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DEHP complexes of lanthanides(III) and actinides(III)

D.N. Suglobov, Yu. I. Trifonov, E.K. Legin and A.G. Tutov
V.G. Khlopin Radium Institute, Shvernic Str. 28, 194021 St. Petersburg, (Russian Federation)

Abstract

Lanthanides di-(2-ethylhexyl)phosphates (LnA_3) crystallize as needle-like samples exhibiting an axial texture with an identity period along texture of 5.3 Å. A hexagonal elementary cell of EuA_3 has the following parameters: $a=18.6$ Å, $c=10.4$ Å, $z=2$. As is evident from IR and luminescence (EuA_3) spectra, LnA_3 molecules form rigid-chain coordination polymer structure with neighbouring coordination octahedra linked by alkylphosphate bridges. LnA_3 is very poorly soluble in alkanes as well as in donor solvents. However, we developed the series systems in which the solubility of LnA_3 increases dramatically as a result of the formation of oligomers or mixed-ligand complexes. Coordination chemical processes occurring in these systems have been studied using thermodynamic and spectroscopic methods. The structural formulae and strength of the complexes formed are discussed. On the decomposition of mixed-ligand complexes, considerable separation in the Am-lanthanides and Eu-lanthanides series occurs.

1. Introduction

The thermodynamic and kinetic behaviour of lanthanides(III) and actinides(III) upon extraction with di-(2-ethylhexyl) phosphoric acid (HA) has been studied rather thoroughly [1,2]. However, some important problems of molecular structure and coordination properties of rare earth (RE) di-(2-ethylhexyl) phosphates remain to be solved. In the present work some normal non-solvated lanthanide di-(2-ethylhexyl) phosphates (LnA_3) were synthesized and their molecular structure and coordination chemical properties were studied. The structural investigations of crystalline samples were performed by X-ray and spectrometric (IR and luminescence) methods. The coordination chemical behaviour was studied in the processes of LnA_3 dissolving in organic solvents on interaction with different ligands. The IR and luminescence spectra were used to bring out the structure and polymerization of complexes formed. The decomposition reactions of soluble alkylphosphate complexes were studied, and considerable separation of lanthanide and americium was established.

2. Experimental details

HEDHP previously purified from pyro- and monoethers was refined from neutral impurities according to Ref. [3] by mixing equivalent quantities of NaA and $La(NO_3)_3 \cdot 6H_2O$ acetone solutions and separation of the LnA_3 precipitate formed. This procedure was also used in the present work for the synthesis of LnA_3 crystalline powders. Needle-like samples of LnA_3 crystals were grown from a solution of polymeric LnA_3 in a CCl_4 (80 vol.%), n-$C_8H_{17}OH$ (20 vol.%) mixture by slow evaporation of CCl_4. LnA_3 samples were analysed by degradation of n-octane solution by contacting with 10 ml HNO_3 and subsequent titrimetric determination of lanthanide and HA in the water and organic phases respectively. Analytical data obtained correspond to the formula LnA_3. IR spectra were recorded on an IRS-29 spectrometer; luminescence spectra were registered on an SDL-2 spectrometer ($\lambda_{Hg}=360$ nm). The X-ray patterns of crystals were measured in a Weissenberg chamber (Cu Kα).

3. Molecular and crystal structure of LnA_3

The X-ray study has shown that the crystals of LnA_3 exhibit an axial texture. The presence of such texture indicates that the molecules of LnA_3 and previously studied $Nd[O_2P(O_2C_2H_5)_2]_3$ [4] have an identical linear rigid-chain coordination polymer structure. An identity period along the LnA_3 texture of 5.3 Å was determined from X-ray patterns. The character of the splitting in the luminescence spectrum ($^5D_0$–$^7F_{1,2}$) corresponds to the octahedral coordination sphere of Eu^{3+} in EuA_3 (Fig. 1). In the IR spectrum there are bands ν_s (PO) at 1090 cm^{-1} and ν_{as}(PO) at 1180 cm^{-1} which are assigned to the PO stretching vibrations of bridged alkyl phosphate groups.

