Monatshefte für Chemie 124, 7–14 (1993)

Monatshefte für Chemie
Chemical Monthly

Complexation in Pr, Sm–SCN⁻ Systems

Paweł Sadowski and **Marek Majdan**

Faculty of Chemistry UMCS, Pl Marii Curie Sklodowskiej 3, PL-20 031 Lublin, Poland

Summary. The stability constants of Pr, Sm thiocyanate complexes were determined. It was found that the stability constants are lower than those found for Nd. The molar absorptivities of Sm thiocyanate solutions changed in a way which suggested the existence of an equilibrium of inner- and outersphere complexation.

Keywords. Stability constant; Lanthamide thiocyanates.

Untersuchung der Komplexierung in Pr, Sm–SCN⁻ Systemen

Zusammenfassung. Es wurden die Stabilitätskonstanten von Praseodymium und Samariumthiocyanaten bestimmt. Es stellte sich heraus, daß diese niedriger sind als die entsprechenden für Neodym. Die Änderung der molaren Absorption von Samariumthiocyanaten mit der Konzentration zeigte ein Gleichgewicht von innerspärischer und außersphärischer Komplexierung an.

Introduction

This report is the continuation of our study concerning the application of the spectrophotometrical method for the determination of the stability constants of lanthanide thiocyanate complexes. As we mentioned previously [1], we decided to investigate thiocyanate system in respect to the important role of the lanthanide thiocyanates in the solvent extraction of these elements [2–7].

Experimental Part

Pr_2O_3 and Sm_2O_3 (purity 99.9%) were kindly provided by Merck. NaSCN, $HClO_4$, $NaClO_4$ supplied by POCH (Gliwice) were used for the preparation of the lanthanide thiocyanates. Lanthanide perchlorates obtained by the dissolution of the respective oxides in $HClO_4$ were mixed with the calculated volume of 4 *M* NaSCN. The constant ionic strength was controlled by $NaClO_4$.

The spectra were recorded using a Specord M40 (Carl Zeiss Jena production) over the whole visible range.

Results and Discussion

Figures 1–2 show the spectra of Pr and Sm thiocyanates in comparison with their perchlorates. There is a marked bathochromic shift of all absorption bands, which is the evidence for the formation of complexes in lanthanide thiocyanates.

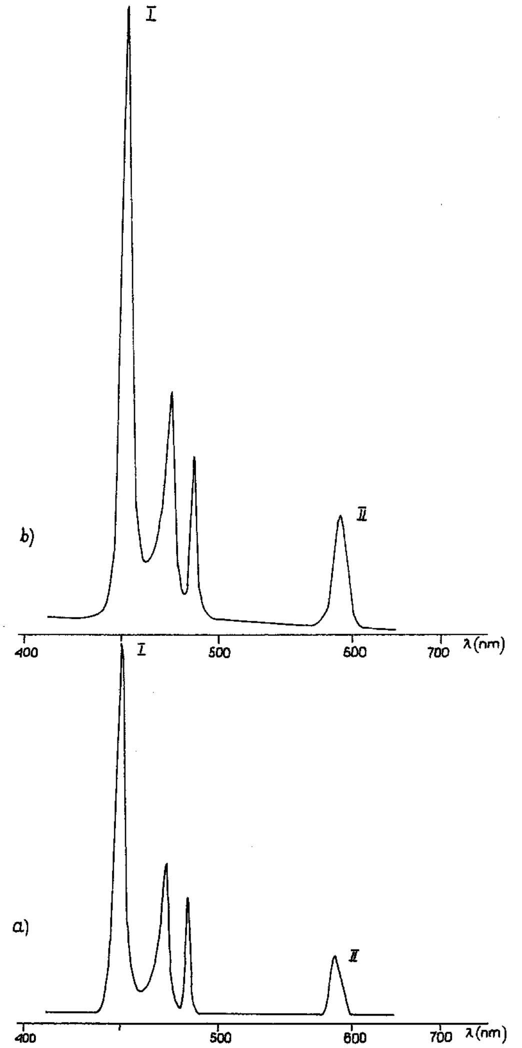

Fig. 1. The spectra of Pr (path length $d = 1$ cm, temp. 25 °C; a and b refer to water and 8 M NaSCN). The absorbances and wavelengths for different bands are as follows: I(a) 0.5143 – 444.2 nm ($^3P_{2,1,0}$–$^3H_4$), 0.2089 – 469.3 nm, 0.1649 – 481.9 nm; II(a) 0.0831 – 590.1 nm ($^1D_2$–$^3H_4$); I(b) 0.8393 – 446.6 nm, 0.3217 – 471.9 nm; 0.2354 – 484.7 nm; II(b) 0.153 – 592.8 nm

