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Thermal decomposition study of some complexes, precursors of mixed oxides, with formula $MM'(L) \cdot nH_2O$ ($M, M' = $ Bi, Pb, Sr, Ca and Cu; $L = $ EDTA-like ligands)

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Abstract

Five compounds of formula $MM'(L) \cdot nH_2O$ [L = ethylenediaminetetraacetic acid (EDTA) or diethylenetriaminepentaacetic acid (DTPA); M, M′ = Bi, Pb, Sr, Ca or Cu, $n = 3$–5] have been synthesized and characterized by elemental analysis, spectroscopic techniques and X-ray diffraction. The thermal behaviour of these complexes has been studied by thermogravimetry and differential thermal analysis. The data set provided by the TG and DSC curves of the complexes shows the occurrence of three consecutive steps: dehydration, ligand pyrolysis and the formation of inorganic residues. The enthalpies of the corresponding dehydration process have been calculated. In considering the last-named stage, the compounds were heated at different temperatures. The final products of the pyrolysis, metallic and bimetallic oxides, were examined by X-ray powder diffraction. Note that the $PbSrO_3$ phase is obtained under normal conditions of pressure.

INTRODUCTION

Since the discovery of high T_c superconductors in 1986, a great deal of study has been devoted to improving knowledge on and characteristics of complex metal oxides, in particular perovskite phase [1]. These compounds are traditionally prepared by the ceramic method, in which reactions are generally slow because of the large diffusion distances. However, alternative syntheses involving low temperature decomposition of suitable precursors hold much promise [2,3]. We have therefore applied this technique to obtain precursors of the family Bi Pb Ca Sr Cu O [4] from metallo-organic derivatives. Thus, different complexes having the general stoichiometry $MM'(L) \cdot nH_2O$ [M, M′ = Bi, Pb, Sr, Ca, Cu; L = EDTA-like ligands;

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$n = 3$–5] have been prepared. The metallic elements in these EDTA derivatives are dispersed but ordered; the relative stoichiometry in the final oxides could thus be controlled. Further studies, for example, of the influence of the type of initial salt on the surface specific properties [5], are nowadays very important, and might offer significant results in discovering synthetic procedures to replace the ceramic method. This kind of work could be better developed in the light of prior understanding of the thermal behaviour of the starting complexes. To research this last question constitutes the fundamental aim of the present paper. In addition, X-ray diffraction techniques have been used to identify the products formed in the production of the inorganic degradation residues.

EXPERIMENTAL

Materials

Five different complexes have been prepared as follows. To an aqueous solution of ligand (EDTA (ethylenediaminetetraacetic acid) or DTPA (diethylenetriaminepentaacetic acid)) (1 mmol) was added the stoichiometric quantity (1 mmol) of the oxide or carbonate of one of the metals (Bi_2O_3, $CaCO_3$, $SrCO_3$, PbO or CuO). After a short period to ensure complexation, an equimolar suspension of the other metal (as oxide or carbonate) was added. The complexes were separated from the solutions as crystalline precipitates by vacuum filtration after addition of acetone. The solids were washed with water and ether and dried over P_2O_5. In this way, the complexes $[CaPb(EDTA)(H_2O)_5]$, and $[SrPb(EDTA)(H_2O)_3]$, $[PbBi(DTPA)(H_2O)_3]$, $[SrCa(EDTA)(H_2O)_5]$ and $[SrCu(EDTA)(H_2O)_4]$ were obtained.

Methods

Carbon, nitrogen and hydrogen contents of the complexes were determined by elemental analysis, and metals were determined by atomic absorption (Table 1).