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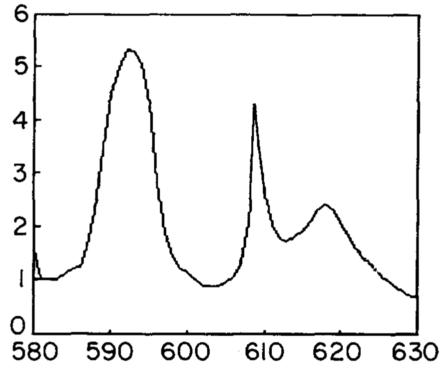


Fig. 1. Luminescence spectrum of polycrystalline EuA_3.

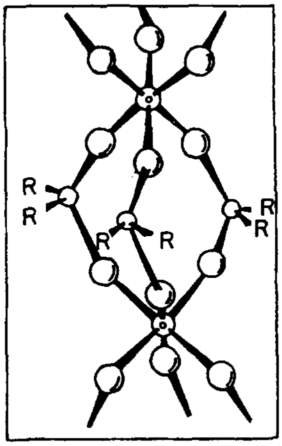


Fig. 2. Model of EuA_3 polymeric molecule: ◎, Eu^{3+}; ○, oxygen; o, phosphorus; R, 2-ethylhexyl radical.

The model of the polymeric molecule $(LnA_3)_n$ was constructed on the basis of X-ray and spectroscopic data (Fig. 2). In compliance with the model, Ln^{3+} ions in LnA_3 have an octahedral coordination sphere and the faces of neighbouring octahedra are linked by alkylphosphate bridges. The distance Ln–Ln calculated from the model is in good agreement with the identity period of the texture (5.3 Å). The 2-ethylhexyl radicals are positioned perpendicular to the polymer axis. The elementary cell of EuA_3 (hexagonal) has the following parameters: $a = 18.6$ Å, $c = 10.4$ Å, $Z = 2$, $\rho_{calc} = 1.16$ g cm^{-3}, $\rho_{exp} = 1.21$ g cm^{-3}. In the crystal lattice each EuA_3 molecule is surrounded by six neighbours at a distance of 18.6 Å and connected with them by Van der Waals forces.

4. Solvation and coordination chemical properties of LnA_3 in organic solution

LnA_3 is very poorly soluble in alkanes as well as in donor solvents (ROH, CH_3COCH_3, H_2O, R_3N, $(RO)_3PO$, etc.). However, LnA_3 forms viscous polymeric solutions in highly polarizable solvents such as CCl_4. Such solutions contain the rigid polymeric molecules $(LnA_3)_n$ and, as shown in Ref. [5], are lyophilic liquid crystals (nematic).

Later we shall consider some systems in which the partial destruction of alkylphosphate bridge bonds in LnA_3 polymers occurs to yield a low viscous solution of oligomers.

4.1. Behaviour of LnA_3 in the system n-octane–n-octanol–ammonia

The solubility of solid LnA_3 in an octane–octanol mixture increases sharply upon addition of gaseous NH_3:

$$LnA_3 + NH_3 \longrightarrow \text{soluble complex (I)} \qquad (1)$$

The solubility of $LnA_3(S)$ as a function of NH_3 partial pressure (P_{NH_3}) is fitted by the equation

$$S = S^0 + kP_{NH_3}{}^n \qquad (2)$$

where S^0 is the solubility of LnA_3 at $P_{NH_3} = 0$; $k = S - S^0$ at $P_{NH_3} = 10^5$ Pa and n is an empirical parameter (Fig. 3).

At a fixed P_{NH_3} the maximum LnA_3 solubility is achieved at 20 vol.% ROH. A considerable quantity of NH_3 was observed to be absorbed by solid LnA_3. This process as seen from X-ray patterns results in a significant distortion of the LnA_3 crystal lattice. However, the bands of coordinated NH_3 molecules are not registered in the IR spectra of solid LnA_3 and samples of solutions saturated by ammonia, which suggests that the NH_3 interaction with LnA_3 is of an outer-sphere character.

The bands corresponding to terminal alkylphosphate group vibrations are not observed in the IR spectra of the above solutions. Consequently the soluble LnA_3 oligomers produced by NH_3 action are rather long.

