ELSEVIER

Journal of Alloys and Compounds 223 (1995) 118–121

Journal of
ALLOYS
AND COMPOUNDS

# Mixed-ligand solid state complexes of cerium with bis-(2-ethylhexyl) phosphoric acid

M.M. Milanova, D.S. Todorovsky, M.G. Arnaudov

*Sofia University, Faculty of Chemistry, 1 J. Bourchier Ave., 1126 Sofia, Bulgaria*

Received 21 September 1994; in final form 3 November 1994

**Abstract**

The elemental composition, IR spectrum and thermal decomposition of the precipitate obtained during interaction of a $Ce(NO_3)_3$–acetone solution and a partially neutralized mixture of bis- and mono-(2-ethylhexyl) phosphoric acid are studied. It is established that the precipitate represents $CeA_3NO_3$, whereas under the same experimental conditions Pr, Nd and Er form $LnA_3$ complexes ($A=/CH_3(CH_2)_3CH(CH_2CH_3)CH_2O_2/POO^-$). The $NO_3$ group is released when the sample is heated to 458 K, and $CeA_3$ is formed as an intermediate. The subsequent thermal decomposition proceeds without melting to $Ce(PO_3)_3$.

*Keywords:* Cerium; Solid state complexes; IR spectra; Thermochemical behaviour

## 1. Introduction

In our previous work [1] it was shown that the behaviour of lanthanum differs significantly from that of Pr, Nd and Er during its interaction with commercially available bis-(2-ethylhexyl) phosphoric acid. The latter commercial acid consists of a mixture of bis- and mono-(2-ethylhexyl) phosphoric acids (resp. HA, $A=/CH_3(CH_2)_3CH(CH_2CH_3)CH_2O/_2POO^-$; $H_2B$, $B=CH_3(CH_2)_3CH(CH_2CH_3)CH_2OPO_3^{2-}$. Reaction of Pr, Nd and Er (i.e. Ln after Ce) with this mixture results in $LnA_3$ type solid state complexes (Ln = rare earth), whereas La forms $La(HB)_2NO_3 \cdot nH_2O$ or $La(HB)_3 \cdot nH_2O$ [1,2]. The properties of these complexes differ sufficiently to allow separation of La during their precipitation [1]. Obviously, it is rather interesting to study the behaviour of Ce under the same experimental conditions, which was the aim of the present work.

$LnA_3$ solid state complexes are relatively well studied [3–13]. Mixed ligand complexes $LaA(NO_3)_2 \cdot nH_2O$ [9] and $LnA(NO_3HA)_2$ [14] have also been prepared. However, the literature data for cerium complexes are rather limited. An $NO_3$-containing complex of Ce(IV) ($CeO_{0.5}A_2NO_3$) was reported long ago [15]. Solid state $CeA_3$ is mentioned in Ref. [5] without any specific information. Its thermochemical decomposition is studied in Ref. [13] along with that of other $LnA_3$.

In the present paper results are reported on the elemental composition, IR spectrum and thermally induced processes in the precipitate formed during the interaction of $Ce^{3+}$ with a partially neutralized mixture of (2-ethylhexyl) phosphoric acids ($HA+H_2B$).

## 2. Experimental

### 2.1. Materials

The reagents used (including $Ce(NO_3)_3$) were of puriss. p.a. grade. $Ln(NO_3)_3$ was prepared from the respective oxides with an assay >99.9%. According to potentiometric titration the bis-(2-ethylhexyl) phosphoric acid (Fluka) contains 62% HA and 37% $H_2B$.

### 2.2. Synthesis

The method for complex preparation was analogous to that applied in Ref. [1]. To the weighed mass of the commercial mixture ($HA+H_2B$) 0.5 M NaOH was added in an amount six times lower than that stoichiometrically required for neutralization of the acids to, respectively, NaA and NaHB. The organic phase was separated after 30 min stirring. It contains NaA and NaHB, dissolved in ($HA+H_2B$) along with 2.2–2.4% $H_2O$. Acetone solutions of the respective $Ln(NO_3)_3$

0925-8388/95/$09.50 © 1995 Elsevier Science S.A. All rights reserved
*SSDI* 0925-8388(94)01477-9

