Solvent Extraction Study of Trivalent Actinide and Lanthanide Complexes in Aqueous Solutions

IV. Thiocyanate Complexes of La(III), Eu(III), Lu(III), and Am(III) in 5 M Na(ClO₄) Solutions at 25°C

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The complex formation of La(III), Eu(III), Lu(III), and Am(III) with thiocyanate ion has been studied in 5 M Na(ClO₄) at 25°C by a distribution method.

The metal ions in aqueous solution were equilibrated with 2-thenoyltrifluoroacetone in carbon tetrachloride containing tributylphosphate or methylisobutylketone, and the complex formation was determined from the decrease of the distribution ratio when various amounts of thiocyanate ion were introduced in the solution.

The stability constants of the thiocyanate complexes were calculated by a generalized least squares method using the LETAGROP VRID computer program.

The results are as follows:

$$\beta_n = [M(SCN)_n{}^{3-n}] \,/\, [M^{3+}][SCN]^n$$

	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$
La(III)	0.24 ± 0.06	(< -0.62)	-0.73 ± 0.12	—
Eu(III)	0.32 ± 0.09	≈ -0.1 (<0.25)	-0.36 ± 0.15	—
Lu(III)	0.45 ± 0.09	≈ -1.3 (< -0.06)	-0.14 ± 0.23	—
Am(III)	0.85 ± 0.05	—	0.55 ± 0.15	0.00 ± 0.15

(limits are $\pm 3\,\sigma$, values in parentheses are $\log (\beta_2 + 3\sigma)$)
These results indicate that (a) Am(III) forms more stable thiocyanate complexes than the other three ions, (b) the second complexes, $M(SCN)_2{}^+$, are not as stable as the other complexes of the same ion.

Not so much attention has been paid to the complex formation of trivalent lanthanide ions with thiocyanate ion because the thiocyanate complexes of these ions are neither so stable to be easily detected nor very useful for the separation of these elements.

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However, a remarkable difference has been reported recently between the ion-exchange behavior of the trivalent actinide and lanthanide ions in thiocyanate media. Following a prediction by Diamond,[1] that thiocyanate should complex more strongly with actinides than with lanthanides, Surls and Choppin [2] studied the elution of these ions from anion- and cation-exchange resins with ammonium thiocyanate solutions. They reported that lanthanides and yttrium are eluted before the actinides from an anion-exchange resin, and that actinides are eluted from a cation-exchange resin before the lanthanides of comparable ionic size. From this they concluded that the actinides form stronger complexes with the thiocyanate ion than the lanthanides do.

The solvent extraction of the trivalent lanthanides from thiocyanate solutions with tributylphosphate (TBP) in various organic solvents has been studied by Yoshida.[3]

Previous work on the metal thiocyanate complexes has been summarized by Bjerrum, Schwarzenbach and Sillén.[4] Recently, Lebedev and Yakovlev [5] determined β_1 and β_3 for thiocyanate complexes of Ce(III), Am(III), and Cm(III).

This series of papers has reported studies on the complex formation of La(III), Eu(III), Lu(III), and Am(III) by a distribution method: Paper I [6] deals with chloride complexes, Paper II [7] with sulfate complexes and Paper III [8] with oxalate complexes. The present paper describes the complex formation of these ions with the thiocyanate ion.

The metal ions in aqueous solutions of 5 M $Na(ClO_4)$ were equilibrated with 2-thenoyltrifluoroacetone (TTA) in carbon tetrachloride containing tributylphosphate (TBP) or methylisobutylketone (hexone). The TBP or hexone was added to form adducts with the chelate complexes. The experiments were carried out in solutions at log $[H^+] = -3$ to -4 since thiocyanic acid is a strong acid ($p\mathrm{K}_a = 0.86$).[9]

The stability constants of the thiocyanate complexes were determined from the decrease of the distribution ratio when various amounts of thiocyanate ion were added to the aqueous phase. The constants were finally refined by a generalized least squares method with the LETAGROP VRID which is an improved version of the LETAGROP computer program.[10]

A short note which contains the present results has been published.[11]

APPLICATION OF THE LAW OF MASS ACTION

The equations used for the calculation of the stability constants were as follows (for details see Paper I [6]):

M^{3+}: trivalent ion.
L^{l-}: complex-forming ligand with negative charge $l-$.
β_n: overall stability constant of the nth complex.
D: net distribution ratio of metal.
HA: organophilic chelating acid.
N: organophilic adduct forming ligand.
K_{ex}: extraction constant, eqn. (3).
β_{An}: overall formation constant for the nth adduct MA_3N_n.