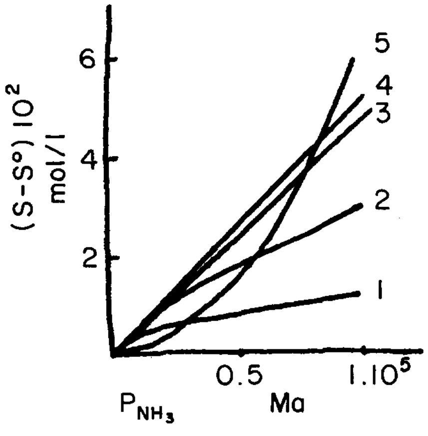


Fig. 3. $S - S^0$ as a function of P_{NH_3} for various lanthanides (n-octane, n-octanol (20 vol.%, 20 °C): 1, NdA_3, $n = 0.5$; 2, CeA_3, $n = 0.75$; 3, GdA_3, $n = 1$; 4, SmA_3, $n = 1$; 5, LaA_3, $n = 2$.

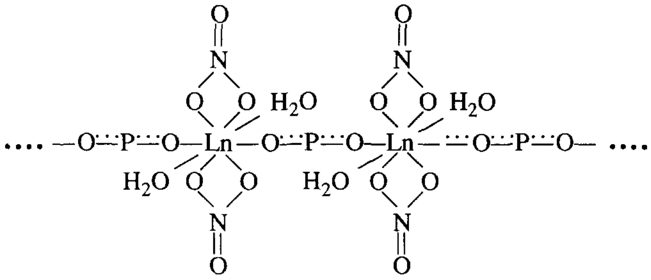
Reaction (1) is shifted to the left during NH_3 removal from solution by blowing with air, yielding solid LnA_3.

4.2. Solubility of LnA_3 in $Ln(NO_3)_3 \cdot 6H_2O$ acetone solutions

Upon addition of $Ln(NO_3)_3 \cdot 6H_2O$ acetone solution to a heterogeneous mixture of solid LnA_3 and acetone, rapid dissolution of the solid occurs as a result of the reaction

$$LnA_3 + 2Ln(NO_3)_3(ac.) = 3LnA(NO_3)_2(ac.) \qquad (3)$$

In the case of LaA_3 this reaction is strongly shifted to the right, which allows one to isolate $LaA(NO_3)_2 \cdot 2H_2O$ (II) as an individual complex. The IR spectrum of (II) shows the bands $\nu_{as}(PO)$ at 1190 cm^{-1} and $\nu_s(PO)$ at 1090 cm^{-1} of bridged alkylphosphates anions, the bands ν_4 at 1507 cm^{-1}, ν_1 at 1275 cm^{-1} and ν_6 at 810 cm^{-1} of bidentately coordinated nitrate anions and the bands ν_{OH} at 3400 cm^{-1} and δ_{H_2O} at 1620 cm^{-1} of coordinated water molecules. According to these data, the following structural formula of (II) may be proposed:



The number of bridged alkylphosphate groups in this polymeric complex is one-third of that in LnA_3, leading to considerable depolymerization of mixed complexes in solution. One of the causes of mixed complex formation is the increase in lanthanide coordination number from six in LnA_3 to eight in (II). Furthermore, the formation of (II) is facilitated by the strengthening of the NO_3^- coordination in the mixed complex ($\nu_4 - \nu_1 = 232$ cm^{-1}, $\nu_6 = 810$ cm^{-1}) in comparison with $Ln(NO_3)_2 \cdot 6H_2O$. ($\nu_4 - \nu_1 = 210$ cm^{-1}, $\nu_6 = 818$ cm^{-1}).

As seen from Fig. 4, the solubility of LnA_3 by reaction (3) is decreased in the series LaA_3–ErA_3 as a result of alkylphosphate bridge bond strengthening.