TABLE 1

Analytical data of the complexes

Compound	Found (calculated), %			M (Pb or Cu)
	C	N	H	
$PbCaC_{10}N_2H_{22}O_{13}$	19.27 (19.20)	4.67 (4.48)	3.32 (3.52)	32.96 (33.13)
$PbSrC_{10}N_2H_{18}O_{11}$	19.03 (18.86)	4.63 (4.40)	2.40 (2.82)	32.67 (32.48)
$PbBiC_{14}N_3H_{24}O_{13}$	19.64 (19.60)	4.79 (4.89)	2.68 (2.80)	24.37 (24.15)
$CaSrC_{10}N_2H_{22}O_{13}$	23.81 (23.72)	5.63 (5.53)	4.16 (4.35)	–
$CuSrC_{10}N_2H_{20}O_{12}$	23.04 (23.50)	5.44 (5.78)	3.34 (3.90)	12.13 (12.45)

Infrared spectra were obtained using KBr discs (2%) on a Perkin–Elmer 1430 spectrophotometer. To follow the thermal complex evolution, TGA and DSC techniques were used. The measurements were carried out with a Perkin–Elmer System-7 DSC–TGA unit. Crucibles containing 20 mg of sample were heated at 10 °C min^{-1} under dry nitrogen and air, respectively. Cylindrical pellets for DSC were made from the powder using a Perkin–Elmer (P/N 15.010) hydraulic press at 5 atm pressure. The complexes were heated at different temperatures in the range 500–900 °C during 2 h, in an atmosphere of air. The resulting products were examined by X-ray powder diffraction. The data were recorded at room temperature with a Philips PW 1710 diffractometer equipped with a graphite monochromator, using Cu Kα radiation. Positions of diffraction were corrected using a separate internal standard for each compound. Journal Cards of Powder Diffraction Files (JCPDS) [16] and the theoretical generated diagrams (LAZY PULVERIX [6]) were utilized as comparative patterns. The different diagrams were indexed with TREOR4 [7] and LSUCRE [8] computer programs.

RESULTS AND DISCUSSION

The different complexes are obtained as polycrystalline powders. For two of them single crystals were obtained, and the preliminary lattice constants and space groups were determined by the symmetry of oscillation and absences on zero and first level Weissenberg photographs. Final unit cell parameters for both single crystals were obtained by least squares refinements, LSUCRE [8], of the indexed powder diffraction patterns. For $[SrCa(EDTA)(H_2O)_5]$, $a = 19.520(4)$, $b = 11.527(2)$, $c = 15.968(3)$ Å, $\beta = 95.3(1)°$, space group $C2/c$ and for $[SrCu(EDTA)(H_2O)_4]$, $a = 8.706(3)$, $b = 10.482(4)$, $c = 19.484(9)$ Å, $\beta = 100.4(2)°$ and space group $P2_1/c$. In the case of $[SrCa(EDTA)(H_2O)_5]$ good quality crystals were isolated and the crystal structure was determined [9]. The indexation of the X-ray diffraction diagrams for the other compounds led to different symmetries (TREOR4 [7]).

The main bands in the infrared spectra for the ligands and their complexes are reported in Table 2.

Stretching vibrations of the OH group of the water molecules appear as broad and complex bands in the 3600–3200 cm^{-1} region. Absorption at 1125–1087 cm^{-1} is attributed tentatively to the C–N group. The splitting of the band at approximately 1100 cm^{-1} in the complexes suggests a metal–nitrogen coordination. The bands in the region of the spectra between 1550 and 1600 cm^{-1} correspond to the C–O stretching vibration. Complexing of the carboxyl groups shifts the carbonyl band toward lower frequencies. The absence of absorption around 1700 cm^{-1} indicates that no –COOH groups are present. These results agree with those previously presented in the literature for compounds of this type [9–12].

TABLE 2

Characteristic bands in the infrared spectra (3500–600 cm^{-1})

Compound	$\nu(OH)H_2O$	$\nu(CO)$	$\nu(CN)$
EDTA	3490 m	1690 s	1090 w
DTPA	3480 m	1635 s	1095 w
$[PbBi(DTPA)(H_2O)_3]$	3350–3550 s, br	1590 s	1087, 1125 m
$[CaPb(EDTA)(H_2O)_5]$	3200–3550 s, br	1590 s	1097, 1110 m
$[SrPb(EDTA)(H_2O)_3]$	3300–3550 s, br	1580 s	1093, 1107 m
$[SrCa(EDTA)(H_2O)_5]$	3250–3550 s, br	1580 s	1108, 1125 m
$[SrCu(EDTA)(H_2O)_4]$	3200–3600 s, br	1600 s	1110, 1125 m

Abbreviations used: s, strong; m, medium; w, weak; br, broad.