Figures 3–4 include the change of the relative molar absorptivities $\varepsilon/\varepsilon_0$ of the lanthanide thiocyanates with the $[SCN^-]$ increase. The well marked "inflection" on the absorptivity curve of Sm occurs. A similar effect was observed by Abrahamer [8] for H_2O–C_2H_5OH solutions of the lanthanide nitrates. The existence of this "inflection" was explained as the result of the replacement of C_2H_5OH from the first coordination sphere of the cation by NO_3^-. Similarly in our case "inflection" results probably from the replacement of H_2O by SCN^- in the first coordination sphere of the lanthanide; the symmetrical $Ln(SCN)_2^+$ complexes changed to more unsymmetrical $Ln(SCN)_3$ species and the molar absorptivity increases again more rapidly.

Tables 1–4 list the values of the relative molar absorptivities of the lanthanide thiocyanates for different SCN^- concentrations. Based on the $\varepsilon/\varepsilon_0$ values we found the stability constants of $Ln(SCN)^{2+}$ and $Ln(SCN)_2^+$ species (see Tables 5–7). The procedure for the determination of the stability constants from the spectral data is

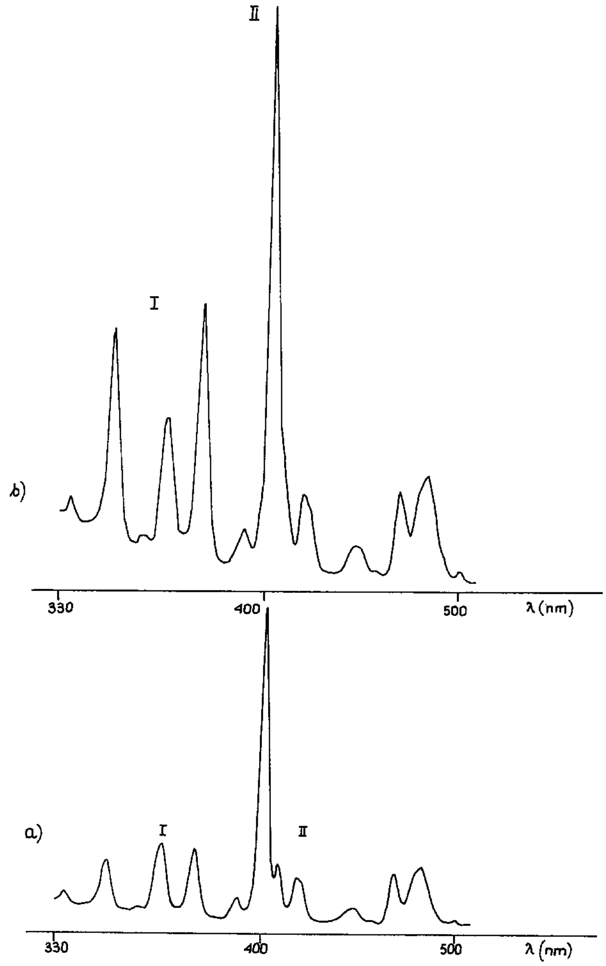

Fig. 2. The spectra of Sm (path length $d = 1$ cm, temp. 25 °C; a and b refer to water and 8 *M* NaSCN). The absorbances and wavelengths for different bands are as follows: I(a) 0.0645 – 344.6 nm ($^4H_{9/2}$, $^4D_{3/2}$, $^6P_{7/2}$–$^6H_{5/2}$), 0.0820 – 362.5 nm, 0.0764 – 374.5 nm; II(a) 0.3218 – 401.6 nm ($^6P_{3/2}$, $^4L_{13/2}$–$^6H_{5/2}$); I(b) 0.2795 – 345.2 nm, 0.1897 – 363.1 nm, 0.3059 – 375.6 nm; II(b) 0.5712 – 402.9 nm