4.3. Solubility of LnA_3 in acidic organic solutions

Upon addition of concentrated HNO_3 (15 mol l^{-1}) dropwise to a heterogeneous mixture of LnA_3 and acetone with stirring, rapid dissolution of the solid occurs as a result of acidic mixed complex (III) formation:

$$LnA_3 + 2HNO_3 = LnA(NO_3HA)_2 \text{ (III)} \qquad (4)$$

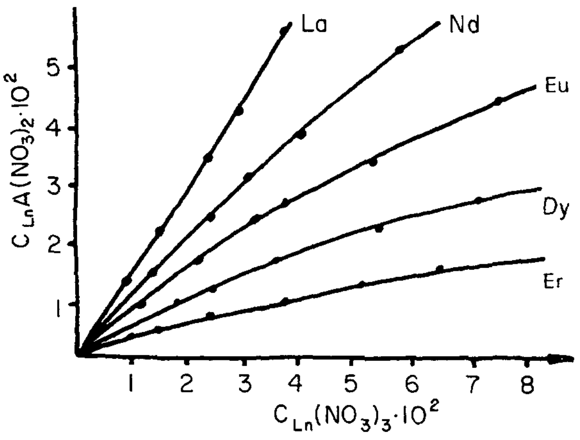


Fig. 4. Solubility of LnA_3 in acetone as a function of $Ln(NO_3)_3$ concentration for various lanthanides (20 °C).

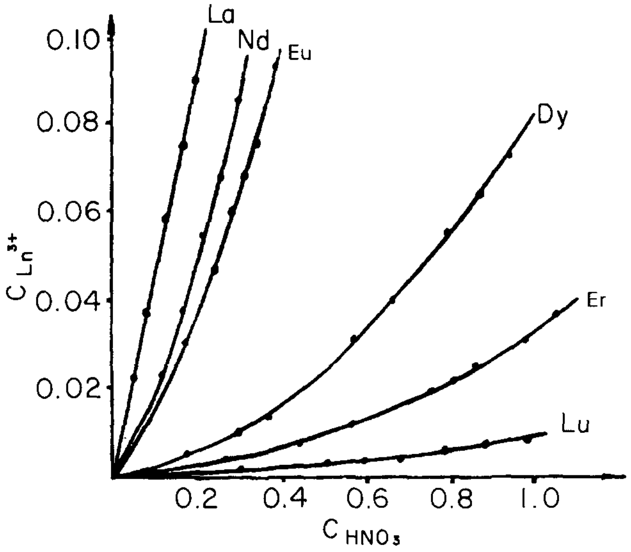
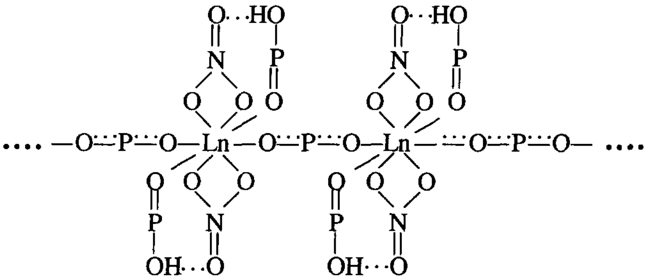


Fig. 5. Solubility of LnA_3 in acetone as a function of HNO_3 concentration for various lanthanides (20 °C).

The equilibrium constants of this reaction decreased along the lanthanide series (Fig. 5). However, in the case of lanthanum reaction (4) is strongly shifted to the right, which allows one to isolate the individual complex (III). This complex may also be prepared by reaction of HA with complex (II):

$$LaA(NO_3)_2 \cdot 2H_2O + 2HA = LaA(NO_3HA)_2 + 2H_2O \qquad (5)$$

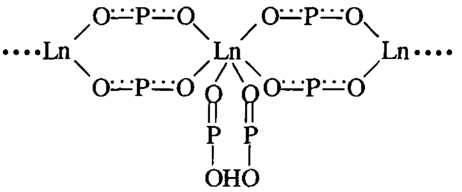
In the IR spectrum of (III) the bands of bidentately coordinated NO_3^- anions (810, 1280, 1510 cm^{-1}), the bands $\nu_{as}(PO)$ and $\nu_S(PO)$ of bridged alkylphosphate groups (1190, 1090 cm^{-1}) and the bands of chelated NO_3HA^- bianions (1030, 1090 cm^{-1}) are observed. The following structural formula of (III) may be proposed on the basis of these data:



