p-TERT-BUTYLCALIX[4]ARENE TETRAKIS(N,N-DIMETHYLACETAMIDE) AS A SECOND LIGAND IN THE COMPLEXATION OF TRIVALENT LANTHANOIDS WITH THENOYLTRIFLUOROACETONE IN SOLUTION AND INVESTIGATION OF A SOLID Eu(III) COMPLEX

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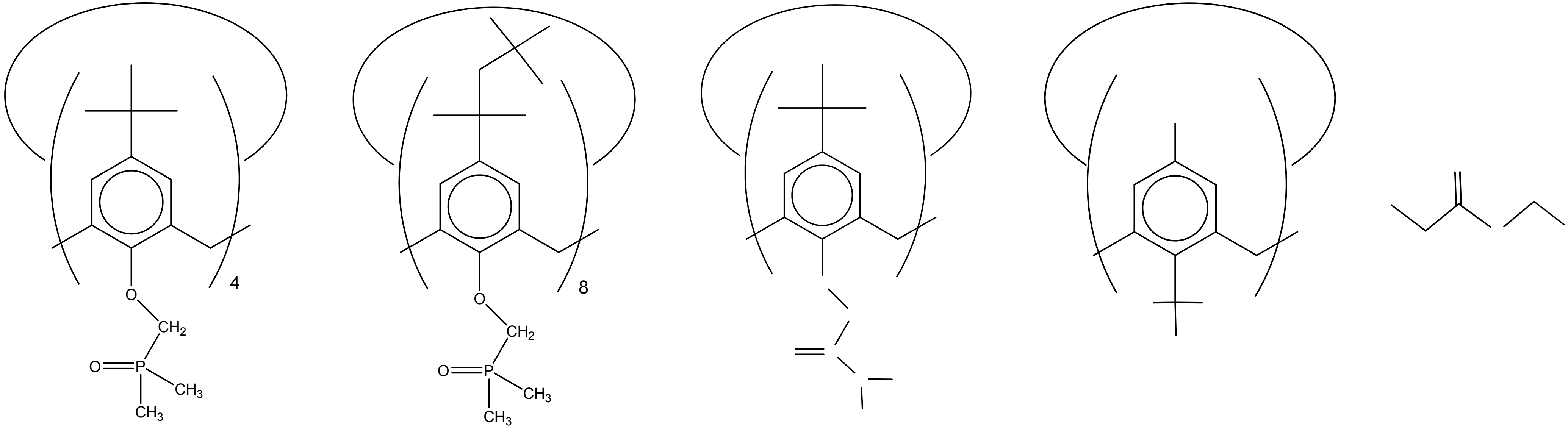
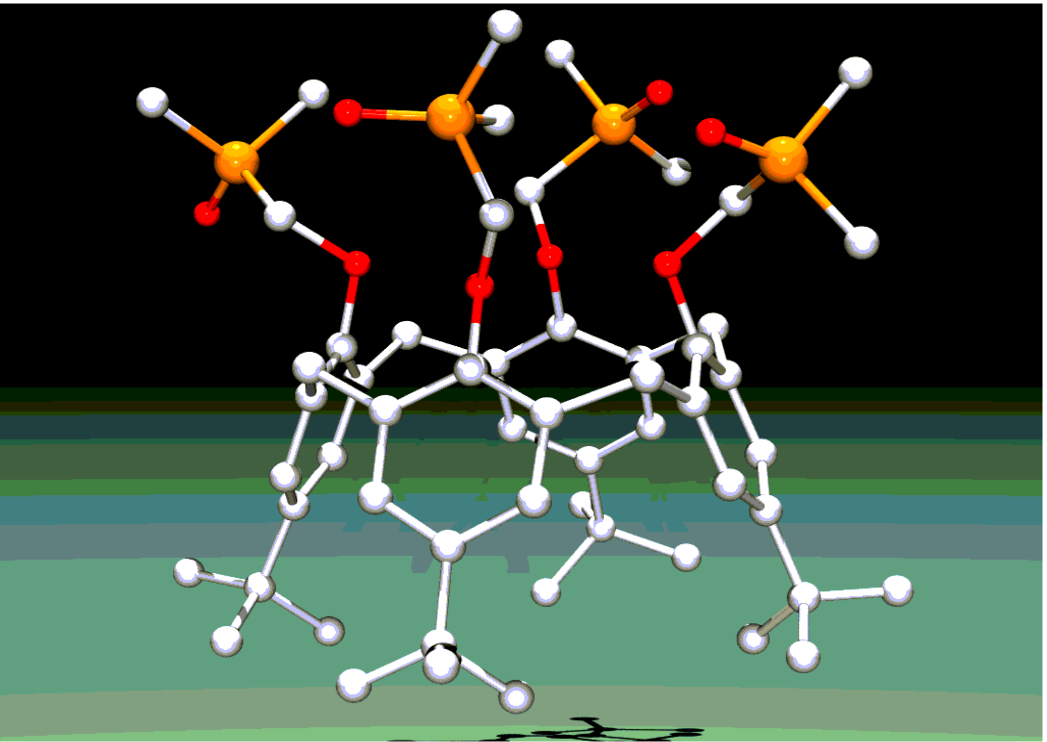