K_{ex}': extraction constant when adduct chelates are formed in the organic phase.

$D_0 D^{-1}$: the ratio of distribution ratios in two systems where $[H^+]$ and $[HA]_{org}$ are the same. D_0 denotes the distribution ratio when L^- is absent and D denotes that when the concentration of L^- is $[L^-]$.

The assumptions made are: (a) No complexes with the chelating acid, MA_n^{3-n}, and no hydrolyzed species are formed in the aqueous phase. (b) MA_3 and its adducts, MA_3N_n, are the only complexes of M^{3+} present in the organic phase.

$$\beta_n = [ML_n^{3-nl}]/[M^{3+}] [L^-]^n \tag{1}$$

$$D = [M(III)]_{org,\ total}/[M(III)]_{aq.\ total} \tag{2}$$

$$K_{ex} = [MA_3]_{org}[H^+]^3[HA]_{org}^{-3}[M^{3+}]^{-1} \tag{3}$$

$$K_{ex}' = [MA_3]_{org}[H^+]^3[HA]_{org}^{-3}[M^{3+}]^{-1}(1 + \sum_1^n \beta_{An}[N]_{org}^n)^{-1} \tag{4}$$

$$D_0 D^{-1} = 1 + \sum_1^n \beta_n[L^-]^n \tag{5}$$

EXPERIMENTAL

Tracers. ^{140}La, $^{152+154}$Eu, ^{177}Lu, and ^{241}Am were used in this study. The preparation of these tracers was described in Paper I.[6] The tracer stock solutions were finally made in 0.1 M $HClO_4$ + 4.9 M $NaClO_4$.

Reagents. All the reagents were of analytical grade. The purification of sodium perchlorate, tributylphosphate, methylisobutylketone and chloroform was described in Papers I and II.[7] Other reagents were used without further purification. TTA solutions in CCl_4 with TBP and hexone were prepared as described in Papers I and II.

Procedures. A 0.1 ml portion of the tracer solution, a certain volume of 5 M NaSCN, and a 1 ml portion of 0.1 M sodium sulfanilate in 5 M $NaClO_4$ were added to a 50 ml stoppered glass tube. The hydrogen ion concentration was adjusted by addition of 0.1 M $HClO_4$ + 4.9 M $NaClO_4$. In some experiments where [SCN$^-$] was very high, a certain volume of 8 M NaSCN, 0.1 ml of the tracer solution and 2 ml of 0.05 M sulfanilic acid solution were added to the tubes; the hydrogen ion concentration was then adjusted with 1 M $HClO_4$, a calculated amount of water was added to adjust the ionic strength at 5 M and finally 5 M $NaClO_4$ was added to make the volume 10.0 ml. A 10.0 ml portion of the organic solution was added. The tubes with the two phases were fixed on a framework which was rotated mechanically for an hour. It was checked by preliminary experiments that the distribution ratio of the metal did not change if the agitation was continued for more than one hour. The two phases were separated by centrifugation, and a 2 ml portion was taken from each phase and transferred into a polyethylene tube. The γ radioactivity was measured with a well-type scintillation counter. A small fraction of the aqueous phase was transferred into a small plastic vessel with a glass cover, and the $-\log [H^+]$ was measured potentiometrically with 0.01 M $HClO_4$ + 4.99 M $NaClO_4$ as the standard with $-\log [H^+] = 2.00$ in $I = 5$ M.

All the procedures were carried out in a thermostated room at 25°C and the pipetting of the two phases was made very carefully to avoid contamination by the other phase.

RESULTS AND DISCUSSION

Table 1 gives the hydrogen ion concentration dependence of the metal distribution between organic phases and 5 M $NaClO_4$.

Table 2 gives the ratio of the distribution ratio defined by eqn. (5) for various thiocyanate concentrations.

Table 1. Distribution of M(III) between the organic phases and 5 M NaClO$_4$ at 25°C. The organic phase was, for La(III): 0.1 M TTA in CCl$_4$ containing 0.0034 M TBP; for Eu(III), Lu(III), and Am(III); 0.1 M TTA in CCl$_4$ containing 10 % (by volume) hexone. The data are given as $-\log$ [H$^+$], $\log$ D, $(-\log$ D [H$^+$]^3 [HA]$_{org}^{-3}$); (*cf.* eqn. (4); [HA]$_{org}$ and [N]$_{org}$ were constant).