Table 1
Elemental composition (%) of the complexes received

| No. | Formula supposed | H |  | C |  | N |  | P |  | Ln |  |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  | Found | Calc. | Found | Calc. | Found | Calc. | Found | Calc. | Found | Calc. |
| 1 | $PrA_3$ | 9.40 | 9.30 | 51.47 | 52.17 | – | – | 8.1 | 8.4 | 13.2 | 12.8 |
| 2 | $NdA_3$ | 9.17 | 9.28 | 51.54 | 51.96 | – | – | 8.2 | 8.4 | 13.4 | 13.1 |
| 3 | $ErA_3$ | 9.10 | 9.28 | 51.12 | 50.95 | – | – | 8.0 | 8.2 | 14.2 | 14.8 |
| 4 | $La(HB)_2NO_3 \cdot 1.5H_2O$ | 5.86 | 6.08 | 29.36 | 29.73 | 2.1 ± 0.2 | 2.2 | 9.4 | 9.6 | 21.3 | 21.5 |
| 5 | $CeA_3NO_3$ | 8.99 | 8.89 | 48.26 | 49.36 | 1.3 ± 0.2 | 1.2 | 8.0 | 8.0 | 12.5 | 12.1 |

Table 2
Thermal decomposition of $CeA_3NO_3$

| Heating atmosphere | DTG peak (K) | Kinetic equation $d\alpha/dt$ [a] = | Activation energy (kJ $mol^{-1}$) |  | Kinetic model | Temperature interval (K) | Process supposed | Mass decrease (%) |  |
|---|---|---|---|---|---|---|---|---|---|
|  |  |  | Calc. | Found |  |  |  | Found | Calc. |
| Air | 448 | $k(1-\alpha)$ | 132 | 138 | Random nucleation | 293–449 | $NO_3$ release | 6.0 | 5.5 |
|  |  |  |  |  |  | 449–518 | Release of 6 mol $CH_3$ | 7.6 | 7.7 |
|  | 538 |  |  |  |  |  |  |  |  |
|  | 551 | $k[-\ln(1-\alpha)]^{-1}$ | 165 | 160 | Random nucleation | 518–568 | Release of 6 mol $C_7H_{14}O_{0.5}$ | 52.1 | 54.5 |
|  |  |  |  |  |  | > 568 | Crystallization | 2.0 | – |
|  |  |  |  |  |  |  | Total [b] | 67.7 | 67.7 |
| $N_2$ | 443 |  |  | 82 |  | 293–453 | Release of $NO_3$ | 6.7 | 5.5 |
|  |  |  |  |  |  | 453–533 | Release of 6 mol $CH_3$ | 6.2 | 7.7 |
|  | 561 |  |  | 118 |  | 533–588 | Release of 6 mol $C_7H_{14}O_{0.5}$ | 54.8 | 54.5 |
|  |  |  |  |  |  | > 588 | Crystallization | 1.2 | – |
|  |  |  |  |  |  |  | Total [b] | 68.9 | 67.7 |

[a] According to Ref. [19], α = mole fraction.

[b] $CeA_3NO_3 \rightarrow Ce(PO_3)_3^-$.

compounds (100 g $dm^{-3}$) were added in mole ratio $A^-/Ce^{3+} > 4$. A precipitate formed during stirring, and its yield increased with addition of acetone. The precipitate was filtered after 24 h, washed with water and acetone and dried for 48 h in a desiccator above concentrated $H_2SO_4$. This precipitate was subjected to study.

The $CeA_3$ complex was prepared from $Ce(NO_3)_3$–acetone solution and sodium salt (NaA) of pure HA. The latter was obtained from the ($HA + H_2B$) mixture by the method proposed in Ref. [16].

### 2.3. Analysis

The content of C, H and N in the precipitates was determined by common organic analysis methods, and that of P and Ln by ICP atomic emission spectroscopy. IR spectra of sample nujol suspensions were recorded by a FT-Bomem Michelson-100 Spectrometer. Thermogravimetric analysis was carried out by a MOM Paulik-Paulik-Erdey derivatograph, heating 0.3 g of the samples in air or in $N_2$ at 5 K $min^{-1}$ up to 773 K in a corundum crucible. $Al_2O_3$ was used as a standard.