Scheme 1. Structural formulas of the 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis-(dimethylphosphinoylmethoxy)calix[4]arene, 5,11,17,23,29,35,41,47-octa(1,1,3,3-tetramethylbutyl)-49,50,51,52,53,54,55,56-octakis(dimethylphosphinoyl-methyleneoxy) calix[8]arene and *tert*-butylcalix[4]arene tetrakis(N,N-dimethylacetamide), 4-*tert*-butylcalix[4]arene-tetraacetic acid tetraethyl ester [R1-R3].



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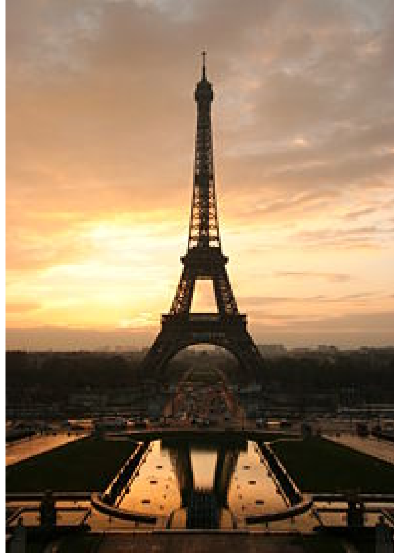
[R1] L. Saulnier, **S. Varbanov**, R. Scopelliti, M. Elhabriri, J.-C. G. Bünzli, J. Chem. Soc. Dalton Trans (1999) 3919.
[R2] F. M. Ramirez, **S. Varbanov**, C. Cecile, G. Muller,N. F. Rouge, R. Scopelliti, J.-C. G. Bünzli, J. Chem. Soc., Dalton Trans. (2002) 4505.
[R3] E. Tashev, M. Atanassova, S. Varbanov, T. Tosheva, S. Shenkov, A.-S. Chauvin, I. Dukov, Sep. Purif. Technol. 64 (2008) 170.

$$SC = \log \frac{D_{1,2}}{D_1 + D_2} \qquad SC > 0$$



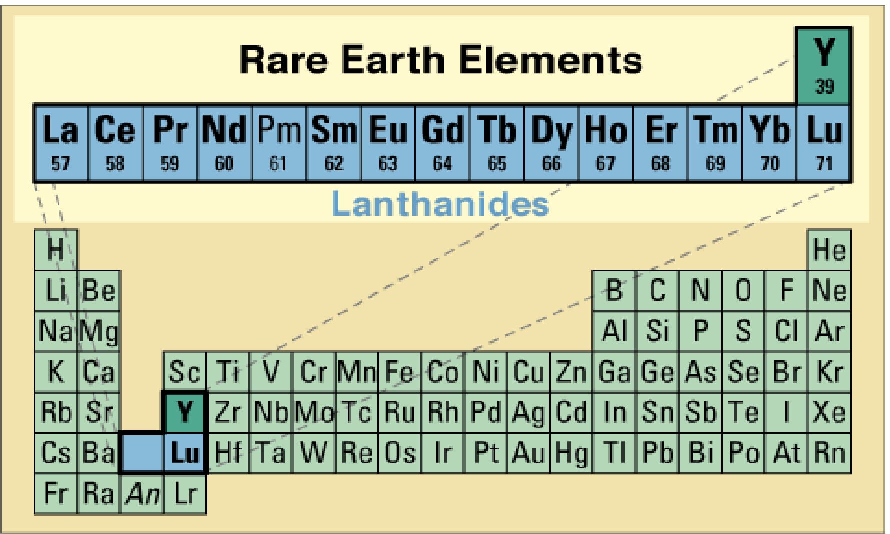
Conditions for synergistic extraction of a metal* [R4]*:

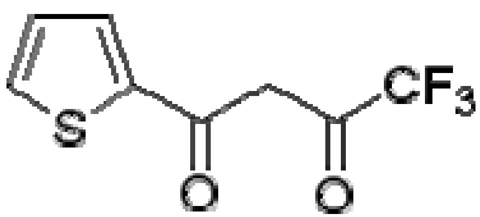
- One of the extractants is capable of neutralizing the charge of the metal ion, preferably forming a chelate complex.
- The second extractant (synergist) is capable of displacing any residual co-ordinated water from the metal complex and of rendering it less hydrophilic.
- The second extractant is not hydrophilic and is co-ordinated less strongly than the first (chelating) extractant.
- The maximum co-ordination number and the geometry of the ligands are favourable.

