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Complexation of f electron (3+) ions with pseudohalide ligands

M. Borkowski[a], S. Lis[b,*], S. Siekierski[a]

[a]*Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warsaw, Poland*
[b]*Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznan, Poland*

Abstract

The coordination sphere of Nd(III) and Eu(III) cations in aqueous solutions containing pseudohalide ligands has been studied by absorption spectroscopy (hypersensitive transition) and luminescence lifetimes. It has been found that the tendency to form inner-sphere complexes increases in the order $NCSe^- < NCS^- < N_3^- < NCO^-$. The study of extraction of tetrahedral Co(II) complexes with NCS^- and N_3^- ligands has shown that the metal-bonded N_3^- ligand interacts with water molecules much stronger than the NCS^- ligand. That explains why extraction of inner-sphere lanthanide complexes by TBP is much less efficient for the azide than for thiocyanate ligand, in spite of similar stability constants. © 1998 Elsevier Science S.A.

Keywords: Lanthanides; Pseudohalide complexes; Luminescence; Solvent extraction

1. Introduction

It is known that with respect to solvent extraction from nitrate solutions yttrium behaves as a heavy lanthanide, while actinides(III) turn out to be similar to light pseudolanthanides [1–3]. On the other hand, in systems containing thiocyanate ions, yttrium becomes a light lanthanide, while actinides are extracted with heavy lanthanides [1–3]. This reversal in extraction behaviour is a basis for group separation of yttrium from lanthanides and of actinides from lanthanides. It was interesting to know whether other pseudohalide ligands ($NCSe^-$, NCO^-, and N_3^-) behave in a similar way. For that purpose a comparative solvent extraction study of Y(III), Am(III) and selected lanthanides into tri-*n*-butyl phosphate, TBP, was previously made [4] and high distribution ratios for NCS^- and $NCSe^-$ and very small distribution ratios for NCO^- and N_3^- were found. Because of higher pK_a values of HN_3 and HNCO than of HNCS and HNCSe, i.e. higher capability to form complexes by the N_3^- and NCO^- than by NCS^- and $NCSe^-$ anions, and because of almost the same partition coefficients of HNCS, HNCO and HN_3 [5] we would expect that an extraction of lanthanides from azide and cyanate solutions, should be similar to those from thiocyanates. We have assumed that partition of HNCS, HNCO and HN_3 acids into TBP can serve as a model for the partition of the respective complexes of trivalent cations, i.e. that each pseudohalide ligand bonded to the metal interacts equally strongly with water molecules. The disagreement between experiment and expected behaviour can be due to the fact that the N_3^- and NCO^- ions prefer formation of unextractable outer-sphere complexes, while the NCS^- and $NCSe^-$ ions form extractable inner-sphere complexes. Another explanation is that the metal-bonded N_3^- and NCO^- ligands interact much stronger with water than the NCS^- and $NCSe^-$ ligands.

To decide between the two possibilities, it is necessary to study both the coordination sphere of the lanthanide(III) ion and partition of the LnX_3 complexes, as a function of the pseudohalide ligand X. It is well known that the luminescence spectroscopy of Eu(III) ion is a useful tool in studying the primary coordination sphere of the cation [6–9], while hypersensitive absorption band of Nd(III) $^4I_{9/2} \rightarrow {}^4G_{5/2}$ (at ~576 nm) is widely used in the study of metal–ligand interaction [9–12]. Therefore, both these methods have been used in this work. Unfortunately, there is no method which makes the determination of the partition constants of the TBP extractable LnX_3 complexes ($X = N_3^-$, NCO^-, NCS^- and $NCSe^-$) possible. Instead of lanthanide complexes we have, therefore, studied the partition between water and TBP of the tetrahedral $[Co(NCS)_4]^{2-}$ and $[Co(N_3)_4]^{2-}$ complexes. Partition constants of the tetrahedral Co(II) complexes can be, under

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[*] Corresponding author.

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certain conditions determined directly by a spectrophotometric method.

2. Experimental details

Pure TBP pure was obtained from Fluka AG and purified by vacuum distillation. NaNCO of analytical grade was from Fluka AG and KNCSe of 97% purity from Aldrich Chemical Company. Other chemicals of analytical grade (NaN_3, NaNCS and $Co(NO_3)_2$) were obtained from POCh, Gliwice, Poland. All these reagents were used as received.

Solutions containing Nd(III) and Eu(III) ions were prepared using $Nd(ClO_4)_3$ and $Eu(ClO_4)_3$, obtained by dissolving Nd_2O_3 and Eu_2O_3 (spectroscopically pure, prepared in the Laboratory of Rare Earths, Faculty of Chemistry, Adam Mickiewicz University, Poznan) in perchloric acid. The Nd(III) and Eu(III) concentrations were 0.01 M in all experiments. The required pH values of the solutions used were adjusted by addition of NaOH and $HClO_4$, and controlled by a pH meter (26, Radiometer, Copenhagen).

