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Complex formation of divalent lanthanides and actinides

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Abstract

This paper reports new data on the behaviour of Ln^{2+}, An^{2+}, and Sr^{2+} in different systems. The data, obtained in this study, allowed us to compare the behaviour of 4f and 5f elements relative to one another and their analogue, strontium.

Keywords: Actinides; Lanthanides; Complex formation

1. Introduction

All lanthanides (Ln), except Gd, and actinides (An) starting from Pu, except Cm, have an f^ns^2 electronic configuration analogous to that of alkaline-earth elements [1]. This might suggest that the basic oxidation state of these elements should be 2+. Yet, the basic oxidation state of Ln and An, starting from americium (except No) is 3+, and the 2+ oxidation state can be provided only under specific conditions. At present, all Ln and An, starting from Th, have been obtained in the 2+ oxidation state. The larger part of them have been obtained in this state only in melts [2–4].

The instability of Ln and An solutions in the 2+ oxidation state (except for No) is one of the reasons complicating their complex formation studies. Obtaining stable Ln^{2+} solutions in protic and aprotic solvents allowed a new class of complex compounds of the composition $[M(crown)]L_2$ ($M=Sr^{2+}$, Ln^{2+}, and An^{2+}, $L=ClO_4^-$, BF_4^-, and BPh_4^-). These compounds simultaneously contain levelling (crown ethers) and differentiating ligands (ClO_4^-, BF_4^-, and BPh_4^-).

This work discusses the latest findings in the coordination chemistry of divalent f elements, focusing on the similarity and differences of f elements in the 2+ oxidation state between one another and between their analog, the strontium ion.

2. Hydrate and solvation properties of Ln^{2+} and An^{2+}

The hydration or solvation of divalent f elements, where water or solvent molecules act as a complex-forming ion can be considered to be a kind of complex formation. The plots of the hydration energies of Ln^{2+} and alkaline earth elements as a function of ionic radii are described by Born's equation [5]. This allows the conclusion that, like alkaline earth elements, Ln^{2+} does not show specific properties at least in water. The similarity of the calculated $-\Delta H_{hydr}$ (M^{2+}) for Ln and An [6] suggests that divalent 4f and 5f elements, as well as alkaline earth elements will behave in a similar manner.

On the other hand, although the properties of divalent 4f and 5f elements, as well as of their analog Sr^{2+}, are similar, their behaviours in aqueous organic and organic solvents are different. Thus, unlike Eu^{2+} and Yb^{2+}, divalent Es forms strong solvate–hydrate complexes at C_2H_5OH: $H_2O=2$: 1, as was shown during the study of the co-crystallization of these ions with the solid-phase $Sr(Sm)SO_4$ from ethanol [7].

Along with aqueous ethanol systems, we studied the behaviour of Eu^{2+}, Yb^{2+}, Es^{2+}, Ce^{3+}, and Am^{3+} during their co-crystallization with the solid phases $SrCl_2$ and $SmCl_2$ from C_2H_5OH, CH_3CN, as well as from the mixed solvent C_2H_5OH–CH_3CN. Table 1 shows the co-crystallization coefficients (D)[1] of Eu^{2+}, Yb^{2+}, Es^{2+}, Ce^{3+}, and Am^{3+} with the solid-phase $SrCl_2$ and $SmCl_2$ from the above solvents. For Eu^{2+}, Yb^{2+}, and Es^{2+}, the coefficients

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[1] The co-crystallization coefficient D was calculated by the equation:

$$\frac{a}{a-x} = D \cdot \frac{b}{b-y},$$

where D is the co-crystallization coefficient; a and b are the contents of macro- and microcomponents in the system; x and y are their contents in the solid phase.

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Table 1
Co-crystallization coefficients (*D*) of di- and trivalent f elements with $SrCl_2$ and $SmCl_2$ solid phases from organic systems

