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Preparation, Characterization and Properties of some Lanthanide Oxides

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Abstract

The formation of oxides of the types Ln_2O_3 and $Ln^1Ln^2O_3$ is reported. They have been obtained by thermal decomposition of homo- and hetero-dinuclear complexes of the type $Ln_2(L)(NO_3)_4 \cdot xH_2O$ or $Ln^1Ln^2(L)(NO_3)_4 \cdot xH_2O$ where H_2L is the macrocycle obtained by condensation of 2,6-diformyl-4-chlorophenol and 1,8-diamino-3,6-dioxaoctane.

The composition and properties of the oxides, particularly of $DyEuO_3$ and $DyNdO_3$, have been studied by means of X-ray powder diffraction, electron microscopy and X-ray fluorescence techniques together with magnetic investigations.

The products obtained have been compared with those prepared by thermal decomposition of the appropriate $Ln(NO_3)_3 \cdot xH_2O$ or, where available, with the commercial oxides. The polymorphism of the oxides has been also investigated.

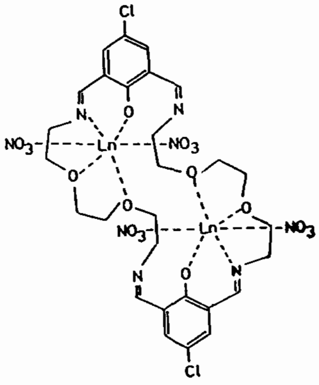
Introduction

Many efforts are currently being made in order to apply the knowledge already acquired on inorganic, coordination or organometallic compounds containing f-ions, to the preparation of inorganic materials. Thus coordination or organometallic compounds can be used in the manufacture of sophisticated molecular devices or as precursors in the preparation of electronic, magnetic, optical materials, etc. [1–7].

The availability of well defined homo- and/or hetero-polynuclear complexes has favoured studies on molecular conductivity, magnetic exchange, reactivity and catalysis, energy transfer processes etc. [1, 2, 8–13].

In these areas polynuclear compounds containing rare earths can have a considerable role owing to the potential of their unique physicochemical properties, especially in the preparation of magnetic and optical systems. To reach this aim, many binucleating ligands have been synthesized, extensively discussed and reviewed [10, 14].

Very recently we have prepared homo- and hetero-dinuclear lanthanide(III) complexes of the types $Ln_2(L)(NO_3)_4 \cdot xH_2O$ and $Ln^1Ln^2(L)(NO_3)_4 \cdot xH_2O$ [15]



$Ln_2(L)(NO_3)_4 \cdot xH_2O$

$Ln^1Ln^2(L)(NO_3)_4 \cdot xH_2O$

These complexes show some interesting optical properties particularly the terbium(III)–europium(III) complex where it was possible to quantify the ligand to Ln(III) and the Tb(III) to Eu(III) energy transfers.

These homo- and hetero-dinuclear complexes have been used as useful precursors in the formation of mixed oxides by their thermal decomposition, focusing particularly on the experimental conditions for the preparation of crystallographically pure species and on their physicochemical properties. By this thermal decomposition procedure, almost the whole series of Ln_2O_3 oxides and several $Ln^1Ln^2O_3$ complexes (Ln^1Ln^2 = LaSm, LaGd, LaDy, NdGd, DyEu, DyNd) have been prepared. The present paper reports the first results obtained, with particular attention to the mixed oxides $DyEuO_3$ and $DyNdO_3$.

Experimental

The homo- and hetero-dinuclear complexes were prepared and characterized according to literature

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procedures [15]. Commercial Ln_2O_3 (at least 99.9 reagent grade; Aldrich) were stored and manipulated in a dry box. The same oxides were also prepared by thermal decomposition of the homo-dinuclear complexes, $Ln_2(L)(NO_3)_4 \cdot xH_2O$ or of $Ln(NO_3)_3 \cdot xH_2O$. The mixed oxides $Ln^1Ln^2O_3$ were obtained by thermal decomposition of the appropriate hetero-dinuclear complexes.

The thermogravimetric and differential thermoanalysis curves were obtained using a NETZSCH STA 429 thermoanalytical equipment. The tests were performed in a nitrogen atmosphere (flux rate 250 ml min^{-1}; heating rate 5 °C min^{-1}) and in air under the same conditions. Neutral alumina (C. Erba product) was used as reference material.

The lanthanide percentage was determined by flame emission by using a Varian AA-257 atomic absorption spectrophotometer.

Lanthanide ratios were conveniently determined by the integral counting of X-ray fluorescence radiation from a Philips SEM model 505 scanning electron microscope equipped with an EDAX analysis system.

Samples suitable for SEM analysis were prepared by suspension of the microcrystalline powders in petroleum ether. Some drops of the resulting suspension were placed on a beryllium plate and, after evaporation of the solvent, the samples were metallized (to take photographs) with graphite or gold by means of an Edward's S150B model sputter coater.