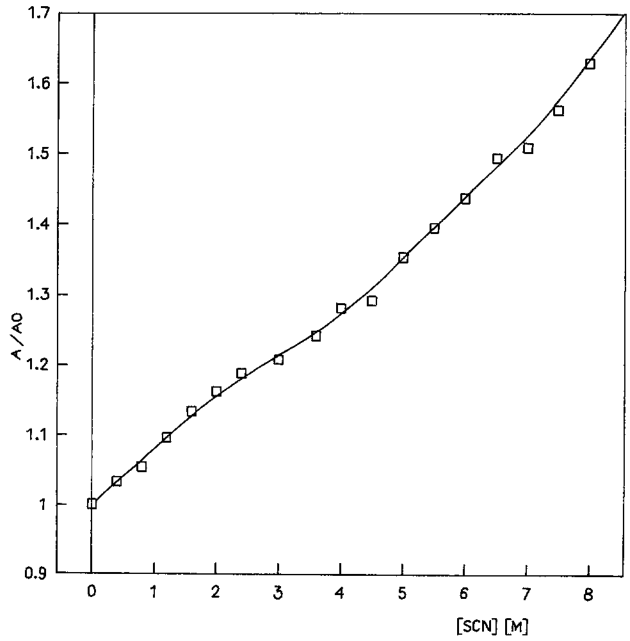

Fig. 3. The change of the relative molar absorptivity of Pr with increasing [SCN$^-$] concentration (the band 444.2 nm was taken for observation, $[Pr]_t = 0.05$ *M*; points in the range 0–4 *M* refer to a constant ionic strength of $I = 4$)

Table 1. The relative molar absorptivities of Pr (the intensity of the bands in the range 444.2–446.6 nm was measured)

Ionic strength $I = 1$		$I = 2$	
[Pr] = 0.025 *M*		[Pr] = 0.025 *M*	
$\varepsilon_0 = 9.02$		$\varepsilon_0 = 9.64$	
[SCN$^-$]	$\varepsilon/\varepsilon_0$	[SCN$^-$]	$\varepsilon/\varepsilon_0$
0	1	0	1
0.1	1	0.2	1.015
0.2	1.015	0.4	1.023
0.3	1.02	0.6	1.038
0.4	1.025	0.8	1.05
0.5	1.025	1.0	1.062
0.6	1.034	1.2	1.062
0.7	1.039	1.4	1.069
0.8	1.044	1.6	1.092
		1.8	1.100

$I = 2$		$I = 2.5$	
[Pr] = 0.05 *M*		[Pr] = 0.05 *M*	
$\varepsilon_0 = 10.33$		$\varepsilon_0 = 10.52$	
[SCN$^-$]	$\varepsilon/\varepsilon_0$	[SCN$^-$]	$\varepsilon/\varepsilon_0$
0	1	0	1
0.2	1	0.25	1
0.4	1.039	0.5	1.023
0.6	1.039	0.75	1.031
0.8	1.054	1.0	1.054
1.0	1.062	1.25	1.078
1.2	1.07	1.5	1.097
1.4	1.093	1.75	1.116
1.6	1.10	2.0	1.136
1.7	1.124		