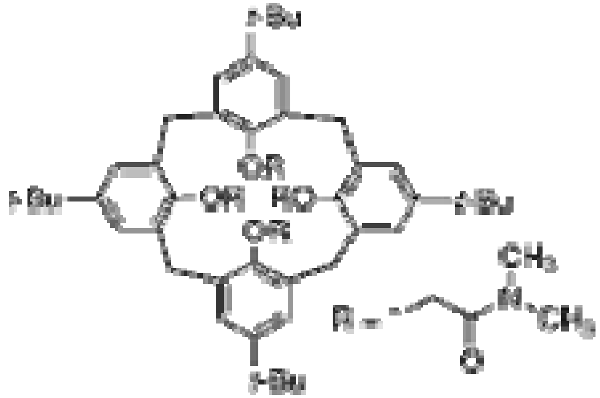
[R4] H. Irving, D. Edgington, J. Inorg. Nucl. Chem., 15(1960) 158.

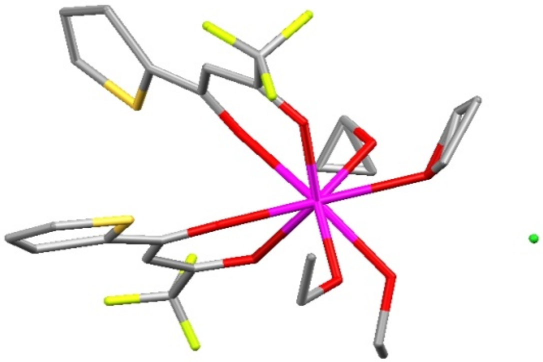
The aims of the present study:

- solvent extraction of the 4f-series metals with mixture of the chelating extractant thenoyltrifluoroacetone (HTTA) and tert-butylcalix[4]arene tetrakis(N,N-dimethylacetamide) (S)
- the stoichiometry of the extracted complexes in the organic phase
- the synergistic enhancement
- the possibilities for the separation of the metals
- to prepare a solid complex of Eu(III) with these extractants and to determine its structure with elemental analysis, IR, ^{1}H NMR and ^{19}F NMR.









$$Ln^{3+}_{(aq)} + 3HTTA_{(o)} \leftrightarrow Ln(TTA)_{3(o)} + 3H^{+}_{(aq)}$$

$$\log K_T = \log D_T - 3pH - 3\log[HTTA]_{(o)}$$

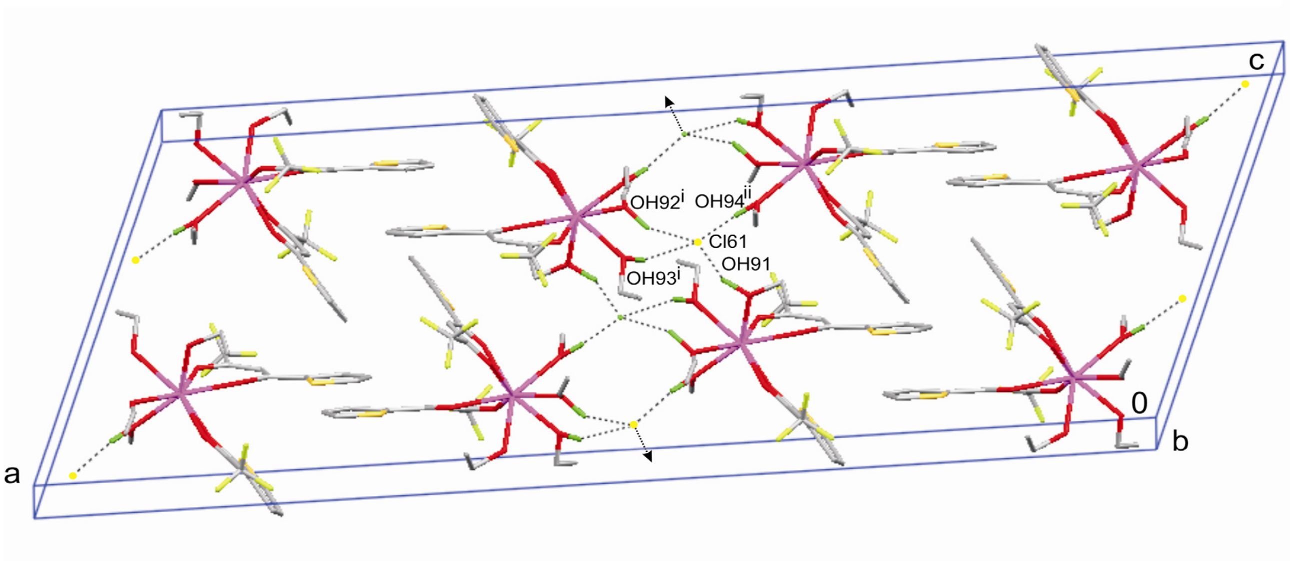


Fig. R1. View of the molecular packing in $[Eu(TTA)_2(C_2H_5OH)_4]Cl$. Hydrogen bonds are represented by dotted lines [R5].