The decomposition steps of the complexes were obtained from their TG and DSC curves (Fig. 1), which could be explained as the occurrence of three consecutive processes, namely dehydration, ligand pyrolysis and inorganic residue formation. Analogous results can be observed in the course of the complex decomposition in a controlled air atmosphere.

Dehydration

The first process in the thermal evolution can be linked with dehydration, which occurs as a one- or two-stage endothermic process in the range 40–160 °C. The thermal data are shown in Table 3.

It can be observed that the dehydration process for $[CaPb(EDTA)(H_2O)_5]$ and $[SrPb(EDTA)(H_2O)_3]$ takes place in only one step (Fig. 1), which suggests that the water molecules are equivalent. The presence of two steps for the other three complexes may be attributed to the liberation of water molecules located in the crystal lattice in a different way. The dehydration process implies a lowering in the coordination number of the hydrated cation (that is, the metal coordinated to different water molecules) and probably concludes with a rearrangement of the EDTA ligand between the two metallic centres [13]. The expected endothermic effect was ob-

TABLE 3

Thermal analysis data for $MM'(L)\cdot nH_2O$ compounds for dehydration step

Compound	T range (°C)	Weight loss Found (calculated) (%)	ΔH (kJ mol^{-1})
$[CaPb(EDTA)(H_2O)_5]$	60–160	14.06 (14.38)	148
$[SrPb(EDTA)(H_2O)_3]$	58–135	8.12 (8.47)	150
$[PbBi(DTPA)(H_2O)_3]$	32–150	6.33 (6.30)	171
$[SrCa(EDTA)(H_2O)_5]$	60–160	17.35 (17.79)	103
$[SrCu(EDTA)(H_2O)_4]$	40–130	14.63 (14.07)	168