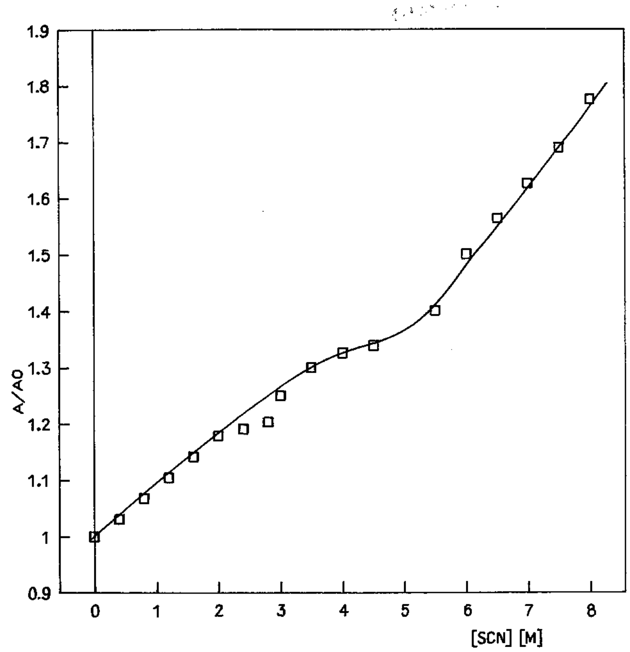

Fig. 4. The change of the relative molar absorptivity of Sm with increasing [SCN$^-$] concentration (the band 344.6 nm was taken for observation, $[\mathrm{Sm}]_t = 0.05\ M$; points in the range 0–4 M refer to a constant ionic strength of $I = 4$)

Table 2. The relative molar absorptivities of Pr

$I = 3$		$I = 4$	
$[\mathrm{Pr}] = 0.05\ M$		$[\mathrm{Pr}] = 0.05\ M$	
$\varepsilon_0 = 10.34$		$\varepsilon_0 = 10.26$	
[SCN$^-$]	$\varepsilon/\varepsilon_0$	[SCN$^-$]	$\varepsilon/\varepsilon_0$
0	1	0	1
0.2	1.012	0.2	1.021
0.4	1.023	0.4	1.033
0.6	1.039	0.6	1.046
0.8	1.039	0.8	1.054
1.0	1.062	1	1.075
1.2	1.078	1.2	1.096
1.4	1.093	1.4	1.117
1.6	1.112	1.6	1.133
1.8	1.112	1.8	1.138
2	1.136	2	1.162
2.2	1.147	2.2	1.162
2.4	1.159	2.4	1.188
2.6	1.171	2.6	1.188
		2.8	1.208
		3.0	1.208
		3.2	1.213
		3.4	1.216
		3.6	1.242

Table 3. The relative molar absorptivities of Sm (the intensity of the bands in the range 401.6–402.9 nm was measured)

$I = 1$		$I = 2$	
[Sm] = 0.025 *M*		[Sm] = 0.025 *M*	
$\varepsilon_0 = 6.3$		$\varepsilon_0 = 6.76$	
[SCN$^-$]	$\varepsilon/\varepsilon_0$	[SCN$^-$]	$\varepsilon/\varepsilon_0$
0	1	0	1
0.1	1.013	0.2	1.01
0.2	1.013	0.4	1.03
0.3	1.025	0.6	1.03
0.4	1.038	0.8	1.055
0.5	1.05	1.0	1.07
0.6	1.054	1.2	1.097
0.7	1.063	1.4	1.11
0.8	1.075	1.6	1.13
		1.8	1.146
$I = 2$		$I = 3$	
[Sm] = 0.05 *M*		[Sm] = 0.05 *M*	
$\varepsilon_0 = 6.48$		$\varepsilon_0 = 7.04$	
0	1	0	1
0.2	1.02	0.2	1.006
0.4	1.034	0.4	1.025
0.6	1.06	0.6	1.037
0.8	1.079	0.8	1.049
1.0	1.079	1.0	1.062
1.2	1.091	1.2	1.08
1.4	1.103	1.4	1.099
1.6	1.13	1.6	1.123
1.7	1.127	1.8	1.136
		2.0	1.142
		2.2	1.172
		2.4	1.172
		2.6	1.185

Table 4. The relative molar absorptivities of Sm

$I = 4$, [Sm] $= 0.05$ *M*, $\varepsilon_0 = 6.81$	
[SCN^-]	$\varepsilon/\varepsilon_0$
0.0	1
0.2	1.018
0.4	1.031
0.6	1.055
0.8	1.068
1.0	1.092
1.2	1.104
1.4	1.117
1.6	1.141
1.8	1.153
2.0	1.178
2.2	1.178
2.4	1.19
2.6	1.19
2.8	1.203
3.0	1.221
3.2	1.226
3.4	1.239
3.6	1.239

Table 5. The stability constants: β_1, β_2 of $Pr(SCN)^{2+}$ and $Pr(SCN)_2^+$ species (the values in brackets denote standard deviations)