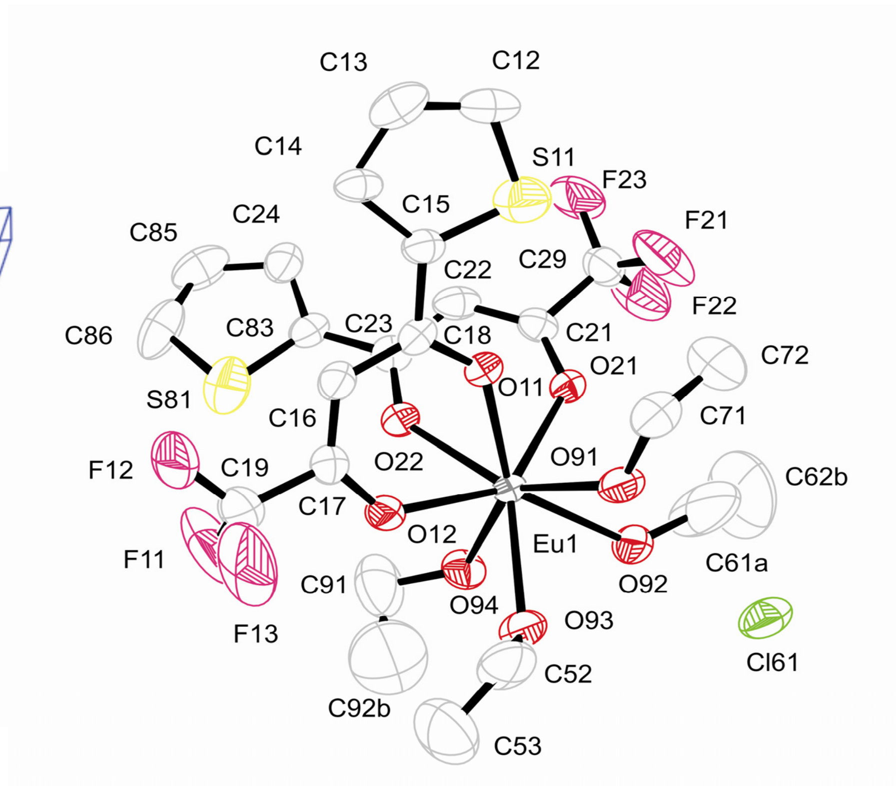


Fig. R2. View of the structure of the complex $[Eu(TTA)_2(C_2H_5OH)_4]Cl$. [R5]

[R5] M.Atanassova, V. Lachkova, N. Vassilev, B. Scivachev, S. Varbanov, I. Dukov, **Polyhedron** 27 (2008) 3306-3312.

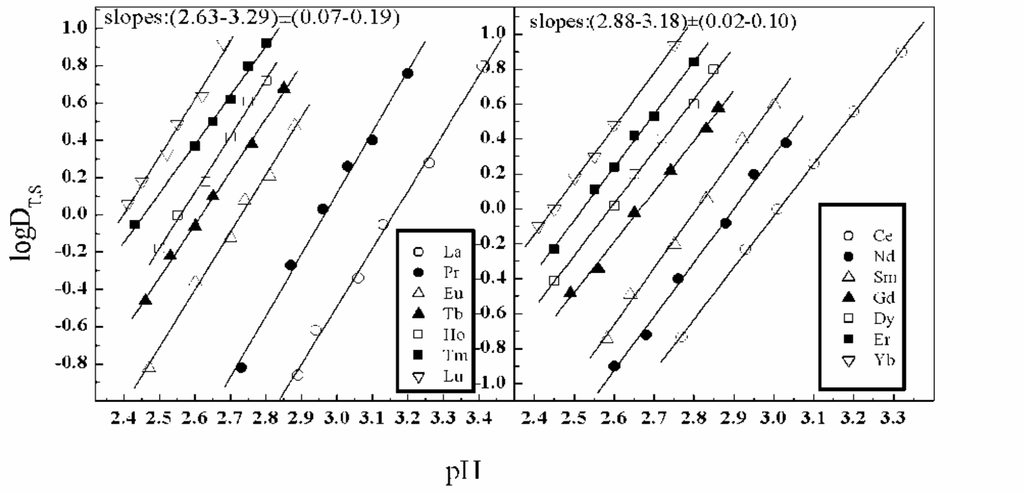


Figure 1. Log$D_{T,S}$ vs pH for the extraction of lanthanoid(III) ions with mixture HTTA–S at [HTTA]=4x10^{-2} mol/dm^3 and [S]=5x10^{-4} mol/dm^3.