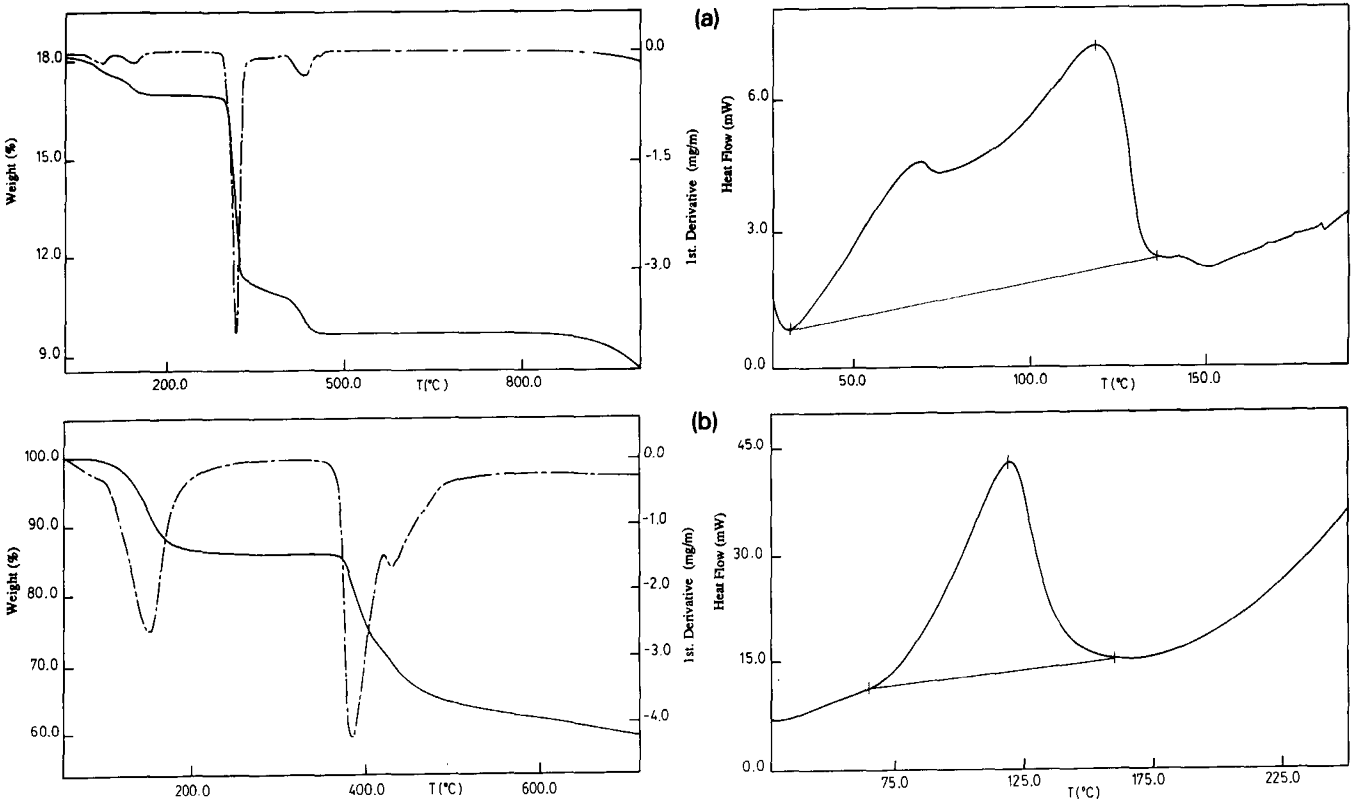

Fig. 1. TG and DSC curves for the different complexes: (a) [PbBi(DTPA)(H_2O)$_3$], (b) [CaPb(EDTA)(H_2O)$_5$], (c) [SrPb(EDTA)(H_2O)$_3$], (d) [SrCa(EDTA)(H_2O)$_5$], (e) [SrCu(EDTA)(H_2O)$_4$].