β_1	β_2	$\varepsilon_1/\varepsilon_0$	$\varepsilon_2/\varepsilon_0$	I	$[Pr]_t$
0.27	0.03	1.27	1.23	1	0.025
(0.03)	(0.03)	(0.11)	(0.19)		
0.28	0.05	1.24	1.44	2	0.025
(0.06)	(0.04)	(0.08)	(0.23)		
0.21	0.056	1.32	1.49	2	0.05
(0.09)	(0.03)	(0.15)	(0.18)		
0.18	0.06	1.2	1.6	2.5	0.05
(0.015)	(0.02)		(0.14)		
0.14	0.05	1.37	1.50	3	0.05
(0.04)	(0.02)	(0.12)	(0.15)		
0.3	0.2	1.2	1.35	4	0.05
(0.1)		(0.1)	(0.05)		

given in our previous paper concerning Nd [1]. If we compare the data for Nd, we can notice that they are evidently higher than those for Pr and Sm. A similar case was found for nitrato complexes of the lanthanides [9] and we explained it as the increase of the innersphere complexation in the lanthanide nitrato complexes in the region La-Nd, Sm.

Table 6. The stability constants of $Nd(SCN)^{2+}$ and $Nd(SCN)_2^+$ species (taken from Ref. [1])

β_1	β_2	$\varepsilon_1/\varepsilon_0$	$\varepsilon_2/\varepsilon_0$	I	$[Nd]_t$
0.33	0.41	1.48	1.55	1	0.025
(0.09)	(0.08)	(0.1)	(0.07)		
0.45	0.45	1.35	1.40	2	0.025
(0.05)	(0.05)	(0.05)			
0.39	0.32	1.47	1.46	2	0.05
(0.1)	(0.14)	(0.11)	(0.10)		
0.37	0.23	1.53	1.57	2.5	0.05
(0.05)	(0.07)	(0.07)	(0.04)		
0.5	0.34	1.33	1.63	3	0.05
(0.08)	(0.05)	(0.04)	(0.04)		
0.4	0.23	1.57	1.73	4	0.05
(0.08)	(0.05)	(0.09)	(0.05)		

Table 7. The stability constants of $Sm(SCN)^{2+}$ and $Sm(SCN)_2^+$ species

β_1	β_2	$\varepsilon_1/\varepsilon_0$	$\varepsilon_2/\varepsilon_0$	I	$[Sm]_t$
0.13	0.13	1.67	1.27	1	0.025
(0.02)	(0.06)	(0.09)	(0.09)		
0.22	0.03	1.49	1.27	2	0.05
(0.05)	(0.04)	(0.11)	(0.24)		
0.14	0.08	1.4	1.6	2	0.025
(0.04)	(0.04)	(0.13)	(0.15)		
0.13	0.05	1.64	1.34	2.5	0.05
(0.30)	(0.07)	(0.13)	(0.24)		
0.08	0.07	1.6	1.45	3.0	0.05
(0.02)	(0.03)	(0.16)	(0.09)		
0.25	0.06	1.4	1.45	4.0	0.05
(0.05)	(0.03)	(0.1)			

References

[1] Sadowski P., Majdan M. (1991) Monatsh. Chem. **122**: 241

[2] Gerontopulos P. Th., Erigali L., Barbano P. G. (1965) Radiochim. Acta **4**: 75

[3] Yoshida H. (1962) J. Inorg. Nucl. Chem. **24**: 1257

[4] Khopkar P. K., Narayankutty P. (1972) J. Inorg. Nucl. Chem. **34**: 2617

[5] Chang C. A., Manchanda V. K., Peng J. (1989) Solv. Extr. Ion Exch. **7**: 413

[6] Gaikwad A. G., Damoda A. D. (1990) Analytical Sciences **6**: 871

[7] Gaudernack B., Hannestadt G., Hundere I., (1973) U.S. Patent: **3**: 751, 553

[8] Abrahamer I., Marcus Y. (1968) J. Inorg. Nucl. Chem. **30**: 1563

[9] Majdan M., Sadowski P. to be published

Received March 2, 1992. Accepted March 24, 1992