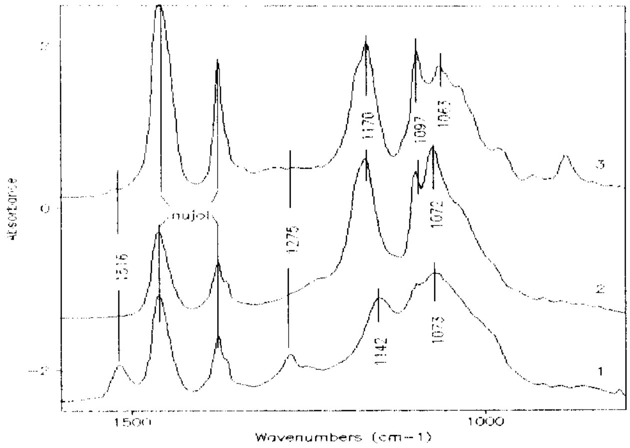

Fig. 1. IR spectrum of $CeA_3NO_3$ (1), the same sample after heating to 458 K (2) and of $CeA_3$ (3).

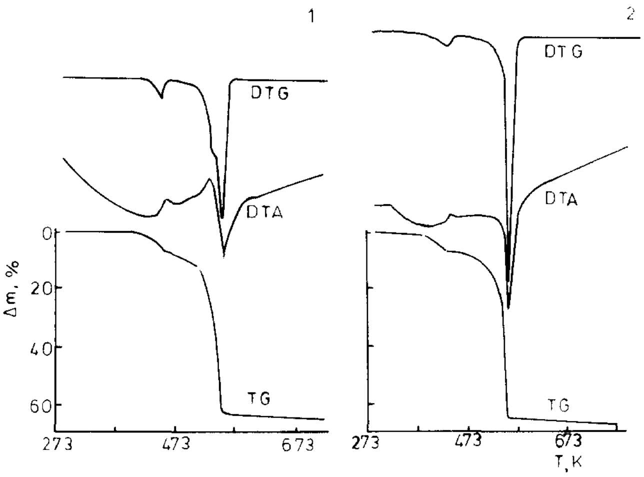

Fig. 2. TG, DTA and DTG curves of $CeA_3NO_3$ heated in air (1) and in $N_2$ (2). DTA sensitivity: 1/5 (1) and 1/3 (2).

Calibration of the TG and DTA curves was carried out with $CaC_2O_4 \cdot H_2O$. TG sensitivity was 2 mg.

## 3. Results and discussion

The main difference between the experimental conditions employed in this work and in previous studies [3–5] is that in the course of this study $HNO_3$ was formed by the reaction $Ln(NO_3)_3 + 3HA \rightarrow LnA_3 + 3HNO_3$. According to the common method for preparation of these complexes [3–5], NaA instead of HA is used; in this way $CeA_3$ was prepared. In the presence of the above shown amount of $HNO_3$ (3 mol/mol $LnA_3$), solid state $LaA_3$ does not form: $HNO_3$ fully destroys its precursor $LaA(NO_3HA)_2$ existing in the solution. However, the respective complex with $H_2B$ could be precipitated [1].

### *3.1. Elemental composition and IR spectra*

The elemental composition of the prepared precipitate is shown in Table 1. The results confirmed the expected composition $LnA_3$ of the compounds of Pr, Nd and Er and $La(HB)_2NO_3 \cdot 1.5H_2O$ [1]. Under the same conditions Ce forms a $CeA_3NO_3$ complex. The formula proposed is based on the absence of an EPR signal from the sample. It must be supposed that an oxidation of Ce(III) to Ce(IV) takes place during the synthesis. The IR spectrum confirms the presence of $NO_3$ (bands at 1275 and 1516 $cm^{-1}$) [18] (Fig. 1). If one excludes this feature, the $CeA_3NO_3$ spectrum is quite similar to that of $CeA_3$ and of the other $LnA_3$.

Taking into account the different behaviour of La, Ce, Pr, Nd and Er under our experimental conditions, one could suppose that the possibility of substitution of $A^-$ by other acidoligands sharply decreases in the order La–Ce–Pr.

