	Exp.	20.65	2.18	3.75	—	—	5.65
	Calc.	20.77	2.32	4.04	40.60	—	5.19
Pr_2(Hnta)$_3$	Exp.	24.72	2.83	4.63	31.32	—	0.0
	Calc.	25.46	2.49	4.95	33.19	—	0.00
(NH_4)Pr(edta)·5H_2O	Exp.	22.11	4.73	7.45	—	—	16.5
	Calc.	22.36	4.88	7.82	26.23	—	16.77
Pr(H_2dtpa)·1.5H_2O	Exp.	29.87	4.04	7.23	24.84	—	3.6
	Calc.	30.12	4.15	7.53	25.24	—	4.84
(gu)$_2$Pr(Httha)·3.5H_2O	Exp.	29.40	5.44	16.95	—	—	7.8
	Calc.	29.53	5.45	17.22	17.32	—	7.75
(agu)$_2$Pr(Httha)·3H_2O	Exp.	28.83	5.47	20.06	—	—	6.6
	Calc.	28.78	5.43	20.14	16.88	—	6.48
Pr_2(ttha)·3.5H_2O	Exp.	25.63	3.65	6.33	35.93	—	7.8
	Calc.	25.95	3.75	6.72	33.82	—	7.57
BiPr(ttha)·7H_2O	Exp.	22.13	3.87	5.21	14.86	22.04	13.5
	Calc.	22.42	3.97	5.81	14.61	21.67	13.08
Pr_4(egta)$_3$·3H_2O	Exp.	26.53	4.13	4.17	29.54	—	2.93
	Calc.	28.88	3.81	4.81	32.27	—	3.09

[a] Elemental analysis.
[b] Complexometric titrations.
[c] TGA analysis.

3.1.4. Heterometallic Bi–La and Bi–Pr Complexes with the ttha Ligand

In addition to these mono- or homopolynuclear complexes, two heterobimetallic complexes were isolated: (triethylenetetraaminehexaacetato) bismuth(III) lanthanum(III) (BiLa(ttha)) and (triethylenetetraaminehexaacetato) bismuth(III) praseodymium(III) (BiPr(ttha)).

3.2. Comments on the Stability and the Solubility of the Various Complexes

As expected, the solubility of the PAC complexes in water increases with their ionicity. For instance, the solubility of the (gu)$_2$Bi(Httha) complex is about tenfold that of Bi(H_3ttha), whereas the dinuclear compound Bi_2(ttha) is insoluble in water. While the presence of ammonium, guanidinium or aminoguanidinium counterions always enhances the solubility, the complexes in which all carboxylate groups are neutralized by the positive charges of the metal cations display usually (except for the egta complexes) very low water solubility: compounds like Pr(nta) and all M_2(ttha) are completely insoluble. On the other hand, all complexes based on the egta ligand exhibit extremely high solubility and could not be isolated upon precipitation either by concentration of the starting solution or by adding organic solvents like ethanol, diethylether, acetone, dichloromethane and even hexane. This extreme solubility probably results from the presence of two ether functions which are able to be involved in hydrogen bonding with water and other solvents. When evaporating a solution containing egta complexes, the solution becomes viscous and transforms itself into a gel which, upon further drying, generates a perfectly homogeneous and transparent glassy material. The potential interest of such a ligand within the frame of precursor methods able to produce mixed oxides appears therefore to be very high. The drawback of this behavior is however related to the fact that during the attempts to isolate egta complexes in their solid-state form, the impurities associated with the starting reagent are carried along in the solid residue; this explains why the agreement between theoretical and experimental contents for egta complexes is poorer than in the other cases.