The absorption spectra of Nd(III) and Co(II) complexes were obtained by means of a Shimadzu UV-2401 PC spectrophotometer. The luminescence lifetime of Eu(III) was measured using the detection system described earlier, which consisted of a nitrogen laser (KB6211) and a tuneable dye laser [13]. The luminescence decay curves observed in this work were analyzed by a single exponential relation. The decay constants were calculated with a computer program using the Simplex procedure [13].

The distribution ratios of tetrahedral Co(II) complexes, D_{tetr}, were determined as a function of TBP concentration in heptane using 0.025 M solutions of $Co(NO_3)_2$ in 4.0 M NaN_3 and in 4.0 M NaCNS. The distribution ratios of tetrahedral Co(II) complexes were calculated from the recorded absorption spectra in the organic and aqueous phases. For the thiocyanate complex the absorption band at ~625 nm and for the azide complex that at ~675 nm were used [14].

3. Results and discussion

3.1. Hypersensitive transition spectra of Nd(III) ion

The Nd(III)-hypersensitive band with the maximum at ~576 nm (${}^4I_{9/2} \rightarrow {}^4G_{5/2}$) was recorded for a wide range of N_3^-, NCO^-, NCS^- and $NCSe^-$ concentrations. The pH of the solutions was 3 for NCS^-, 5.5 for N_3^- and $NCSe^-$, and about 6 for NCO^-. Fig. 1 shows the hypersensitive spectrum of Nd(III) as a function of the azide concentration. It can be seen that the absorption band in the region 570–595 nm increases markedly with N_3^- concentration. A similar behaviour has been also found for the NCO^- ligand. In the case of the NCS^- ligand an increase of absorption is also observed, but for thiocyanate concentrations higher than 1.0 M (Fig. 2). For selenocyanates we observed that the Nd(III)-hypersensitive band remains

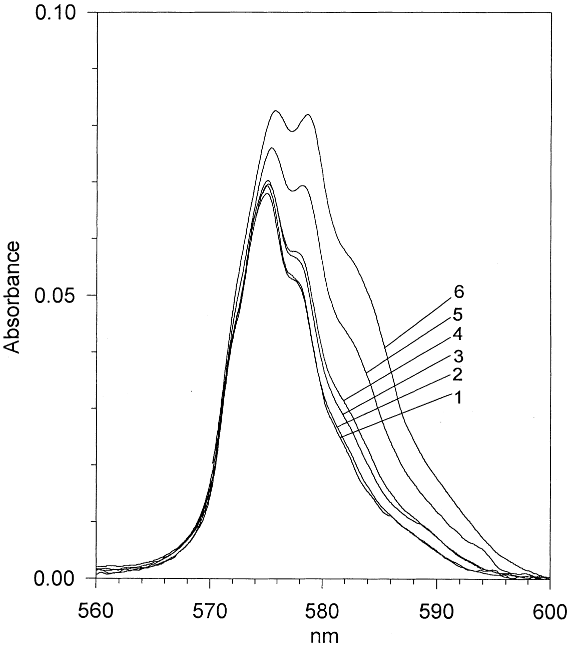

Fig. 1. The effect of azide ion concentration on the ${}^4I_{9/2} \rightarrow {}^4G_{5/2}$ hypersensitive transition of Nd(III); $c_{Nd(III)} = 0.01$. Molar concentrations of azide ions are: (1) none, (2) 0.01, (3) 0.05, (4) 0.10, (5) 0.50 and (6) 1.00.