System	*D*				
	Eu^{2+}	Yb^{2+}	Es^{2+}	Ce^{3+}	Am^{3+}
	Solid-phase $SrCl_2$				
CH_3CN	1.12±0.13	0.99±0.10	1.26±0.14	0.12±0.02	0.10±0.02
C_2H_5OH–CH_3CN (7.5 mol/l)	0.18±0.03	0.14±0.02	0.15±0.03	0.31±0.04	0.34±0.04
C_2H_5OH	0.69±0.07	0.62±0.06	0.82±0.09	0.74±0.08	0.78±0.09
	Solid-phase $SmCl_2$				
CH_3CN	1.18±0.12	0.93±0.10	1.09±0.11	0.03±0.01	0.02±0.01
C_2H_5OH–CH_3CN (7.5 mol/l)	0.77±0.09	0.75±0.08	0.91±0.09	0.07±0.01	0.06±0.01
C_2H_5OH	0.64±0.07	0.55±0.06	0.79±0.09	0.24±0.03	0.21±0.03

of cocrystallization with $SrCl_2$ drastically decrease in the mixed solvent. The cocrystallization coefficients of Ce^{3+} and Am^{3+} monotonically increase in passing from CH_3CN to C_2H_5OH, assuming an intermediate value in the mixed solvent. Unlike the case with $SrCl_2$, the *D* values for Eu^{2+}, Yb^{2+}, Es^{2+}, Ce^{3+}, and Am^{3+} during their co-crystallization with the solid-phase $SmCl_2$ change monotonically in passing from CH_3CN to C_2H_5OH, assuming an intermediate value in the mixed solvent. These results have led us to conclude that Sr^{2+} and divalent f elements behave differently in C_2H_5OH–CH_3CN (7.5 mol/l).

Our calculations showed [8] that the anomalous solvation effect observed in the mixed solvent results in a 5-fold increase in the solubility products of $EuCl_2$ and $YbCl_2$ and a 7-fold increase in $EsCl_2$.

The results presented above suggest that, unlike Sr^{2+}, Ln^{3+}, and An^{3+}, divalent Ln and An, being strong electron donors, can form strong coordination bonds due to the charge transfer to σ- and π- bonds of the solvent of the ligand. An example of this complex formation is the interaction of Ln^{2+} and An^{2+} with perchlorate (ClO_4^-), terafluorborate (BF_4^-), and tetraphenyl borate (BPh_4^-) ions in various solvents.

3. Complex formation of Ln^{2+} and Es^{2+} with ClO_4^-, BF_4^- and BPh_4^--ions

Although ClO_4^-, BF_4^-, and BPh_4^- ions belong to reagents having a weak ability to form coordination bonds with metals, the presence of σ- and π- bonds in them may lead to the formation of complex compounds with metal ions that are electron donors, thanks to the charge transfer. These metal ions are Ln^{2+} and An^{2+}.

Previously, we established that aqueous and aqueous ethanol solutions of Eu, Yb, and Sm dichlorides could be stabilized by adding $NaBPh_4$. The stabilities of the solutions increased fifty- to hundredfold, depending on the sodium tetraphenyl borate concentration [9]. Later, it was shown that this stabilization was due to the formation of outer-sphere complexes of the composition $[M(H_2O)_n](BPh_4)_2$ ($M=Ln^{2+}$ and An^{2+}). Note that unlike Ln^{2+} and An^{2+}, the Sr^{2+} ion does not form complex compounds with BPh_4^- [10]. The formation and stabilization of these complexes may be due to the charge tunnelling from the Ln^{2+} and An^{2+} ions to the nonsaturated bonds of the phenyl groups BPh_4^-. The size and character of the solvent molecules forming the first coordination sphere of the central atom should have a strong influence on this charge transfer. In order to establish the role of these parameters on the formation of complexes, we studied the complex formation of Ln^{2+} and Es^{2+} with BPh_4^- in CH_3CN and THF.

Table 2 shows the complex formation constants for Eu^{2+}, Yb^{2+}, and Es^{2+} with BPh_4^- in various solvents. The stability of the complexes increases with a decrease in the size of the solvent molecule forming the first coordination sphere. This does not contradict the suggestion that the formation of complexes of divalent f elements with BPh_4^-

Table 2
The stability constants of Yb^{2+}, Eu^{2+}, and Es^{2+} with BPh_4^- in other solvents

System	Solvent in the first coordination sphere and its molecule volume, (cm^3/mol)		Yb^{2+}		Eu^{2+}		Es^{2+}	
			β_1	β_2	β_1	β_2	β_1	β_2
C_2H_5OH–H_2O (10 mol/l)	H_2O	18.07	6.5	25.7	1.7	52.7	6.2	106.4
CH_3CN	CH_3CN	52.9	$<10^{-2}$	$<10^{-2}$	0.3	9.3	6.6	16.0
THF	THF	81.6	$<10^{-3}$	$<10^{-3}$	$<10^{-3}$	$<10^{-3}$	$<10^{-3}$	$<10^{-3}$

Table 3
The colour of the solution of LnL_2 ($L=I^-$, ClO_4^-, BF_4^-, BPh_4^-) in THF

Ln^{2+}	Anion			
	I^-	ClO_4^-	BF_4^-	BPh_4^-
Eu	yellow	limon	limon	yellow
Yb	yellow	light yellow	light yellow	yellow
Sm	bluish–green	red	brownish–red	bluish–green
Tm	green	–	greyish–brown	green

is due to the electron tunnelling leading to a single-electron exchange chemical bonding [10,11].