Table 6 summarizes the values of stability constants reported in the literature for some Bi(III), La(III) and Pr(III) PAC complexes (22–25). Because of their very high stability, the PAC complexes of Bi(III) could be synthesized and isolated at the low pH value obtained after adding the starting polyaminocarboxylic acid. In the case of lanthanum and praseodymium, the stability constants are lower but remain sufficiently high to allow the La(III)

TABLE 6
Complex Stability Constants at 25°C (log K_f)[a] (22)

	Bi^{3+}	La^{3+}	Pr^{3+}
nta	18.2 17.55 (23)	10.47	10.87 10.31 (24)
edta	27.8 26.41 (23)	15.46	16.36 15.98 (24)
dtpa	30.7 29.29 (23) 35.6 (25)	19.49	21.10
ttha	—	22.4	22.7
egta	23.8[b]	15.77	16.17[b]
Cydta	31.9 (25)	17.10	18.07
hedta	22.3	13.56	14.71
hpdta	12.0[b]	11.61	12.57

[a] $M^{n+} + L^{x-} \rightleftharpoons ML^{(x-n)^-}$, $K_f = [ML^{(x-n)^-}]/[M^{n+}][L^{x-}]$.
[b] $T = 20°C$.

TABLE 7
Representative IR Data of Bi(III), La(III), and Pr(III) PAC Complexes

Ligands	$\nu(C=O)$ (cm^{-1})	Complexes	$\nu_{as}(COO-)$ (cm^{-1})	$\nu_s(COO-)$ (cm^{-1})	$\Delta\nu$ (cm^{-1})	Number μ- COO–
H_3nta	1719	Bi(nta)	1626, 1572	1390	236, 182	2
		Pr(nta)	1605	1460, 1410	195, 145	2
		$Pr_2(Hnta)_3$	1710, 1605, 1565			
H_4edta	1700	Bi(Hedta)	1596	1382	214	1
		(NH_4)La(edta)	1667, 1589, 1561			
		(NH_4)Pr(edta)	1589			
H_5dtpa	1734	$(gu)_2$Bi(dtpa)	1670, 1582	1399, 1385	285, 183	1
	1702	La(H_2dtpa)	1740, 1580			
	1636	Pr(H_2dtpa)	1725, 1588			
			1735, 1632			
H_6ttha	1737	Bi(H_3ttha)	1703, 1690, 1610	1435, 1377	313, 175	0
	1700	La(H_3ttha)	1720, 1589			
		Ce(H_3ttha)	1591			
		$(gu)_2$Bi(Httha)	1740, 1676, 1591	1402, 1375	301, 189	0
		$(gu)_2$La(Httha)	1700,1680,1654, 1584	1437, 1391	289, 193	0
		$(gu)_2$Pr(Httha)	1670, 1585	1435, 1395	275, 150	0
		$(agu)_2$Pr(Httha)	1685, 1596			0
		Bi_2(ttha)	1631, 1600	1384, 1354	277, 216	—
		La_2(ttha)	1597, 1550	1440, 1411	186, 110	—
		Pr_2(ttha)	1583, 1536	1449, 1408	175, 87	—
		BiLa(ttha)	1589	1442, 1414	175, 147	—
		BiPr(ttha)	1653, 1588	1438, 1403	250, 150	—
H_4egta	1742	Bi(Hegta)	1615			
		$La_4(egta)_3$	1584			
		$Pr_4(egta)_3$	1582			
H_4hedta	1679	Bi(Hhedta)	1617, 1553			
	1626					
H_5hpdta	1718	Bi(H_2hpdta)	1735, 1619			
		La(H_2hpdta)	1587			
H_4Cydta	1752	Bi(HCydta)	1656, 1594	1376	280, 218	2
	1730	La(HCydta)	1660, 1616, 1580			
	1708	(gu)La(Cydta)	1664, 1607			
	1656					
	1586					

and Pr(III) complexes to be formed at acidic pH except for edta. Reaction times are usually much smaller for La and Pr than for Bi. Another difference is related to the fact that the 1:1 metal:ligand stoichiometry is quite easily overcome in the case of La. Consequently, the $Ln(H_3ttha)$ complexes ($Ln = La$, Pr) are readily converted into the 2:1 complex according to the disproportionation reaction

$$2Ln(H_3ttha) \leftrightarrows Ln_2(ttha) + H_6ttha$$

even when the reagents were engaged in the equimolar ratio.