X-ray diffraction patterns were recorded by transmission technique, using a GD 2000 Ital Structures diffractometer operating in the Seemann-Bohlin geometry, with a quartz monochromator on the primary beam and a NaI(Tl) scintillation counter; Cu Kα_1 radiation was employed. The step-scanning recording was performed in the 5–60° (2θ) range at 0.02° steps and with a counting time of 15 s per step. In the present paper the diffractograms are reported in the usual way, i.e. 2θ angle against intensity in arbitrary units.

Results and Discussion

The homo- and hetero-dinuclear lanthanide(III) complexes $Ln_2(L)(NO_3)_4 \cdot xH_2O$ and $Ln^1Ln^2(L)(NO_3)_4 \cdot xH_2O$ were prepared by reaction of 2,6-diformyl-4-chlorophenol with 1,8-diamino-3,6-dioxaoctane in the presence of the appropriate lanthanide(III) nitrate hydrate [15]. IR, Raman and luminescence data, magnetic susceptibility, EPR and electron microscopy investigations together with X-ray fluorescence analysis agree with a binuclear structure, where the macrocycle H_2L has incorporated, in its coordination moiety, two equal or different lanthanide ions. The coordination, almost equal about each metal ion, is completed by two bidentate nitrate anions. By using particular experimental procedures [15], it is possible to vary the Ln^1/Ln^2 ratio in the hetero-dinuclear complexes. X-ray powder diffraction patterns show the homo- and hetero-dinuclear complexes are all isostructural, independently of the metal/metal ratio.

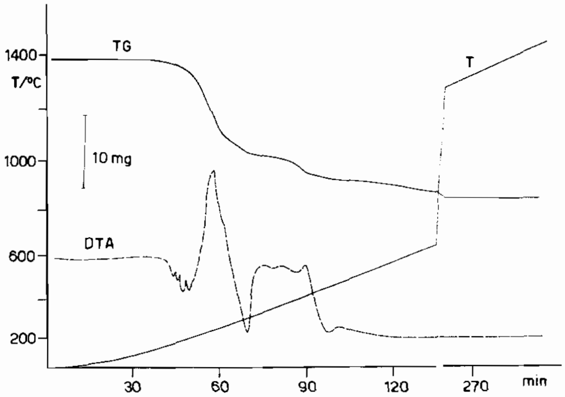

Fig. 1. Thermograms of $[DyEu(L)(NO_3)_4] \cdot H_2O$ (43.60 mg).

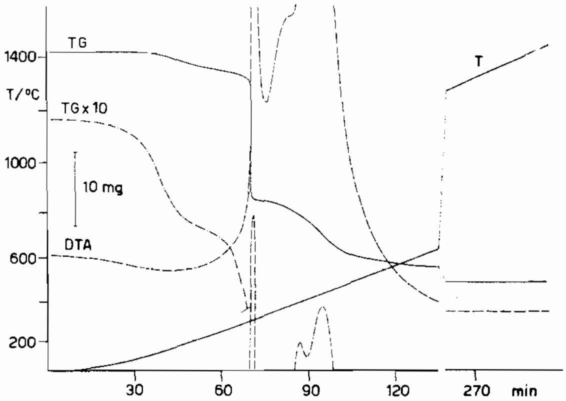

Fig. 2. Thermal behaviour of an equimolar mixture of $Dy(NO_3)_3 \cdot nH_2O$ and $Eu(NO_3)_3 \cdot nH_2O$ (37.04 mg).

The thermal decomposition in air and in nitrogen of these homo- and hetero-dinuclear complexes was followed by TG and DTA up to 1600 °C and compared respectively with that of the corresponding $Ln(NO_3)_3 \cdot nH_2O$ or of equimolar mixtures of lanthanide(III) nitrate hydrates. The final products are the oxides Ln_2O_3 or $Ln^1Ln^2O_3$, according to the starting compounds used as precursors. The oxides, obtained from the complexes, are often crystallographically purer than the commercial products; as an example commercial Eu_2O_3 appears to be quite amorphous; in its XRD pattern only one strong line at 2θ = 28.3° is clearly detectable. Figure 1 reports the thermal behaviour of the hetero-dinuclear complex $[DyEu(L)(NO_3)_4] \cdot H_2O$ whereas Fig. 2 shows the thermal decomposition of an equimolar mixture of $Dy(NO_3)_3 \cdot H_2O$ and $Eu(NO_3)_3 \cdot H_2O$.