The interaction of Ln^{2+} and Es^{2+} with other tetrahedral anions (ClO_4^- and BF_4^-) in the THF solution was also studied. The absorption spectra of the f–d transitions of LnI_2 in THF show that, in contrast to BPh_4^-, ClO_4^- and BF_4^- change the colour of the solution (Table 3) and the absorption spectrum of the f–d transitions [12]. The effects of ClO_4^- and BF_4^- are different and begin at different threshold concentrations (0.04 and 0.09 mol/l for ClO_4^- and BF_4^-, respectively). This suggests that the extent of the metal–ligand interaction increases in the series $BPh_4^- < BF_4^- < ClO_4^-$. The changes observed in the absorption spectra of the Ln^{2+} f–d transitions indicate a radical rearrangement of the cationic coordination sphere and, consequently, the occurrence of complex-formation processes in these systems.

A solubility study of $SrCl_2$ and $SmCl_2$ in THF has shown that the solubility of $SrCl_2$ does not change in the presence of BPh_4^-, BF_4^-, and ClO_4^-. On the other hand, the solubility of $SmCl_2$ increases with an increase in the concentrations of these anions, with the largest effect being observed for ClO_4^- and the lowest, for BPh_4^-. This suggests that Sr^{2+} does not form complexes with these ligands in THF [13].

A study of the co-crystallization of Eu^{2+}, Yb^{2+}, and Es^{2+} with the solid phase [Sr(18-crown-6)]I_2 from THF has shown that the addition of ClO_4^- to the system has the strongest effect on the cocrystallization coefficient (D), whereas BPh_4^- does not influence D. For BF_4^-, as in the $SmCl_2$ solubility experiments, an intermediate complex formation between ClO_4^- and BPh_4^- is observed. Thus, the stability of the complexes increases in passing from ClO_4^- to BF_4^-, whereas BPh_4^- does not form any complexes with divalent f elements.

The above-described results indicate that unlike Sr^{2+}, Ln^{2+} and An^{2+}, which are strong electron donors, can form strong coordination bonds with ClO_4^-, BF_4^-, and BPh_4^- thanks to the charge transfer. It was of interest to determine whether the difference in the behavior of f elements and Sr^{2+} in these systems would be retained in the presence of 18-crown-6 or it would disappear as was the case with the iodide ion [14].

4. Complex compounds of the composition [M(18-crown-6)]L_2 ($M=Ln^{2+}$, Es^{2+}, and Sr^{2+}; $L=ClO_4^-$, BF_4^-, and BPh_4^-)

The simplest method to obtain Ln^{2+} complex compounds with crown ethers is to react LnI_2 with crown ethers in THF, which leads to the formation of difficultly soluble products of a specific color [15]. We used the method to obtain the complex compounds [M(18-crown-6)]I_2 ($M=Ln^{2+}$, An^{2+}, and Sr^{2+}) [14]. However, at specific $LiClO_4$, $LiBF_4$, and $LiBPh_4$ concentrations in MI_2 ($M=Ln^{2+}$ and Sr^{2+}) in THF, the addition of 18-crown-6 leads to the precipitation of a complex compound, in which ClO_4^-, BF_4^-, and BPh_4^- act as anions.

The Ln^{2+} complexes synthesized (some of their properties are presented in Table 4), are extremely sensitive to traces of moisture and oxygen, in whose presence they get oxidized very rapidly (within less than 1 min). The Ln^{2+} characteristic colour disappears, and the complexes turn white.

The thermal stabilities of the complexes increase in the series $Tm^{2+} < Sm^{2+} < Yb^{2+} < Eu^{2+}$, which agrees well with an increase in the oxidation potentials of the Ln^{3+}/Ln^{2+} pairs [16]. The complexes decompose in several consecutive stages. Therefore, it is impossible to give a definite answer to the question about the reason for the increase in the thermal stabilities in passing from BPh_4^- to ClO_4^-.

Unlike complexes with ClO_4^- and BF_4^-, compounds with BPh_4^- are poorly soluble not only in THF but also in H_2O, C_2H_5OH, and their mixtures. Table 5 shows the solubility data for Ln^{2+} and Sr^{2+} complexes, obtained using the radioactive tracer technique, and for Ln^{2+} and Es^{2+} complexes, obtained using the co-rystallization technique.