In the same way, the stoichiometry $M_4(egta)_3$ which has been observed for La and Pr could not be obtained in the case of Bi. All Pr complexes were found to be highly hygroscopic and this explains the poorer agreement for the results of the elemental analyses.

3.3. *Spectroscopic Characterization*

The IR spectra of the various complexes and starting ligands display a very intense absorption band in the region 3600–3000 cm^{-1} which corresponds to the stretching $\nu(OH)$. In the PAC complexes, this band appears very

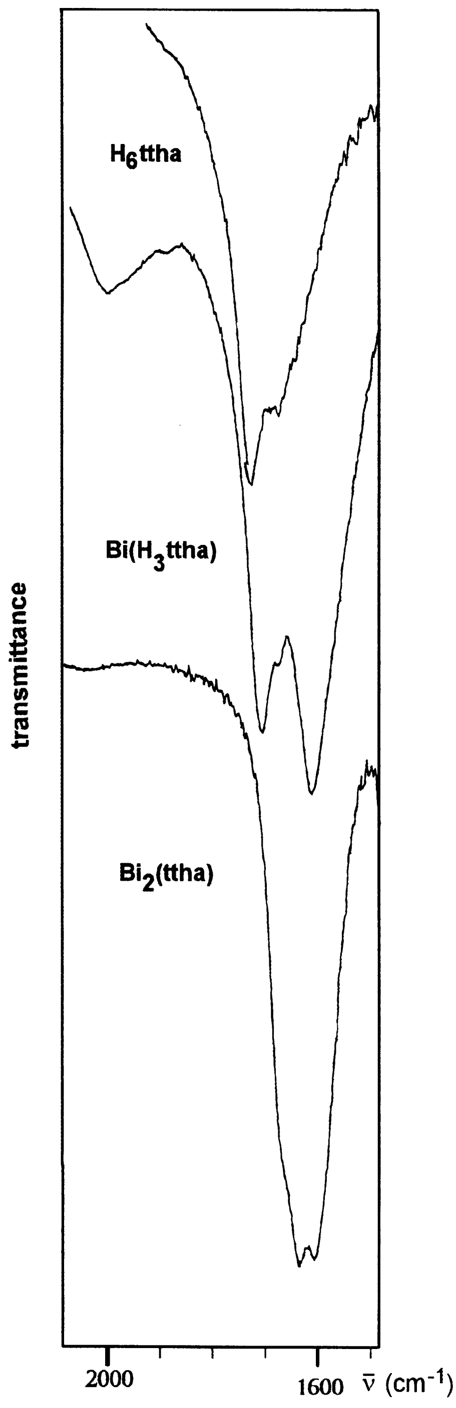


FIG. 1. FTIR spectra (carbonyl region) of H_6ttha, Bi(H_3ttha) and Bi_2(ttha).

broad in consequence of the intricate network of hydrogen bonds involving non-ionized and ionized carboxylic groups and the water molecules. In their free form, the polyaminocarboxylic acids exist as zwitterions resulting from proton exchange between the –COOH and amine groups. However, the corresponding N–H bands which are expected for free ligands in the 3500–3300 cm^{-1} region are weak and overlap those of ν(OH). The most interesting region ranges between 1800 and 1550 cm^{-1}, and corresponds to the antisymmetrical stretching of the carboxylic group, a vibration mode which is quite influenced by its ionization. Their symmetrical counterpart appears in the region 1420–1370 cm^{-1}, but is much less affected by the complexation process. The most relevant values characterizing the ν_s(COO) and ν_{as}(COO) in the free ligands and the various complexes are listed in Table 7. In addition to these bands, weak absorptions assigned to ν(C–N) and out-of-plane bending of the carboxylate group, δ_{oop}(COO), appear at 1100 and 900 cm^{-1}, respectively.