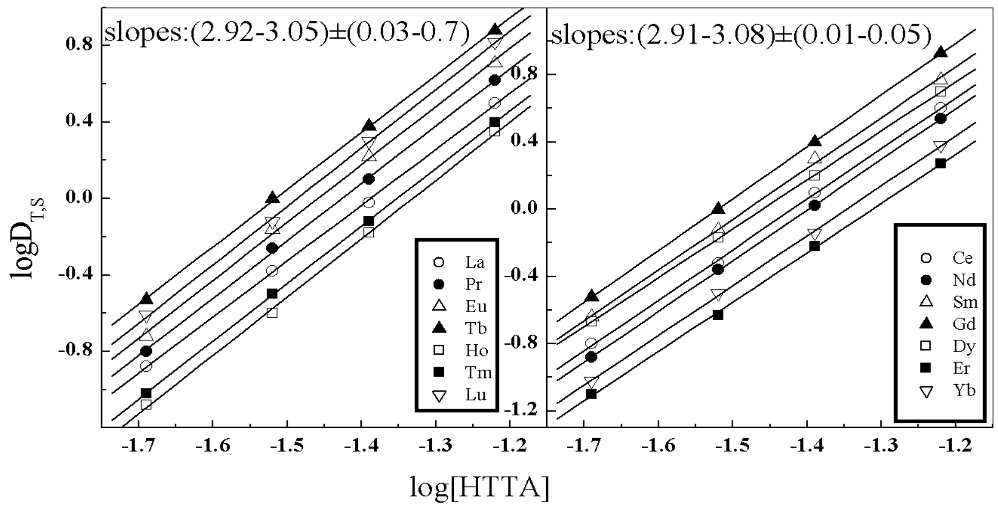


Figure 2. Log$D_{T,S}$ vs [HTTA] for the extraction of lanthanoid(III) ions with mixture HTTA–S at [S]=5x10^{-4} mol/dm^3.
La, pH=3.15; Pr, pH=3.00; Eu, pH=2.80; Tb, pH=2.75;
Ho, pH=2.50; Tm, pH=2.45; Lu, pH=2.50.
Ce, pH=3.05 ; Nd, pH=2.90 ; Sm, pH=2.90; Gd, pH=2.80;
Dy, pH=2.65; Er, pH=2.45; Yb, pH=2.40.

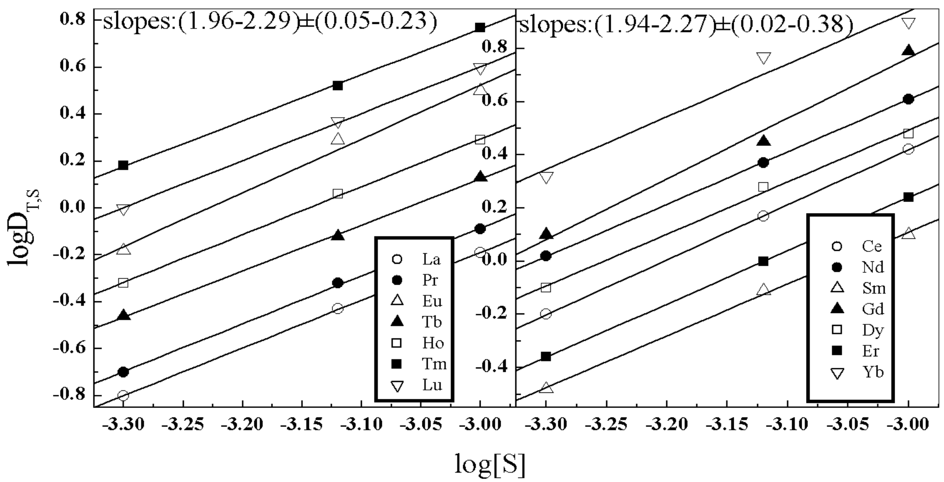


Figure 3. Log*D*T,S vs. [S] for the extraction of lanthanoid(III) ions with mixture HTTA–S at [HTTA]=4x10^{-2} mol/dm^3.
La, pH=2.90; Pr, pH=2.75; Eu, pH=2.70; Tb, pH=2.45;
Ho, pH=2.45; Tm, pH=2.55; Lu, pH=2.40.
Ce, pH=2.95; Nd, pH=2.90; Sm, pH=2.65; Gd, pH=2.70;
Dy, pH=2.55; Er, pH=2.40; Yb, pH=2.55.

$$Ln^{3+}_{(aq)} + 3HTTA_{(o)} + 2S_{(o)} \leftrightarrow Ln(TTA)_3{\cdot}2S_{(o)} + 3H^{+}_{(aq)}$$