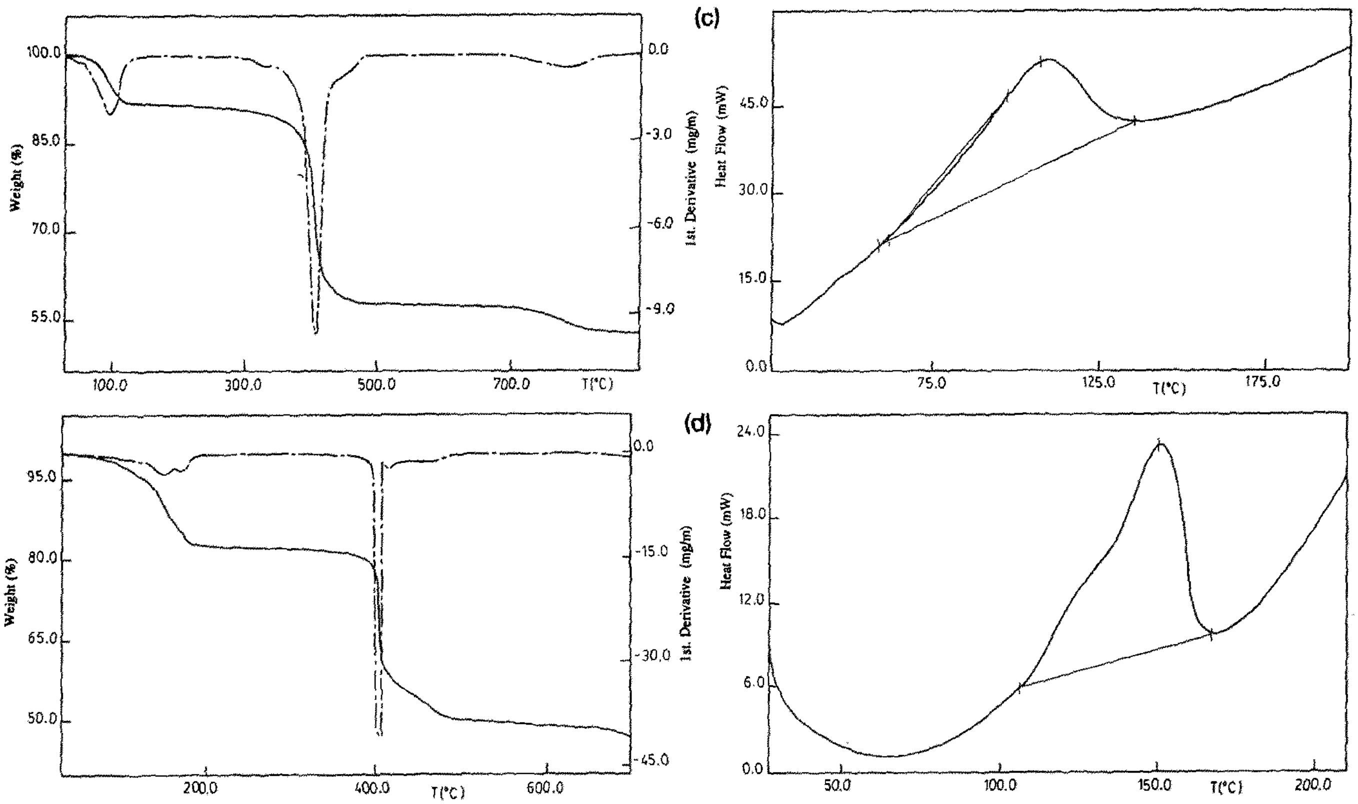

Fig. 1 (continued).

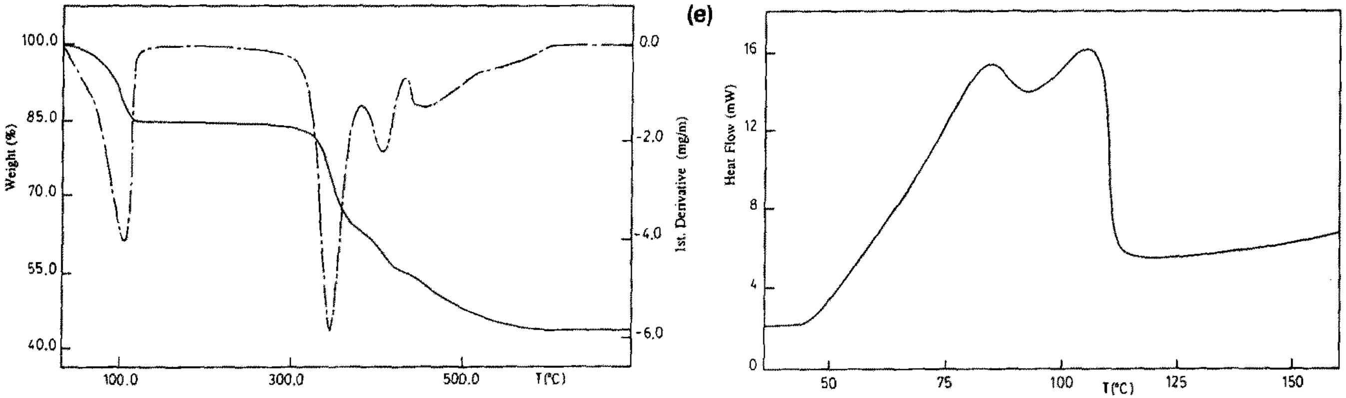

Fig. 1 (continued).

served in the DSC curves, from which the dehydration enthalpies were calculated. These are of the same magnitude as those obtained previously for this type of complex [14]. The high values obtained indicate that the water molecules could be directly linked to the metal ions, in agreement with the results obtained from determination of the structure of these complexes [9,10]. In order to analyze the dehydration kinetics, Satava's least squares fit has been used. Since the analyzed models corresponding to different mechanisms led systematically to similar correlation factors, general assignments could not be assumed for the dehydration process.