The frequencies associated with the ν_{as}(COOH) mode are typically higher than those corresponding to the ionized groups. Values in the range 1680–1700 cm^{-1} or higher can be assigned to non-ionized carboxylic groups. Fig. 1 allows to compare the FTIR spectra of the mononuclear and dinuclear Bi–ttha complexes with that of the free H_6ttha ligand. In several IR spectra of the free ligands, bands occurring below 1680 cm^{-1} can be assigned to the $–COO^-$ of the zwitterionic form. In this case, the band expected for –COOH does not appear clearly because of its overlap with the broadband from the carboxylate group. As for carboxylates, the carboxylic acid functions can be involved in metal coordination. This is reflected by the shift of their absorption bands above or below 1700 cm^{-1}, higher values being assigned to non-coordinating groups. When comparing the IR spectra of the three $(gu)_2M$(Httha) complexes (M = Bi, La, Pr), it appears that the Bi compound is the only one giving rise to an absorption band at 1740 cm^{-1}. In the Bi complex, the Bi atom was found to be ninefold coordinated (8), without involvement of the –COOH group in the coordination sphere, this group being responsible for the high wavenumber value. In the corresponding La and Pr complexes, this –COOH group is involved in metal bonding and this results in a tenfold coordination, as proven by the crystal structure determinations (19, 21). First attempts to correlate the $\nu_{as}(COO^-)$ values with the ionicity of the metal–oxygen bonding were described in the literature for a wide range of edta complexes (26). However, the conclusions of these studies, for instance in the case of Bi(III) and Pb(II) edta complexes, were not supported by the corresponding crystal structures.

Another approach reported in the literature is based on the fact that, in some favorable cases, the differences between the $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ values can be interpreted in terms of coordination mode of the carboxylate groups (27). This was first established by considering a large number of spectroscopic and crystallographic data collected with acetates and trifluoroacetates. Differences $\Delta\nu = \nu_{as}(COO^-) - \nu_s(COO^-)$ larger than 200 cm^{-1} were suggested to be related to essentially unidentate carboxylate,

TABLE 8
TGA Results of Bi(III) PAC Complexes

	Decomposition steps				Δm tot. (%)[b]	
	I	II	III	T_f[a] (°C)	Exp.	Calc.[c]
$Bi(nta) \cdot 2H_2O$	160–190	290–295	295–315 315–375	375	45.2	46.21
$Bi(Hedta) \cdot 2H_2O$	130–160	310–335	335–455 455–485	485	56.3	56.39
$(gu)_2Bi(dtpa) \cdot 2H_2O$	80–125	290–320 320–445 445–450	450–480	480	67.3	69.08
$Bi(H_3ttha) \cdot 2.5H_2O$	100–145	280–300 300–510	510–560	560	66.1	68.75
$(gu)_2Bi(Httha) \cdot 2H_2O$	80–160	280–320 320–465 465–475	475–505	505	72.4	72.74
$Bi_2(ttha) \cdot 3.5H_2O$	70–120	270–370	370–465	465	51.3	51.93
$Bi(Hegta) \cdot 2H_2O$	70–145	215–280 280–420	420–460	460	58.3[d]	62.56
$Bi(Hhedta) \cdot 1.5H_2O$	70–160	250–290 290–500	500–570	570	54.2	54.43
$Bi(H_2hpdta) \cdot 2H_2O$	70–240	240–280 280–300	300–405 405–440 440–475	475	56.5	58.71
$Bi(HCydta) \cdot H_2O$	80–140	305–330	490–540	540	56.3[d]	59.15

[a] Final decomposition temperature.
[b] Total weight loss (25°C- T_f).
[c] Weight loss calculated with respect to Bi_2O_3.
[d] Significant upwards baseline shift.

while values smaller than this were assumed to reflect a symmetrical coordination mode, either bidentate, or bidentate and bridging. These purely empirical considerations were also verified in the case of Bi(III) complexes based on pyrazine- or pyrazoledicarboxylic acids (28, 29). As obvious from the values listed in Table 7, the interest of this approach seems to be very limited in the case of the PAC complexes presently reported. The main reason for this seems to be related to the large variety of metal–ligand interactions present in the corresponding structures, reflected namely by the broad range of metal–oxygen distances measured by X-ray diffraction in the case of the crystalline materials already described. The involvement of these carboxylate groups in an extended network of hydrogen bonding complicates this situation even further, in the sense that unidentate carboxylates involved in a strong hydrogen bond with an adjacent ligand should actually be considered as ‘‘pseudo-bridging,’’ while bidentate and bridging carboxylates in highly asymmetrical environments should be considered as ‘‘pseudo-unidentate.’’