(a) La(III): 3.924, 2.079 (6.69); 3.608, 1.158 (6.67); 3.572, 1.086 (6.63); 3.550, 1.017 (6.63); 3.479, 0.806 (6.63); 3.473, 0.790 (6.63); 3.151, -0.147 (6.60); 2.899, -0.879 (6.58); 2.671 -1.537 (6.55).

(b) Eu(III): 3.795, 1.682 (6.70); 3.755, 1.551 (6.71); 3.740, 1.606 (6.61); 3.643, 1.167 (6.76); 3.601, 1.137 (6.67); 3.501, 0.824 (6.68); 3.324, 0.364, (6.61); 2.906, -0.947 (6.67).

(c) Lu(III): 4.061, 2.907 (6.28); 3.638, 1.656 (6.26); 3.396, 1.021 (6.17); 3.325, 0.788 (6.19); 3.221, 0.483 (6.18); 3.156, 0.316 (6.15); 2.955, -0.267 (6.13); 2.867, -0.530 (6.13).

(d) Am(III): 4.059, 2.140 (7.04); 3.899, 1.834 (6.88); 3.733, 1.250 (6.95); 3.679, 1.045 (6.99); 3.677, 1.140 (6.89); 3.672, 1.041 (6.98); 3.587, 0.821 (6.94); 3.249, 0.009 (6.74); 3.031, -0.742 (6.84).

Figs. 1 to 4 give the plots $\log$ $D_0 D^{-1}$ *versus* $\log$ [SCN$^-$]
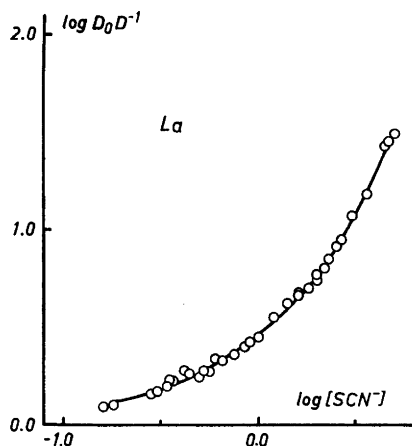

Fig. 1. The variation of the distribution of lanthanum(III) as a function of the concentration of thiocyanate ion. $D_0 D^{-1}$ gives $1 + \sum_1^n \beta_n$[SCN]^n (*cf.* eqn. (5)). The curve is calculated from the constants in Table 3. Aqueous phase: 5 M Na(ClO$_4$). Organic phase: 0.1 M TTA in CCl$_4$ containing 0.0034 M TBP.
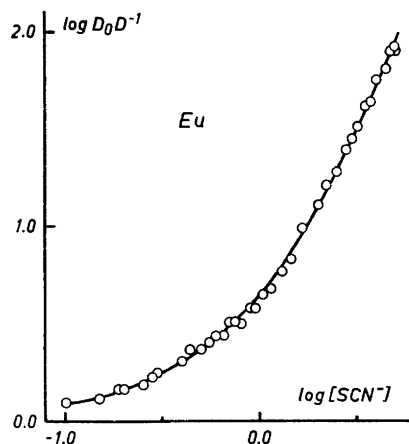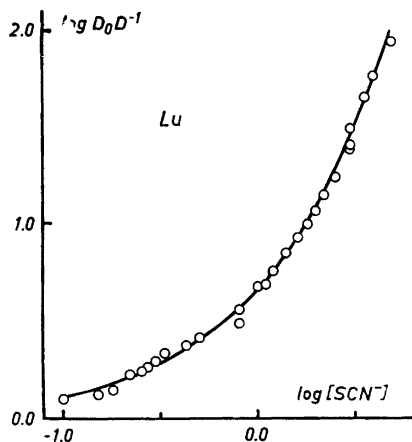
Fig. 2. The variation of the distribution of europium(III) as a function of the concentration of thiocyanate ion. $D_0 D^{-1}$ gives $1 + \sum_1^n \beta_n$[SCN]^n (*cf.* eqn. (5)). The curve is calculated from the constants in Table 3. Aqueous phase: 5 M Na(ClO$_4$). Organic phase: 0.1 M TTA in CCl$_4$ containing 10 % (by volume) hexone.
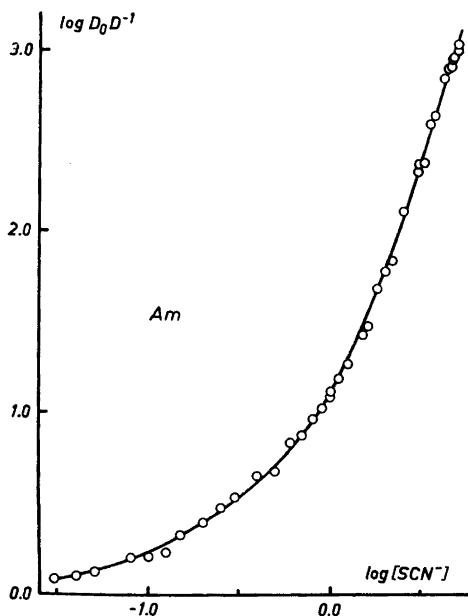
Fig. 3. The variation of the distribution of lutetium(III) as a function of the concentration of thiocyanate ion. $D_0 D^{-1}$ gives $1 + \sum_1^n \beta_n [SCN]^n$ (cf. eqn. (5)). The curve is calculated from the constants in Table 3. Aqueous phase: 5 M $Na(ClO_4)$. Organic phase: 0.1 M TTA in CCl_4 containing 10 % (by volume) hexone.