In all cases, but for complexes with BPh_4^- in THF, the solubilities of complexes of divalent f elements and Sr^{2+} are very similar. For complexes with BPh_4^-, the solubilties of Sr^{2+} complexes and divalent f elements in THF differ more than ten fold, although this difference was not

Table 4
The colour and decomposition temperature (T_{decomp}) of complexes [M(18-crown-6)]L_2 ($M=Ln^{2+}$, Sr^{2+}; $L=ClO_4^-$, BF_4^-, BPh_4^-)

Complex	Colour	T_{decomp}, K
[Sr(18-crown-6)]$(ClO_4)_2$	white	618
[Sr(18-crown-6)]$(BF_4)_2$	white	551
[Sr(18-crown-6)]$(BPh_4)_2$	white	539
[Eu(18-crown-6)]$(ClO_4)_2$	light yellow	578
[Eu(18-crown-6)]$(BF_4)_2$	yellowish–white	472
[Eu(18-crown-6)]$(BPh_4)_2$	light yellow	406
[Yb(18-crown-6)]$(ClO_4)_2$	yellowish–white	565
[Yb(18-crown-6)]$(BF_4)_2$	yellowish–white	461
[Yb(18-crown-6)]$(BPh_4)_2$	yellowish–white	395
[Sm(18-crown-6)]$(ClO_4)_2$	dark-red	553
[Sm(18-crown-6)]$(BF_4)_2$	violet	451
[Sm(18-crown-6)]$(BPh_4)_2$	lilac	390
[Tm(18-crown-6)]$(BPh_4)_2$	violet	385

Table 5
Solubility of complexes [M(18-crown-6)]L_2 (M=Ln^{2+}, Es^{2+}, Sr^{2+}; L=ClO_4^-, BF_4^-, BPh_4^-) in different systems

Ion	System	Anion	Solubility, mol/l	
			Calculated	Experimental
Sr^{2+}	C_2H_5OH-H_2O (7.5 mol/l)	BPh_4^-	–	6.7×10^{-3}
Eu^{2+}			$(6.5\pm0.3)\times10^{-3}$	–
Yb^{2+}			$(6.6\pm0.7)\times10^{-3}$	–
Es^{2+}			$(6.6\pm0.3)\times10^{-3}$	–
Sr^{2+}	C_2H_5OH	BPh_4^-	–	4.3×10^{-3}
Eu^{2+}			–	4.4×10^{-3}
Yb^{2+}			–	4.6×10^{-3}
Sm^{2+}			–	4.2×10^{-3}
Es^{2+}			$(4.3\pm0.2)\times10^{-3}$	–
Sr^{2+}	THF	ClO_4^-	–	3.4×10^{-4}
Eu^{2+}			$(3.3\pm0.1)\times10^{-4}$	3.4×10^{-4}
Yb^{2+}			$(3.9\pm0.4)\times10^{-4}$	3.6×10^{-4}
Sm^{2+}			–	3.3×10^{-4}
Es^{2+}			$(3.3\pm0.2)\times10^{-4}$	–
Sr^{2+}	THF	BF_4^-	–	2.5×10^{-4}
Eu^{2+}			$(2.5\pm0.1)\times10^{-4}$	2.5×10^{-4}
Yb^{2+}			$(2.7\pm0.2)\times10^{-4}$	2.6×10^{-4}
Sm^{2+}			–	2.4×10^{-4}
Es^{2+}			$(2.5\pm0.3)\times10^{-4}$	–
Sr^{2+}	THF	BPh_4^-	–	0.9×10^{-4}
Eu^{2+}			$(8.2\pm0.2)\times10^{-4}$	8.3×10^{-4}
Yb^{2+}			$(9.0\pm0.3)\times10^{-4}$	9.1×10^{-4}
Sm^{2+}			$(7.0\pm0.3)\times10^{-4}$	7.2×10^{-4}
Tm^{2+}			–	8.7×10^{-4}
Es^{2+}			$(8.2\pm0.3)\times10^{-4}$	–

observed in aqueous ethanol solutions. This can be attributed to the substitution of BPh_4^- ions for THF molecules in the inner coordination sphere. This process can be accompanied by a partial 'pseudooxidation' of Ln^{2+} due to the electron delocalization to the unsaturated π- bonds of the phenyl groups. This pseudooxidation results in the formation of complex compound, whose solubility is intermediate between those of Ln^{2+} and Ln^{3+} complexes equal to ~10^{-4} and ≈10^{-2} mol/l, respectively. As to the ethanol solution, no electron delocalization takes place, because the inner-sphere water has a higher solvating ability than BPh_4^-. In the presence of 18-crown-6, the solvated water is likely to prevent the charge transfer from the Ln^{2+} ion to BPh_4^-, and the difference in the behaviours of Ln^{2+} and Sr^{2+} disappears.