$$\log K_{T,S} = \log D_{T,S} - 3\log[HTTA] - 2\log[S] - 3\,pH$$

$$Ln(TTA)_{3(o)} + 2S_{(o)} \leftrightarrow Ln(TTA)_3{\cdot}2S_{(o)}$$

$$\log \beta_{T,S} = \log K_{T,S} - \log K_T$$

Ho
Tm
Yb
Tb

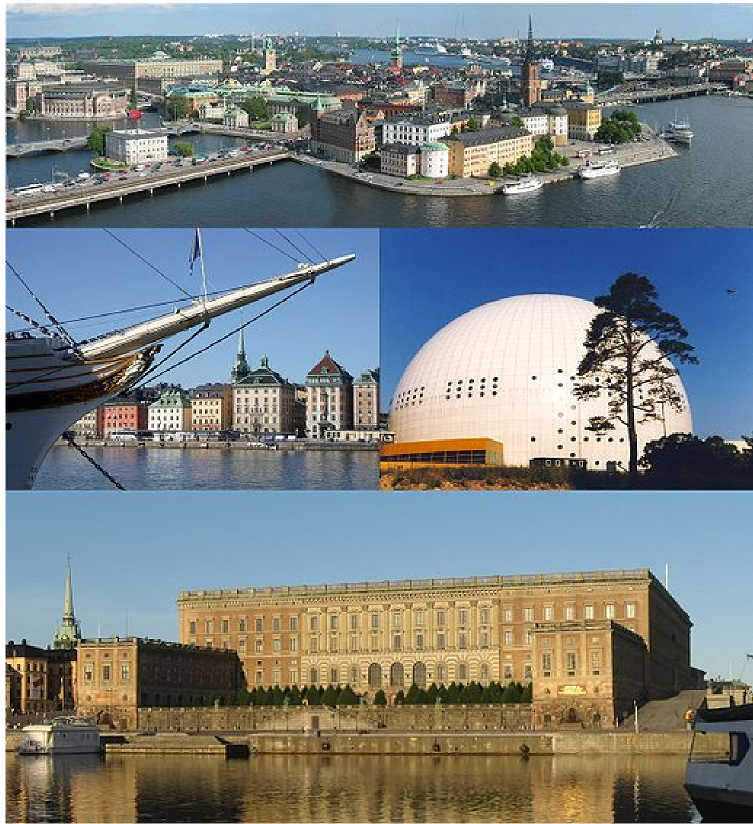


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Table 1. Values of the equilibrium constants K_T, $K_{T,S}$, and $\beta_{T,S}$ and synergistic coefficients for lanthanoids extraction with the HTTA–S mixture.

Ln^{3+}	$\log K_T$[30]	$\log K_{T,S}$	$\log \beta_{T,S}$	pH_{50} (HTTA)	pH_{50} (HTTA–S)	SC	S.F. (HTTA)
La	-10.50	1.29	11.79	4.89	3.16	5.19	3.24
Ce	-9.99	1.74	11.73	4.72	3.02	5.13	2.89
Pr	-9.53	1.90	11.43	4.57	2.97	4.83	1.51
Nd	-9.35	2.10	11.45	4.51	2.89	4.85	4.67
Sm	-8.68	2.38	11.06	4.29	2.80	4.46	1.0
Eu	-8.55	2.61	11.16	4.24	2.73	4.56	1.99
Gd	-8.40	2.78	11.18	4.19	2.66	4.58	2.0
Tb	-8.22	2.92	11.14	4.13	2.62	4.54	1.74
Dy	-7.98	3.03	11.01	4.05	2.59	4.41	1.34
Ho	-7.87	3.11	10.98	4.02	2.56	4.38	1.34
Er	-7.76	3.23	10.99	3.98	2.52	4.39	2.34
Tm	-7.40	3.33	10.73	3.86	2.49	4.13	1.85
Yb	-7.14	3.47	10.61	3.77	2.45	4.01	1.42
Lu	-6.99	3.60	10.59	3.72	2.41	3.99	

Notes: The values of the equilibrium constants are calculated on the basis of the 42 experimental points; statistical confidence is 95% and standard deviation is less than ±0.05.

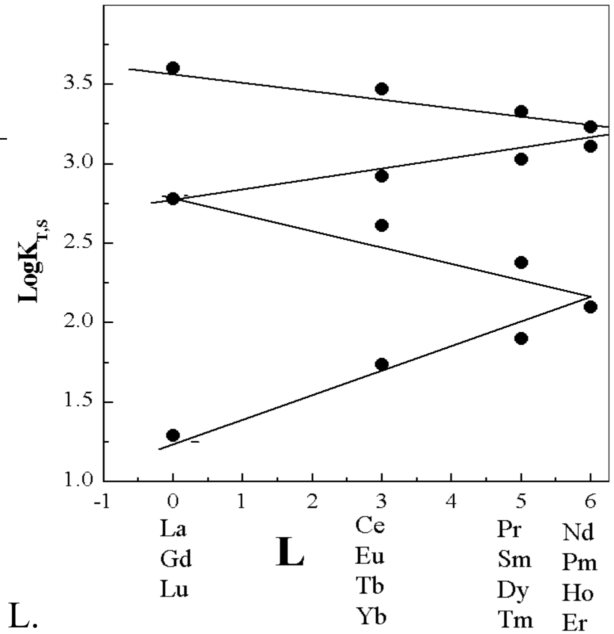

Figure 4. $\log K_{T,S}$ vs. L.

[R6] S. Sinha, Helvetica Chim. Acta 58 (1975) 1978.