Fig. 4. The variation of the distribution of americium(III) as a function of the concentration of thiocyanate ion. $D_0 D^{-1}$ gives $1 + \sum_1^n \beta_n [SCN]^n$ (cf. eqn. (5)). The curve is calculated from the constants in Table 3. Aqueous phase: 5 M $Na(ClO_4)$. Organic phase: 0.1 M TTA in CCl_4 containing 10 % (by volume) hexone.

The stability constants of the thiocyanate complexes of these metal ions were first estimated graphically with Figs. 1 to 4 and finally calculated by a generalized least squares method using the LETAGROP VRID computer program which is an improved version of LETAGROP.[10] The constants were adjusted to minimize the error square sum U

$$U = \sum (\log D_0 D_{exp}^{-1} - \log(1 + \sum_1^n \beta_n [SCN^-]^n)_{calc})^2$$

The constants for the complexes of La(III), Eu(III), and Lu(III) were calculated with three parameters, β_1, β_2, and β_3. After the "best-fit" constants were found for these complexes, attempts were made to find β_4. However, it was concluded that any positive value of β_4 gave a larger error square sum. On the other hand, four parameters, β_1, β_2, β_3, and β_4 were used for the calculation of the Am(III) thiocyanate complexes. It was found in these calculations that any positive value of β_2 gave a larger error square sum than when β_2 was zero, and so, the calculation was finally carried out with three parameters, β_1, β_3, and β_4.

Table 2. Distribution of M(III) between the organic phase (composition, see Table 1) and aqueous phases which contain various amounts of SCN^- ($I = 5$ M at 25°C).

The data are given as: log $[SCN^-]$ (log D_0D^{-1}), where $D_0D^{-1} = 1 + \sum_n^1 \beta_n[SCN]^n$ (*cf.* eqn. (5)).

(a) La(III): 0.699 (1.49); 0.672 (1.45); 0.653 (1.43); 0.556 (1.18); 0.477 (1.07); 0.431 (0.95); 0.398 (0.91); 0.362 (0.85); 0.342 (0.80); 0.301 (0.77); 0.301 (0.70); 0.255 (0.69); 0.204 (0.68); 0.204 (0.66); 0.146 (0.62); 0.079 (0.55); 0.000 (0.45); −0.046 (0.42); −0.071 (0.40); −0.125 (0.36); −0.187 (0.33); −0.194 (0.31); −0.222 (0.34); −0.252 (0.27); −0.284 (0.28); −0.301 (0.25); −0.356 (0.26); −0.377 (0.28); −0.444 (0.23); −0.456 (0.23); −0.468 (0.20); −0.523 (0.17); −0.553 (0.16); −0.745 (0.10); −0.796 (0.09).

(b) Eu(III): 0.699 (1.92); 0.699 (1.91); 0.672 (1.90); 0.655 (1.81); 0.602 (1.75); 0.574 (1.64); 0.544 (1.62); 0.505 (1.51); 0.477 (1.45); 0.447 (1.39); 0.398 (1.28); 0.342 (1.21); 0.301 (1.11); 0.218 (0.99); 0.164 (0.83); 0.117 (0.77); 0.061 (0.68); 0.017 (0.65); −0.017 (0.58); −0.046 (0.58); −0.097 (0.50); −0.125 (0.51); −0.155 (0.51); −0.183 (0.44); −0.222 (0.44); −0.260 (0.41); −0.301 (0.37); −0.356 (0.37); −0.398 (0.31); −0.523 (0.25); −0.553 (0.23); −0.602 (0.19); −0.699 (0.17); −0.730 (0.17); −0.824 (0.12); −1.000 (0.10).