5. Conclusion

The new data on the behaviour of Ln^{2+}, An^{2+}, and Sr^{2+} in different systems, obtained in this study, allowed us to compare the behaviour of 4f and 5f elements relative to one another and their analogue, strontium.

The co-crystallization study of Ln^{2+} and Es^{2+} in different solvents revealed singular points consistent with the formation of stable solvate complexes of divalent f elements.

The complex formation between divalent f elements and ClO_4^- and BF_4^- ions in THF solutions was established for the first time. ClO_4^- and BF_4^- were established to form inner-sphere complexes with Ln^{2+} and An^{2+}. The stability of the complexes increases in passing from BF_4^- to ClO_4^-. On the other hand, the complex-formation data for Ln^{2+} and Es^{2+} with BPh_4^- in different media led us to suggest that the formation of outer-sphere complexes between divalent f elements and BPh_4^- was due to the electron tunnelling from the cation to the unsaturated π- bonds of the phenyl groups of the anion, leading to a single-electron exchange bonding. Unlike the divalent f element, these ligands do not form complexes with Sr^{2+} in any of the solvents studied.

The Ln^{2+} and Sr^{2+} complexes of the composition [M(18-crown-6)]L_2 (M=Ln^{2+} and Sr^{2+}; L=ClO_4^-, BF_4^-, and BPh_4^-) were synthesized and studied for the first time, and the solubilities of analogous Es^{2+} complexes were determined. In most cases, the presence of 18-crown-6 narrows the difference in the behaviour of divalent f elements and Sr^{2+}, which is confirmed by the similarity of the solubilities of the complex compounds. Note, however, that although the ClO_4^-, BF_4^-, and BPh_4^- anions are isotypical, the complexes significantly differ in their physicochemical properties.

References

[1] L. Brewer, J. Opt. Soc. Am. 61 (1971) 1666.
[2] N.B. Mikheev, L.N. Auerman, I.A. Rumer, A.N. Kamenskaya, M.Z. Kazakevich, Uspekhi Khimii 61 (1995) 1805.
[3] N.B. Mikheev, A.N. Kamenskaya, S.A. Kulyukhin, I.A. Rumer, Mendeleev Commun. 5 (1993) 198.
[4] N.B. Mikheev, M.Z. Kazakevich, I.A. Rumer, A.N. Kamenskaya, S.A. Kulyukhin, Radiokhimiya 38 (1996) 416.
[5] N.B. Mikheev, I.A. Rumer, Inorg. Chim. Acta 145 (1987) 139.
[6] F. David, J. Less-Common Met. 121 (1986) 27.
[7] N.B. Mikheev, A.N. Kamenskaya, S.A. Kulyukhin, Radiokhimiya 30 (1988) 213.
[8] I.E. Veleshko, N.B. Mikheev, S.A. Kulyukhin, L.N. Auerman, Radiokhimiya 34 (1992) 22.
[9] A.N. Kamenskaya, N.B. Mikheev, A.N. Strekalov, Zh. Neorg. Khim. 28 (1983) 1711.
[10] N.B. Mikheev, S.A. Kulyukhin, I.A. Rumer, A.N. Kamenskaya, J. Radioanal. Nucl. Chem., Articles 134 (1990) 317.
[11] N.B. Mikheev, S.A. Kulyukhin, Radiokhimiya 35 (1993) 36.
[12] S.A. Kulyukhin, N.B. Mikheev, I.E. Veleshko, Radiokhimiya 33 (1991) 29.
[13] V.G. Vasil'ev, Analiticheskaya Khimiya (Analytical Chemistry), Moscow, Vysshaya Shkola, 1989.
[14] N.B. Mikheev, A.N. Kamenskaya, S. A Kulyukhin, Radiokhimiya 30 (1988) 56.
[15] S.A. Kulyukhin, A.N. Kamenskaya, L.N. Auerman, Radiokhimiya 34 (1992) 35.
[16] S.G. Bratsch, J.J. Lagowski, J. Phys. Chem. 89 (1985) 3310.