SF	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
La	2.82	4.07	6.45	12.3	20.89	30.9	42.65	54.95	66.06	87.9	109.6	151.4	204.2
Ce		1.44	2.29	4.36	7.41	10.9	15.13	19.49	23.44	30.9	38.9	53.7	72.4
Pr			1.58	3.02	5.12	7.58	10.47	13.48	16.22	21.37	26.9	37.2	50.1
Nd				1.9	3.23	4.78	6.6	8.51	10.23	13.48	16.9	23.4	31.6
Sm					1.69	2.51	3.46	4.46	5.37	7.07	8.91	12.3	16.5
Eu						1.47	2.04	2.63	3.16	4.16	5.24	7.24	9.77
Gd							1.38	1.77	2.13	2.82	3.54	4.89	6.60
Tb								1.28	1.54	2.04	2.57	3.54	4.78
Dy									1.20	1.58	1.99	2.75	3.72
Ho										1.32	1.66	2.29	3.09
Er											1.25	1.74	2.34
Tm												1.38	1.86
Yb													1.34

Table 2. Values of separation factors between the adjacent lanthanoid elements obtained using a mixture HTTA−S.

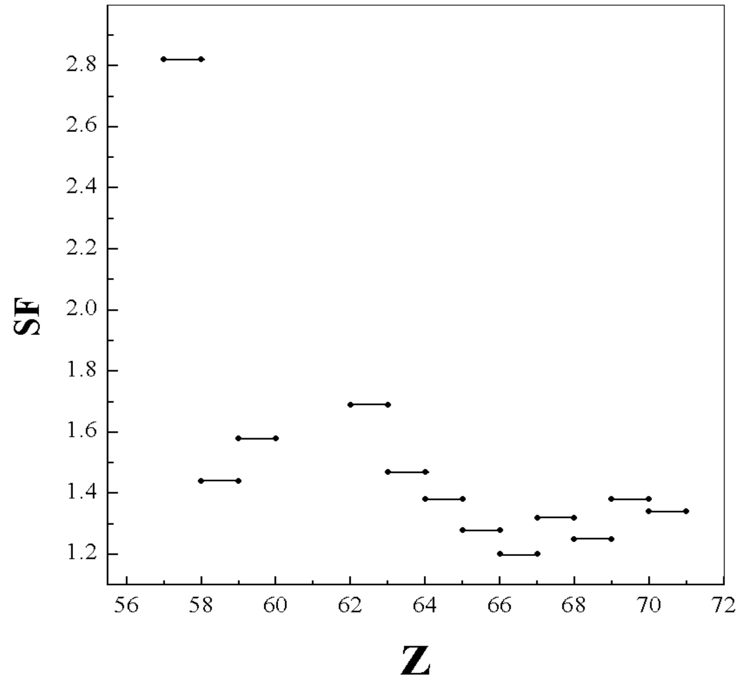

Figure 5. SFs of adjacent lanthanoid pairs vs. Z.

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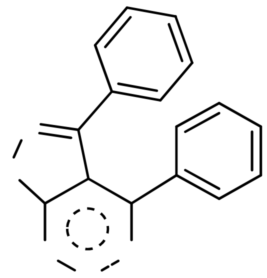
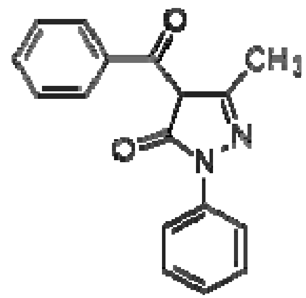
Table R1. Values of separation factors of some lanthanoid pairs obtained with different systems [R7].].

Systems	Nd/La	Eu/Nd	Ho/Eu	Lu/Ho
HTTA–calix[4]arene with P=O donor groups [R6]	**21.37**	**6.60**	**3.72**	**3.80**
HTTA-amidecalix[4]arene present study	**6.45**	**3.23**	**3.16**	**3.08**
HTTA–DPSO [R10]	41.74	4.26	5.24	3.46
HTTA–DB24C8 [R9]	6.76	3.31	5.37	3.16
HTTA – DB18C6 [R9]	13.58	3.72	6.45	7.94
HTTA–calix[4]arene with C=O donor groups [R7]	4.07	2.69	5.12	4.57
HP–calix[4]arene with P=O donor groups [R8]	15.1	3.98	4.57	2.75
HP–calix[8]arene with P=O donor groups [R4]	14.2	4.46	2.57	2.88
HPBI–amedecalix[4]arene [R11]	**3.38**	**2.04**	**3.09**	**3.31**
HPBI–calix[4]arene with P=O donor groups [R12]	6.20	3.90	1.90	2.20
N1923–^{t}Bu[4]CH2COOH [R14]	6.38	3.88	1.01	0.43
HP–sec-octylphenoxyacetic acid [R13]	3.14	1.03	1.09	0.99



HPBI



HP

[R7] Atanassova M., (2011) Microchimica Acta DOI 10.1007/s00604-011-0609-0.
[R8] Atanassova M, Lachkova V, Vassilev N, Varbanov S, Dukov I (2007) J Inclus Phenom Macrocycl Chem58:173.
[R9] Atanassova M, Dukov I (2005) Sep Sci Technol 40:1103.
[R10] Atanassova M, Dukov I (2009) J Solut Chem 38:289.
[R11] Petrova M A, Lachkova V, Vassilev N, Varbanov S (2010) Ind Eng Chem Res 49:6189.
[R12] Atanassova M, Lachkova V, Vassilev N, Varbanov S, Dukov I (2010) Polyhedron 29:655.
[R13] Tong S, Song N, Jia Q, Liao W (2009) Sep Purif Technol 69:97.
[R14] He W, Liao W, Niu C, Li D (2008) Sep Purif Technol 62:674.