(c) Lu(III): 0.699 (1.93); 0.602 (1.75); 0.556 (1.64); 0.477 (1.48); 0.477 (1.40); 0.477(1.38); 0.398 (1.23); 0.342 (1.14); 0.301 (1.06); 0.255 (0.99); 0.204 (0.92); 0.146 (0.84); 0.079 (0.75); 0.041 (0.68); 0.000 (0.67); −0.097 (0.48); −0.097 (0.55); −0.301 (0.41); −0.398 (0.37); −0.481 (0.33); −0.523 (0.29); −0.569 (0.26); −0.602 (0.24); −0.658 (0.22); −0.745 (0.14); −0.824 (0.12); −1.000 (0.10).

(d) Am(III): 0.699 (3.02); 0.699 (2.99); 0.681 (2.95); 0.672 (2.94); 0.663 (2.90); 0.655 (2.89); 0.623 (2.83); 0.574 (2.63); 0.544 (2.58); 0.512 (2.37); 0.477 (2.36); 0.477 (2.36); 0.477 (2.32); 0.398 (2.10); 0.342 (1.83); 0.301 (1.77); 0.301 (1.77); 0.255 (1.67); 0.204 (1.47); 0.176 (1.42); 0.097 (1.26); 0.046 (1.18); 0.000 (1.11); 0.000 (1.08); −0.046 (1.02); −0.097 (0.96); −0.155 (0.87); −0.222 (0.83); −0.301 (0.67); −0.398 (0.65); −0.523 (0.53); −0.602 (0.47); −0.699 (0.39); −0.824 (0.32); −0. 903 (0.23); −1.000 (0.20); −1.097 (0.20); −1.301 (0.12); −1.398 (0.10); −1.523 (0.08).

The "best-fit" constants thus obtained are given in Table 3. The solid curves given in Figs. 1 to 4 show the distribution curves calculated by the stability constants in Table 3.

Table 3. Stability constants of thiocyanate complexes of lanthanum(III), europium(III), lutetium(III), and americium(III) in 5 M Na(ClO$_4$) at 25°C.

	log β_1	log β_2	log β_3	log β_4
La^{3+}	0.24 ± 0.06	−^{a} (< −0.62)^b	−0.73 ± 0.12	−^{c}
Eu^{3+}	0.32 ± 0.09	≈ −0.1 (<0.25)^b	−0.36 ± 0.15	−^{c}
Lu^{3+}	0.45 ± 0.09	≈ −1.3 (< −0.06)^b	−0.14 ± 0.23	−^{c}
Am^{3+}	0.85 ± 0.05	− − − − −^{c}	0.55 ± 0.15	0.00 ± 0.15

The range of error gives three times the standard deviation.

^{a} The result of the LETAGROP VRID calculation was $\beta_2 \pm 3\sigma = -0.02 \pm 0.24$
^{b} The values give log $(\beta_2 + 3\sigma)$
^{c} No positive value for β_2 or β_4 made the error square sum smaller than when $\beta_2 = 0$ or $\beta_4 = 0$.

The present results may be compared with those of Lebedev and Yakovlev.[5] They gave for Ce(III): log $\beta_1 = 0.10$; log $\beta_3 = 0.28$; for Am(III): log $\beta_1 = 0.24$, log $\beta_3 = -0.04$ and for Cm(III): log $\beta_1 = 0.27$, log $\beta_3 = 0.00$ in 5 M NaClO$_4$. We see from Table 3 that the stability constants of the present work

for Am(III) are about four times larger than their results, but β_3/β_1 is nearly the same. The error given for β_2 in Table 3 is much larger than that for β_1 and β_3. This seems to be caused by the instability of the second complexes, $M(SCN)_2{}^+$.

Am(III) thiocyanate complexes are more stable than those of the other three lanthanide ions, and the differences are larger in β_3 than in β_1. Such differences have not been observed in the chloride, sulfate or oxalate complexes of these ions. Surls and Choppin [2] pointed out that the difference in the ion-exchange behavior of these ions in thiocyanate media agrees with the prediction by Diamond,[1] based on the assumption of f-orbital hybridization, that thiocyanate should complex more strongly with actinides than with lanthanides.

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