### *3.2. Thermal behaviour*

$CeA_3NO_3$ is stable up to 393 K. The TG curve (Fig. 2) has a clearly expressed two-stage pattern. As can be seen from Table 2, endothermic release of $NO_3$ most probably takes place up to 453 K, accompanied by the beginning of decomposition of hydrocarbon radicals. The IR spectrum of the heated sample (Fig. 1) confirms the $NO_3$ release. Obviously, a reduction of Ce(IV) to Ce(III) and some reconstruction takes place during the heating and the intermediate IR spectrum is very close to that of $CeA_3$. A kinetic analysis of the data for the decreasing mass shows that the rate-determining process at this stage is random nucleation independent of the heating atmosphere. The activation energy (calculated by the method proposed in Ref. [17]) is a little lower when the sample is heated in $N_2$. This is in agreement with the supposed reduction process. The decomposition starts with the release of 6 mol $CH_3$; the same process was observed in $CeA_3$ [13]. The next stages of the process, observed in Ref. [13], are strongly overlapped. The mass loss, elemental analysis and IR spectroscopy prove that $Ce(PO_3)_3$ is a final product of the heating, as was found for $LnA_3$ [10,13]. Comparing the DTA curves of the samples heated in air and in $N_2$ one can see that the oxidation of the decomposition products has some contribution to the observed effects (Fig. 2).

## 4. Conclusion

The results show that, reacting with a partially neutralized mixture of bis- and mono-(2-ethylhexyl) phosphoric acid, $Pr^{3+}$, $Nd^{3+}$ and $Er^{3+}$ form $LnA_3$-type complexes but $Ce^{3+}$ produces $CeA_3NO_3$. Its thermal decomposition proceeds without melting in several stages (forming $CeA_3$ as an intermediate) to $Ce(PO_3)_3$. The investigation of the reported Ce complex will be enlarged to clarify its potential significance for Ln separation processes.

## Acknowledgement

This research is supported by a grant under contract with the Sofia University Science Foundation.

## References

[1] M. Milanova, D. Todorovsky, M. Arnaudov and N. Minkova, *Sep. Sci. Tech., 30* (1995) 821.
[2] M. Arnaudov, M. Milanova and D. Todorovsky, in preparation.
[3] E.K. Legin and V.P. Arsenteva. *Avt. svidetelstvo SSSR*, No. 642 315, C01F 17/00, 18.01.1979.

[4] N.N. Bogushevich, *Avt. svidetelstvo SSSR*, No. 759 522, CO7 F9/O9, 30.08.1980.

[5] Yu.I. Trifonov, E.K. Legin and D.N. Suglobov, *Radiokhimija*, (4) (1985) 422.

[6] T. Harada, M. Smutz and R.G. Bautista, *J. Chem. Eng. Data, 17* (1972) 203.

[7] G.P. Giganov, M.M. Schokarev, F.I. Verschinina and E.W. Karimov, in *Sbornik nauchnykh trudov VNIICVETMET, 12* (1968) 10.

[8] G. Hongcheng, Wu Jinguang, Ch. Dian, Y. Zhai and Xu Guangxian, *J. Chinese Rare Earth Soc., 4* (1986) 71.

[9] Yu.I. Trifonov, E.K. Legin and D.N. Suglobov, *Radiokhimija*, (1) (1990) 6.

[10] Chen Tien, Ko-Han Chen, Wu Chin-Kwang, Kao Hung-cheng and Hsu Kwang-Hsien, *K'Hsueh T'ung Pao, 26* (1981) 794.

[11] Yu.I. Trifonov, E.K. Legin and D.N. Suglobov, *Radiokhimija*, (3) (1991) 63.

[12] Yu.I. Trifonov, E.K. Legin and D.N. Suglobov, *Radiokhimija*, (6) (1987) 850.

[13] M. Milanova and D. Todorovsky, *Thermochim. Acta, 243* (1994) 27.

[14] Yu.I. Trifonov, E.K. Legin and D.N. Suglobov, *Radiokhimija*, (3) (1992) 143.

[15] D.F. Peppard and J.R. Ferraro, *JINC, 10* (1959) 275.

[16] S. Acharya and A. Nayak, *Hydrometallurgy, 19* (1988) 309.

[17] H. Horowitz and G. Metzger, *Anal. Chem., 35* (1963) 1464.

[18] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd edn., Wiley, New York, 1978, p. 448.

[19] M. Brown, A.D. Dollimore and A. Galvey, *Reactcii Twerdikh Tel*, Mir, Moscow, 1983.