3.4. *Thermal Behavior*

Detailed thermal degradation studies were carried out in order to (i) determine the hydration content, (ii) validate the assumed stoichiometry on the basis of the total measured weight loss, (iii) determine the final decomposition temperature and (iv) investigate the thermal degradation scheme of the PAC complexes. The temperature ranges characterizing the successive degradation steps in air of the various Bi, La and Pr PAC complexes, together with the corresponding final decomposition temperatures, are listed in Tables 8, 9 and 10, respectively. These tables also allow to compare the total experimental weight loss with the value calculated assuming that the final residue

TABLE 9
TGA Results of La(III) Complexes

	Decomposition steps				Δm tot. (%)[b]	
	I	II	III	T_f[a] (°C)	Exp.	Calc.[c]
$(NH_4)La(edta) \cdot 3H_2O$	130–180	260–350 360–375 500–530	530–780 780–810	810	66.0	67.37
$La(H_2dtpa) \cdot 2.5\ H_2O$	100–250	250–370 370–385 510–555	555-x[d]	x[d]	x[d]	71.63
$La(H_3ttha) \cdot 4\ H_2O$	70–240	240–360 360–385 385–490 490–530	530–700 700–735	735	76.7	76.81
$(gu)_2La(Httha) \cdot 3.5H_2O$	80–170	290–400 400–475 475–530	530–700 700–735	735	76.6	79.93
$La_2(ttha) \cdot 4.5H_2O$	110–145 190–210	310–390	390–705 705–745	745	60.0	61.55
$BiLa(ttha) \cdot 4H_2O$	60–85 160–190	280–340	340–510	510	56.1	56.42[e]
$La_4(egta)_3 \cdot 10H_2O$	70–195	280–350 350–400 400–515	515–550 695–725	725	61.1[f]	65.06
$La(H_2hpdta) \cdot 3H_2O$	150–175	250–350	350–750[g]	750	65.0[c]	68.20
$La(HCydta) \cdot 4.5H_2O$	60–80 140–170	235–300 300–370 440–535	535–745 745–770	770	73.9	71.08
$(gu)La(Cydta) \cdot 3H_2O$	75–100 180–215	300–360 475–540	540–780 780–810	810	70.0	72.64

[a] Final decomposition temperature.
[b] Total weight loss (25°C$-T_f$).
[c] Weight loss calculated with respect to La_2O_3.
[d] Unavailable.
[e] Weight loss calculated with respect to $BiLaO_3$.
[f] Significant upwards baseline shift.
[g] Cumulated steps IIb and III.

corresponds to α-Bi_2O_3, La_2O_3 or Pr_6O_{11}, respectively, as determined by XRD.

In general, the TGA curves display three successive steps, corresponding to dehydration, ligand pyrolysis and final evolution of CO_2 leaving the oxide.

3.4.1. Bi PAC Complexes

In most Bi PAC complexes (Table 8), dehydration starts at 70–80°C and ends between 120°C and 160°C. However, in the nta, edta and hpdta complexes, this step is shifted towards higher temperatures and extends beyond 200°C in Bi(H_2hpdta). Such a broad dehydration step originates in the presence of different types of water molecules in these complexes: some of them directly coordinate the metal cation and are hard to remove, while others are included in the crystal lattice, either involved in hydrogen bonding to carboxylate groups, or as isolated lattice molecules which are very loosely bound to other water molecules or carboxylic oxygens. The latter are responsible for the cohesion of the crystal lattice but can be removed upon mere drying of the crystals at ambient temperature. The second decomposition step, ligand pyrolysis, usually starts around 300°C, but earlier (220–250°C) in hedta, hpdta and