Ligand pyrolysis

Decomposition of the anhydrous compounds follows immediately after dehydration in the temperature range 300–500 °C. For this step, kinetic parameters have not been calculated because of the complexity of the process. The process generally involves two overlapping steps, namely decarboxylation (in one or more stages) and breakdown of the ethylenediamine structure; furthermore, the great diversity of possible products, as is the case with carbonates, precludes exhaustive interpretations. The following reaction schemes are the most reasonable to describe the decomposition process

$$\mathrm{MM'(EDTA)(s)} \rightarrow \mathrm{MCO_3(s)} + \mathrm{M'CO_3(s)} + \mathrm{R(g)}$$

$$\mathrm{MM'(EDTA)(s)} \rightarrow \mathrm{MO(s)} + \mathrm{M'CO_3(s)} + \mathrm{R(g)}$$

$$\mathrm{MM'(EDTA)(s)} \rightarrow \mathrm{MO(s)} + \mathrm{M'O(s)} + \mathrm{R(g)}$$

$\mathrm{R(g)}$ = gas residue (CO_2, CO...)

The nature of the cation coordinated to the ligand may be the main factor in determining the results of pyrolysis [15]. Depending on the stability of the metal carbonates, monodentate carboxylates could yield the first gas evolved in the form of CO_2, and the cations could be stabilized as oxides. Otherwise, if the chelated cation gives rise to a stable carbonate, the inorganic residue would be composed of only carbonates.

Inorganic residue formation

An understanding of the stage which the inorganic residue undergoes after ligand pyrolysis is required for a study of the final products. In this step, metal oxides and carbonates can be formed, which can be used as precursors of superconductor phases. Evolution of the resulting phases has been monitored by firing the metallo-organic complexes at different temperatures in an air atmosphere. In all cases, X-ray diffraction patterns of the final products were taken.

After heating the complex [CaPb(EDTA)(H_2O)$_5$] at different temperatures in the range 600–900 ° C, two unique phases, PbO [16] and $PbCa_2O_4$ [17], were found. These results agree with the temperature versus composition diagram presented by Kitaguchi et al. [18], confirming the formation of $PbCa_2O_4$ in the temperature range mentioned above. The X-ray diffraction peaks corresponding to the $PbCa_2O_4$ phase have been indexed (LSUCRE [8]), and do not show any significant variation of the unit cell parameters on increasing the temperature.

In the case of [SrPb(EDTA)(H_2O)$_3$], a mixture of $SrCO_3$ [16], PbO [16] and $PbSrO_3$ [19] can be observed upon heating to 700 ° C. However, at 800 ° C the X-ray diffraction pattern has been indexed on the basis of a single phase corresponding to $PbSrO_3$, with the unit cell parameters: $a = 5.939(1)$, $b = 8.319(4)$, $c = 5.824(4)$ Å; space group *Pnma*. According to the results obtained, it might be mentioned that the preparation of $PbSrO_3$ from the [SrPb(EDTA)(H_2O)$_3$] complex is a relatively simple method of synthesis in favourable conditions, taking account of the high values given in the literature ($P_{O_2} > 3500$ atm and $T = 450$ ° C) [19]. The appearance of oxides of Pb(IV), as has been reported in the literature [20], could be explained because of the presence of alkaline earth metals.

The reaction of the precursor [PbBi(DTPA)(H_2O)$_3$] at different temperatures (500, 600 and 700 ° C) yielded a mixture of PbO and another phase. These have not been identified according to the PbO–Bi_2O_3 phase diagram [21]. As the compounds in this system have attracted great interest in recent years, owing to the discovery of their specific semiconductor and dielectric properties [22], a detailed study has been made of the remaining unidentified peaks. The different X-ray diffraction patterns obtained in the temperature range 500–700 ° C were indexed with a trial and error indexing program, TREOR4 [7], on the basis of a monoclinic unit cell with the following parameters: $a = 11.788(2)$, $b = 14.423(3)$, $c = 10.478(3)$ Å and $\beta = 107(1)°$.

In the case of the complexes [SrCa(EDTA)(H_2O)$_5$] and [SrCu(EDTA)(H_2O)$_4$] a mixture of phases is obtained in each case, $SrCO_3$ and the oxide of the other metal, CaO or CuO respectively. For [SrCu(EDTA)(H_2O)$_4$], some diffraction maxima could not be identified according to the different bimetallic oxides presented in the JCPDS [16].

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