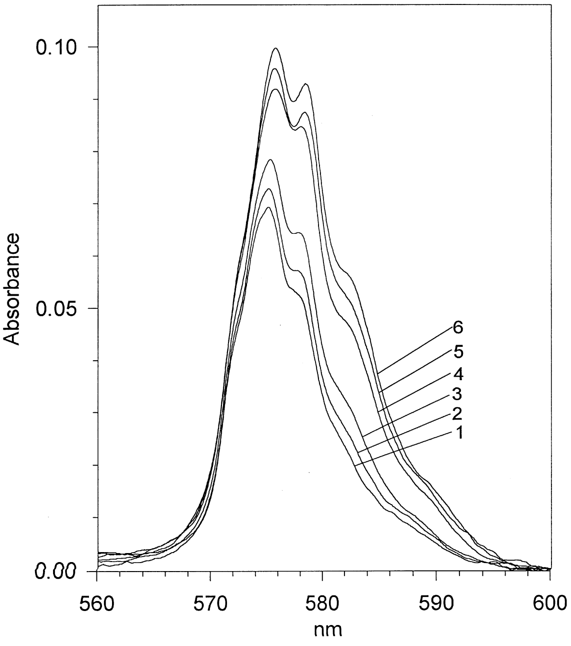

Fig. 2. The effect of thiocyanate ion concentration on the ${}^4I_{9/2} \rightarrow {}^4G_{5/2}$ hypersensitive transition of Nd(III); $c_{Nd(III)} = 0.01$. Molar concentrations of thiocyanate ions are: (1) none, (2) 0.10, (3) 1.0, (4) 1.5, (5) 2.0 and (6) 2.4.

constant up to 0.75 M KNCSe, which is the highest experimentally available concentration. The increase in the hypersensitive absorption band points out to formation of inner-sphere complexes. Spectra of all the systems studied and of the perchlorate solution as a reference, recorded for a metal to ligand ratio=1:50, are presented in Fig. 3. The effect of the ligand on the height of the hypersensitive absorption band of Nd(III) is evidence for the following tendency in formation of inner-sphere complexes:

$$NCSe^- < NCS^- < N_3^- < NCO^-.$$

3.2. Luminescence lifetimes of the Eu(III) ion

The luminescence lifetime of Eu(III) in aqueous solution decreases linearly with increasing number of water molecules in the inner coordination sphere as a result of an efficient energy transfer from the exited ($^5D_0$) state of the Eu(III) ion to the O–H oscillator in the coordinated water molecule(s) [15]. Substitution of D_2O for H_2O eliminates this quenching, since coupling with the D_2O oscillators is much less effective. Complexation of Eu(III) by a ligand results in removal of coordinated water molecule(s) and, consequently, an increase in the luminescence lifetime. An average number of water molecules, n_{H_2O}, present in the complexed Eu(III) cation can be determined by measuring the excited-state lifetimes, τ, separately in H_2O and D_2O solutions. The decay constants, $k=\tau^{-1}$, are used to calculate the average number of water molecules with an uncertainty of ±0.5, by the relationship [15]:

$$n_{H_2O} = 1.05 \cdot (k_{H_2O} - k_{D_2O})$$

The luminescence lifetimes of Eu(III) were measured for azide, thiocyanate, selenocyanate and cyanate solutions. Plots in Fig. 4 show the effect of N_3^-, NCS^- and $NCSe^-$ concentration on the τ value for Eu(III). A dramatic decrease of τ for the azide and selenocyanate ligands is observed even at low concentrations. This suggests that the azide and selenocyanate ligands enter the inner coordination sphere and are more effective quenchers of Eu(III) luminescence than water molecules. The chance that two ligands, if present in the outer coordination sphere, could affect to such an extent the quenching properties of inner-sphere water molecules seems to be highly improbable. In the case of thiocyanate solutions the measured luminescence lifetime of Eu(III) is constant (~0.109 ms) up to 1 M NCS^- and decreases at higher concentrations. Because calculation of the number of water molecules present in the inner-sphere of a complexed cation is based on the assumption that water is usually a much more efficient luminescence quencher than a ligand, calculation of n_{H_2O} in Eu complexes with N_3^-, $NCSe^-$ and NCS^- ligands was not possible. By contrast, τ_{H_2O} in the Eu(III)/cyanate system increases with ligand concentration, which makes such calculations possible. The values of τ_{H_2O}, τ_{D_2O} and n_{H_2O}, for the Eu(III)/NCO^- system are presented in Table 1. It can be seen that n_{H_2O} decreases from 9 to 7 as the NCO^- concentration increases, which is an evidence for formation of inner sphere complexes between Eu(III) and