TABLE 10
TGA Results of Pr(III) PAC Complexes

	Decomposition steps				Δm tot. (%)[b]	
	I	II	III	T_f[a] (°C)	Exp.	Calc.[c]
$Pr(nta) \cdot H_2O$	220–380	380–485	580–640	640	49.8	50.95
$Pr_2(Hnta)_3$	—	260–275 275–395 395–455	575–620	620	62.0	59.91
$(NH_4)Pr(edta) \cdot 5H_2O$	70–170	275–360 360–390 500–570	570–650	650	71.0	68.31
$Pr(H_2dtpa) \cdot 3H_2O$	90–250	250–390 390–500 500–540	540–580	580	71.5	70.91
$(gu)_2Pr(Httha) \cdot 3.5H_2O$	75–185	290–490 490–585	—	585	76.0	79.07
$(agu)_2Pr(Httha) \cdot 3H_2O$	80–200	250–500 500–740	—	740	79.0	79.60
$Pr_2(ttha) \cdot 3.5H_2O$	85–220	340–385	500–555 610–650	650	60.0	59.14
$BiPr(ttha) \cdot 7H_2O$	85–160	280–340	340–420 420–520	520	60.2	58.74[d]
$Pr_4(egta)_3 \cdot 3H_2O$	85–220	360–520 520–555	—	555	62.2	61.01

[a] Final decomposition temperature.
[b] Total weight loss (25°C$-T_f$).
[c] Weight loss calculated with respect to Pr_6O_{11}.
[d] Weight loss calculated with respect to $BiPrO_3$.

egta complexes, in which additional non-carboxylic oxygen atoms are present (alcohol or ether groups). It is sometimes possible to identify two or three successive substeps, like in the $(gu)_2Bi(dtpa)$ and $(gu)_2Bi(Httha)$ complexes. In other cases, pyrolysis proceeds in one single sharp weight loss, like in the complexes Bi(nta), Bi(Hedta), Bi(HCydta) and $Bi_2(ttha)$. At the end of this second step, carbonate-type compounds ($Bi_2(CO_3)_3$, $Bi_2O(CO_3)_2$, $Bi_2O_2CO_3$) are probably present, which could unfortunately not be identified by XRD because of their amorphous nature. The third step follows immediately the previous one because the intermediate species is poorly stable. Taking into account the three different carbonated species postulated in the thermograms, this step would correspond to the following decomposition scheme:

$$Bi_2(CO_3)_3 \rightarrow Bi_2O(CO_3)_2 \rightarrow Bi_2O_2CO_3 \rightarrow Bi_2O_3,$$

in which the oxocarbonate $Bi_2O_2CO_3$ is actually the so far only well-identified Bi carbonate compound. The final decomposition temperatures range between 375°C and 570°C. The intermediate formation of an oxocarbonate has been mentioned only in very limited cases, like in NaBi(edta) (30). Such species were never reported as degradation products of simple Bi(III) carboxylates, many of which proceeding through an intermediate oxocarboxylate (bismuthyl carboxylate) Bi*OL* stage (*L* = acetate (31), ethylhexanoate (32), citrate (33)). In other cases, like the formate, propionate, lactate and oxalate complexes, such an intermediate was not reported and the compounds undergo a quite simple decomposition process leading directly to Bi_2O_3 (31). It should however be mentioned that $Bi_2O_2CO_3$ and α-Bi_2O_3 were both detected by XRD in the thermal residue of $Bi(HCOO)_3$ at 375°C, whereas there was no clear evidence for the oxocarbonate stage in the TGA curve (31).