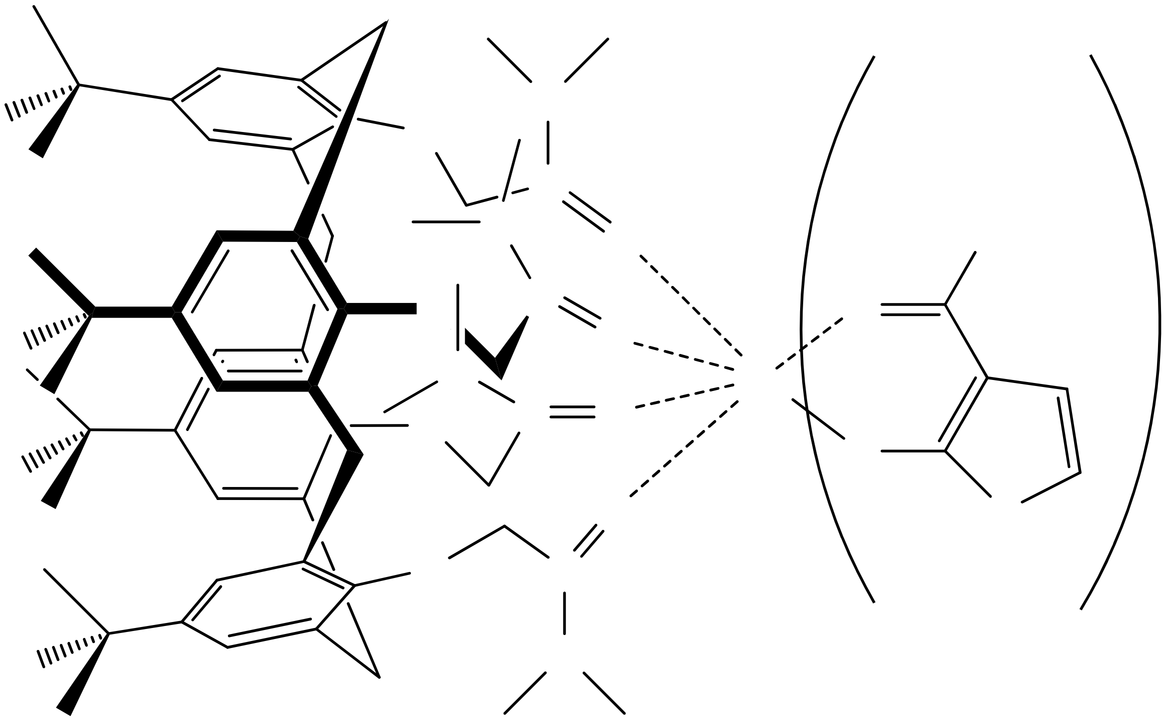
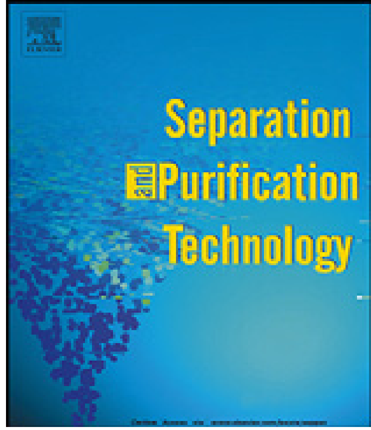


Figure 6. Proposed structure of the solid complex Eu(TTA)$_3$·S with m.p. 360°C on the basis of elemental analysis, IR, ^{1}H and ^{19}F NMR data.

Acknowledgements

The financial support by the National Research Fund of Bulgaria for the purchase of Bruker Avance II+ 600 NMR spectrometer in the framework of the Program "Promotion of the Research Potential through Unique Scientific Equipment" (Project UNA-17/2005) is gratefully acknowledged.

Conclusion



- 14 lanthanoids were synergistically extracted
- thenoyltrifluoroacetone and amide-containing calix[4]arene were used
- the composition of the extracted species were $Ln(TTA)_3{\cdot}2S$
- the stoichiometry of the solid Eu^{3+} complex was found to be $Eu(TTA)_3{\cdot}S$
- the used system offer higher synergistic enhancements and good selectivity

M. Atanassova, N. Vassilev, I. Dukov, Sep. Purif. Technol. 78 (2011) 214.

Thank you for your attention!

Henri Louis le Chatelier