All the homo- and hetero-dinuclear complexes lose a water molecule in the 80–100 °C temperature

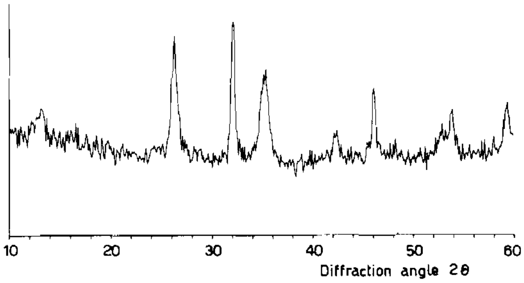

Fig. 3. Diffraction pattern of $DyEuO_2CO_3$.

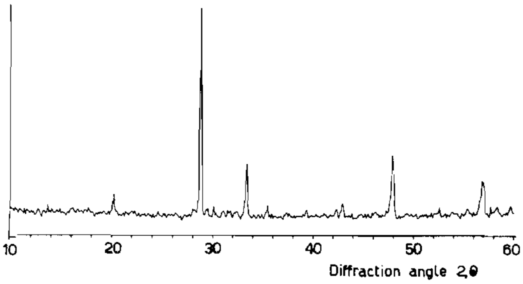

Fig. 4. X-ray diffraction pattern of cubic $DyEuO_3$.

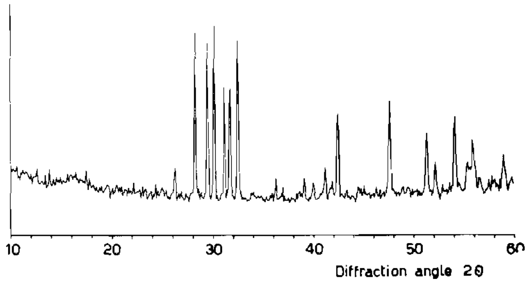

Fig. 5. X-ray diffraction pattern of monoclinic $DyEuO_3$.

range; this indicates that the water molecule is not coordinated to the central metal ion but is a solvate molecule present in the lattice. At about 300 °C the complexes suffer an exothermic decomposition, which causes also microexplosions of the samples. The phenomena were not observed during the thermal decomposition of other lanthanide compounds; and hence they seem to be due to the particular structure of the macrocyclic complexes prepared. These problems have been partially overcome by hooding the samples by fibre quartz; this procedure, however, did not allow a correct evaluation of the weight loss of the samples, consequently the assignment of the degradation pathway from 300 to 600 °C was quite impossible. At about 600 °C there is a range of stability of the formed sample which has been determined to be $Ln_2O_2CO_3$ (Fig. 3) [17]. The subsequent thermal decomposition produces Ln_2O_3 or $Ln^1Ln^2O_3$, in different and pure crystallographic forms [16, 18, 19].

These oxides were characterized by X-ray powder diffraction (XRD) and electron microscopy with X-ray fluorescence analysis. In particular the metal ratio and the homogeneity of the mixed oxides were determined by electron microscopy and X-ray fluorescence spectroscopy. As an example, $DyEuO_3$ shows the presence of both ions in all microcrystals of the mixed oxide while a non-homogeneity is well detectable in an equimolar mixture of Dy_2O_3 and Eu_2O_3. In both samples the lanthanide ratio agrees with the proposed formulation. For $DyEuO_3$, obtained by thermal decomposition of the related complex, the absence of carbon or nitrogen containing residues was also checked.

The XRD pattern of $DyEuO_3$ obtained by decomposition up to 1200 °C (Fig. 4) completely fits for a cubic symmetry and the refined value of the unit cell parameter is $a = 10.773$ Å, to be compared with $a = 10.665$ (Dy_2O_3) and $a = 10.869$ (Eu_2O_3) Å in the cubic form described in the JCPDS cards [16].

The thermal decomposition at 1600 °C of the hetero-dinuclear complex produces a new structure whose XRD pattern, reported in Fig. 5, clearly shows a non-cubic symmetry.

A monoclinic symmetry has been reported in the JCPDS cards for some other mixed oxides of the type $Ln^1Ln^2O_3$, obtained by decomposition of the corresponding nitrates at 1200 °C, for 5 days. Effectively, the XRD pattern of $DyEuO_3$ completely fits for a monoclinc symmetry and the refined parameters of the unit cell are: $a = 14.004$; $b = 3.728$; $c = 8.722$ Å; $\beta = 100°7'$, in very good agreement with the values reported in JCPDS for the monoclinic Eu_2O_3 [16].

A magnetic investigation, carried out at room temperature, has shown that generally there is not a remarkable change of the magnetic moment on going from the complexes to the oxides. As an example $DyNd(L)(NO_3)_4 \cdot 2H_2O$ and the related $DyNdO_3$ have a μ_B of 8.17 and 8.23 BM respectively. The precursor $DyEu(L)(NO_3)_4 \cdot 2H_2O$ has a $\mu_B = 11.02$ BM while $DyEuO_3$ has a $\mu_B = 10.36$ BM.

A more appropriate study on the correlation of the magnetic properties of the mixed oxides to their structures is under investigation.

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