3.4.2. *La PAC Complexes*

The La complexes (Table 9) exhibit essentially the same overall decomposition scheme in three successive steps, but with some minor differences. The dehydration step proceeds from 70°C to 240°C, with two distinct substeps in the case of La_2(ttha), BiLa(ttha), (gu)La(Cydta) and La(HCydta). The ligand pyrolysis step is slower, extending over a much wider temperature range, and can be clearly divided into several (mostly three) different steps, in all cases but La_2(ttha). In the latter compound, a fast degradation process leads directly to $La_2(CO_3)_3$. This carbonate appears as the final intermediate product in all cases at temperatures between 520°C and 550°C. It was already reported in the thermal degradation schemes of some other La compounds, like the acetate (34) and acetylacetonate (35). However, in most other complexes previously reported in the literature (36), the dioxocarbonate $La_2O_2CO_3$ appears to be the usual intermediate. More thorough investigations of the thermal behavior of these complexes using DTA would most probably have allowed to identify $La_2(CO_3)_3$ as intermediate species in a much wider series of compounds. On the other hand, the previously reported $La_2O(CO_3)_2$ intermediate (37) has never been detected in the present work. The heteronuclear BiLa(ttha) complex displays an intermediate behavior between those of Bi_2(ttha) and La_2(ttha), the second step ending with the formation of $BiLa(CO_3)_3$ which in turn decomposes into the mixed oxide $BiLaO_3$. The third step, from 520–550°C to 725–810°C, corresponds to the slow conversion of the carbonate intermediate into La_2O_3, in two stages: transformation of $La_2(CO_3)_3$ into $La_2O_2CO_3$ over a temperature range of 200–300°C, followed by further fast CO_2 evolution leaving La_2O_3. This overall scheme is common to all La complexes investigated, including La_2(ttha), except for the following cases:

— La(H_2hpdta) in which the second and third steps overlap;

— BiLa(ttha) where decarbonatation is much faster due to the presence of Bi and

— $La_4(egta)_3$ in which the conversion of $La_2(CO_3)_3$ into $La_2O_2CO_3$ is much faster and separated by some 150°C of the further decomposition of $La_2O_2CO_3$ into La_2O_3.

The final decomposition temperatures range between 725°C and 810°C, except for BiLa(ttha). Globally, these final temperatures extend over a narrower range than for the Bi complexes, but are some 250–350°C higher.

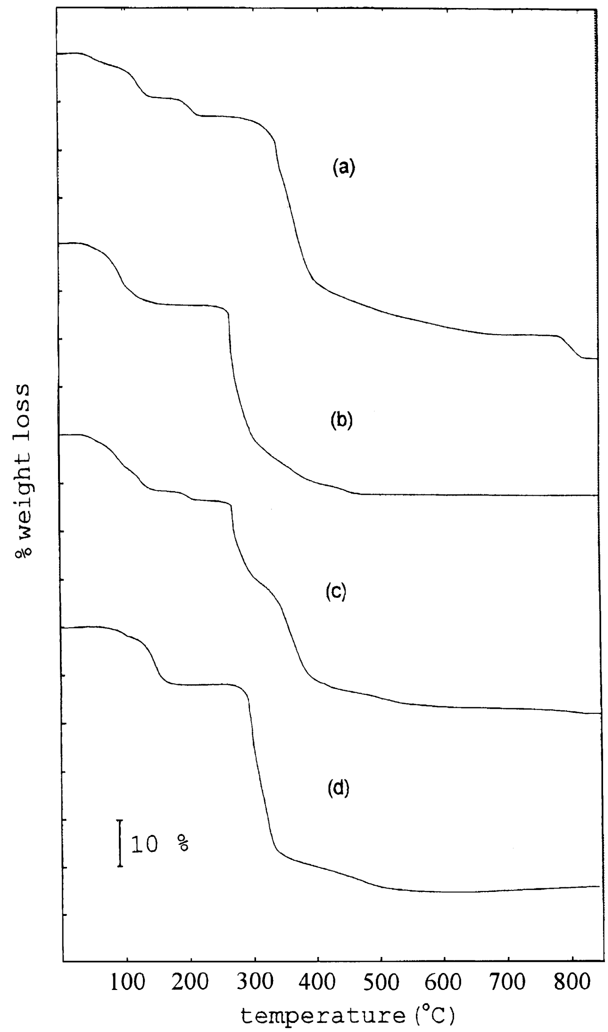


FIG. 2. TGA analysis results of ttha complexes under air (10°/min): (a) La_2(ttha), (b) Bi_2(ttha), (c) equimolar mixture of Bi_2(ttha) + La_2(ttha) and (d) BiLa(ttha).