If a solution of HA in octane is used as acidic reagent, rapid dissolution of LnA_3 occurs by the reaction

$$\mathrm{LnA_3+HA=LnA_2(AHA)}\ \text{(IV)} \tag{6}$$

The equilibrium constants of this reaction decrease along the lanthanide series: La, 2.5×10^{-1}; Nd, 1.1×10^{-1}; Eu, 4.9×10^{-2}; Dy, 1.1×10^{-2}; Er, 2.8×10^{-3}. The bands $\nu_{as}(PO)$ and $\nu_s(PO)$ of bridged alkylphosphate groups (1180, 1090 cm^{-1}) are present in the IR spectrum of (IV). The hyperfine splitting in the luminescence spectrum corresponds to the distorted octahedral symmetry of the Eu^{3+} coordination sphere in $EuA_2(AHA)$. We propose the following structural formula of (IV):



4.4. *Separation of americium and lanthanide in reactions of soluble complex decomposition*

The complexes (I–IV) have low thermodynamic stability and therefore may be degraded by reaction with rather "soft" chemical reagents. The decomposition reactions yield the soluble lanthanide complexes and a solid precipitate of LnA_3. The complex (I) may be decomposed by removal of NH_3 by blowing air through the solution. The complexes (II) and (III) may be decomposed by addition of the small portion of water. The complex (IV) is degraded upon addition of polar compounds such as R(OH), $(RO)_3PO$, etc.

The distribution of metals between the soluble and solid decomposition products of complex (I) is considerably dependent on the metallic ion nature. Figure 6 shows the distribution of Am and Eu between solid phase (LnA_3) and solution as a function of the degree of complex (I) decomposition. According to this dependence, the preferential concentration of Am rather than Eu in solution is observed. This separation effect is caused by the formation of a more soluble fraction of AmA_3 oligomers in process (1).

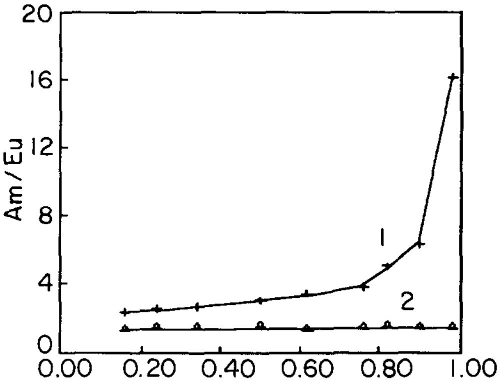


Fig. 6. Ratio of $^{241}Am/^{152}Eu$ in (1) solution and (2) precipitate as a function of EuA_3 fraction in precipitate.

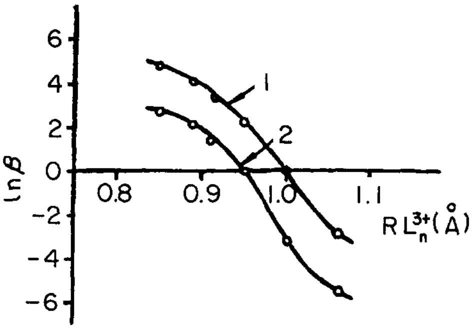


Fig. 7. Dependence of (1) Am–lanthanide and (2) Eu–lanthanide separation (reaction (7)) on lanthanide nature: $\beta(Am/Ln)=C_{am}(sol.)C_{Ln}(prec.)/C_{Am}(prec.)C_{Ln}(sol.)$; β(Eu/Ln) is defined analogously.

The effect of metal separation in the Am–lanthanide and Eu–lanthanide series during the decomposition of (II) with water according to

$$\mathrm{LnA(NO_3HA)_2+H_2O=LnA_3+2HNO_3} \tag{7}$$

is shown in Fig. 7. From these data it is seen that Am is preferentially concentrated in solution from mixtures with heavy lanthanides. Am and Nd show similar behaviour and the inversion of separation occurs in the Am–light lanthanide series. For the separation in the Eu–lanthanide series similar regularities were observed, but shifted along the abscissa.

The separation of metals in the systems studied was established to be independent of the complex decomposition degree. However, the separation may be increased by addition of specific reagents. For example, an increase in β (Am/Eu) from 10 to 40 is observed in system (III) upon increasing the HNO_3 concentration from the minimal required for dissolving LnA_3 to 0.25 mol l^{-1}. An increase in β (Am/Eu) from 10 to 40 is also achieved upon addition of strong complexing reagents (EDTA, DTPA).

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