3.4.3. Pr PAC Complexes

The Pr complexes (Table 10) behave essentially like the La complexes, with similar ranges for the dehydration (70–250°C) and pyrolysis steps (ending at 540–580°C). In most cases, the dioxocarbonate $Pr_2O_2CO_3$ is formed at the end of the second step, except for $(gu)_2$Pr(Httha), $(agu)_2$Pr(Httha) and $Pr_4(egta)_3$, which produce directly Pr_6O_{11}. There is no evidence for the formation of $Pr_2(CO_3)_3$ and this is a striking difference with respect to the corresponding La complexes, for which $La_2(CO_3)_3$ was systematically observed. The formation of $Pr_2O_2CO_3$ has been mentioned in most previously reported cases (34, 37–39), sometimes as further degradation product of the $Pr_2O(CO_3)_2$ intermediate (39). When present, the third step corresponds to the transformation of $Pr_2O_2CO_3$ into Pr_6O_{11}, i.e., decarbonatation is accompanied by the partial oxidation of Pr(III) into Pr(IV). Despite similar final temperatures for the second step, the ultimate decomposition temperatures are lower than for La (555–740°C), meaning that in the case of Pr, the carbonate-to-oxide conversion is facilitated, probably because decarbonatation is assisted by the exothermal oxidation of Pr(III) into Pr(IV).

3.4.4. Heterodinuclear MM′ttha Complexes

In general, the thermal degradation scheme of the heterodinuclear MM'(ttha) complexes is intermediate between those of M_2(ttha) and M'_2(ttha), exhibiting the same three major decomposition steps as the homonuclear complexes. After dehydration in one or two stages, a single and fast pyrolytic decomposition results in the formation of the mixed carbonate $BiLa(CO_3)_3$ in the case of BiLa(ttha), which decomposes further into a mixed dioxocarbonate $BiLaO_2CO_3$, whereas the corresponding compound $BiPrO_2CO_3$ was obtained without any intermediate in the case of BiPr(ttha). The XRD characterization of the final oxides indicated the presence of ternary oxides corresponding to the formula $BiLaO_3$ and $BiPrO_3$. However, in the latter case, as shown by the XRD pattern of the mixed oxide obtained (10), which is intermediate between those of δ-Bi_2O_3 and Pr_6O_{11}, an alternative formulation such as $BiPr^{III}_{1-x}Pr^{IV}_xO_{3+0.5x}$, taking into account the simultaneous presence of Pr(III) and Pr(IV) in the final residue, can also been proposed. The final decomposition temperatures of the heterodinuclear complexes are intermediate between those of the corresponding homodinuclear complexes. As illustrated in Fig. 2 for the Bi–La system, the TGA curve of BiLa(ttha) (Fig. 2d) is characteristic of this formulation and does not correspond to the superimposed curves from La_2(ttha) (Fig. 2a) and Bi_2(ttha) (Fig. 2b), as those obtained when an equimolar mixture of the two homodinuclear complexes are heated under the same conditions (Fig. 2c).

4. CONCLUSIONS

A wide series of new polyaminocarboxylate complexes of Bi(III), La(III) and Pr(III) with the edta, dtpa, ttha, Cydta, hpdta and egta ligands has been synthesized and characterized. In addition to mononuclear and homopolynuclear complexes of these three elements, a unique opportunity of synthesizing heterobinuclear Bi-*Ln* complexes involving two different trivalent elements was encountered with the decadentate ttha ligand. Detailed investigations of the thermal behavior of these complexes was carried out in view of their use as molecular solid-state precursors for Bi–*Ln*–O phases which display a great interest as inorganic materials.

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