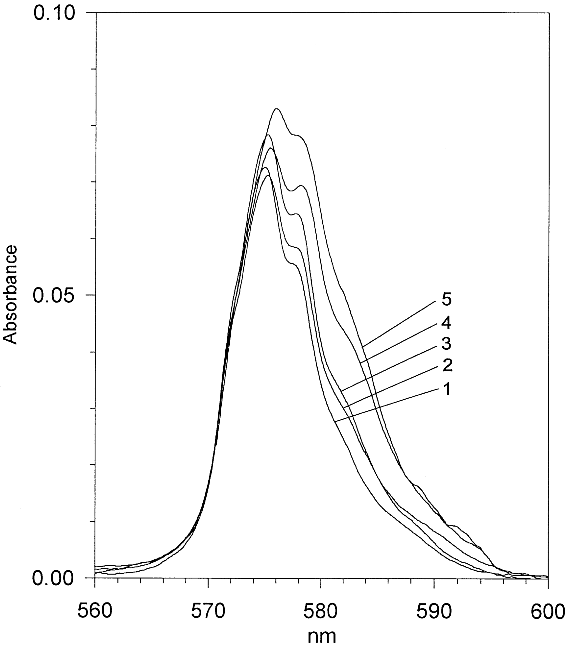

Fig. 3. Changes of the Nd(III)-hypersensitive transition band ($^4I_{9/2} \rightarrow {}^4G_{5/2}$) as a function of the ligand; $c_{Nd(III)}=0.01$ M, ligand concentration 0.5 M. (1) Perchlorate, (2) selenocyanate, (3) thiocyanate, (4) azide and (5) cyanate.

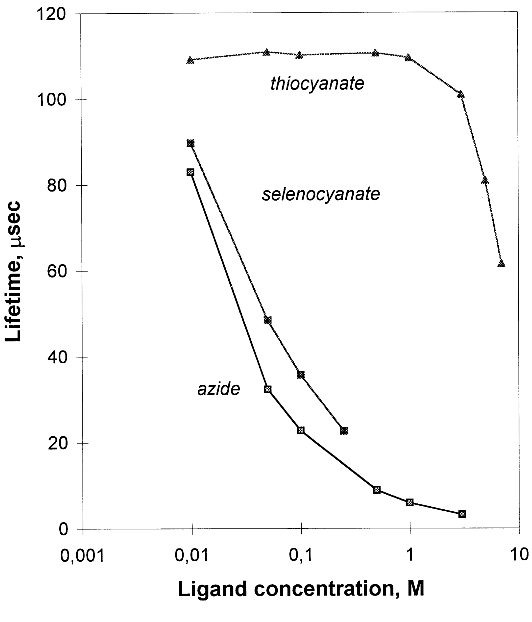

Fig. 4. The variation of the Eu(III) luminescence lifetime, τ, with azide, thiocyanate and selenocyanate concentration.

Table 1
Luminescence lifetimes of Eu(III) in H_2O and in D_2O solutions containing various amounts of sodium cyanate

NCO− conc. (M)	$\tau_{(H_2O)}$ (ms)	$\tau_{(D_2O)}$ (ms)	n_{H_2O}
0	0.1096	3.846	9.3
0.012	0.1113	3.668	9.1
0.024	0.1124	3.342	9.0
0.048	0.1143	3.417	8.9
0.096	0.1160	3.461	8.7
0.192	0.1209	3.338	8.4
0.576	0.1441	3.226	6.9

Eu(III) concentration was equal to 0.01 M.

NCO^- ions. These results are in agreement with those following from our studies on the hypersensitive absorption spectra.

3.3. Partition of azido- and thiocyanato-complexes of Co(II)

The data on Eu(III) luminescence lifetimes and on Nd(III) absorption spectroscopy have shown that the azide and cyanate ions form even stronger inner-sphere complexes than the thiocyanate ions. If so, then the difference in extraction between the azide and thiocyanate complexes must be due to different partition, in spite of the same partition of the respective acids.

In the extraction of lanthanides by TBP, the neutral LnX_3 complex is transferred from the aqueous into the organic phase. Determination of the constant for the transfer reaction which also contains the exchange of water molecules for TBP molecules

$$LnX_3(H_2O)_{n,aq} \rightarrow LnX_3(TBP)_{k,org}$$

is not possible. The reason is that concentrations of the individual LnX_n^{3-n} in the aqueous phase species cannot be determined. Therefore, interaction of lanthanide azido- and lanthanide thiocyanato-complexes with water molecules cannot be directly compared. However, a comparison between the metal bonded N_3^- and NCS^- ligands with respect to interaction with water molecules is possible by studying partition of tetrahedral, colored, $[CoX_4]^{2-}$ complexes. Fig. 5 shows the distribution ratios of tetrahedral $[Co(NCS)_4]^{2-}$ and $[Co(N_3)_4]^{2-}$ complexes, at pH 7, as a function of TBP concentration in heptane. It follows from the presented data that the distribution ratio of $[Co(NCS)_4]^{2-}$ is about 6 orders of magnitude higher than that of $[Co(N_3)_4]^{2-}$. It means that cobalt(II)-bonded N_3^- ligands interact much stronger with water molecules than cobalt(II)-bonded NCS^- ligands. In view of these results it is reasonable to assume that the lanthanide bonded N_3^- ligands also interact much stronger with water molecules than the NCS^- ligands. Thus, in spite of greater tendency to form inner-sphere complexes with lanthanide ions by the azide than the thiocyanate ions the distribution ratio is lower for the azide complexes, because of much lower transfer (partition) constant.

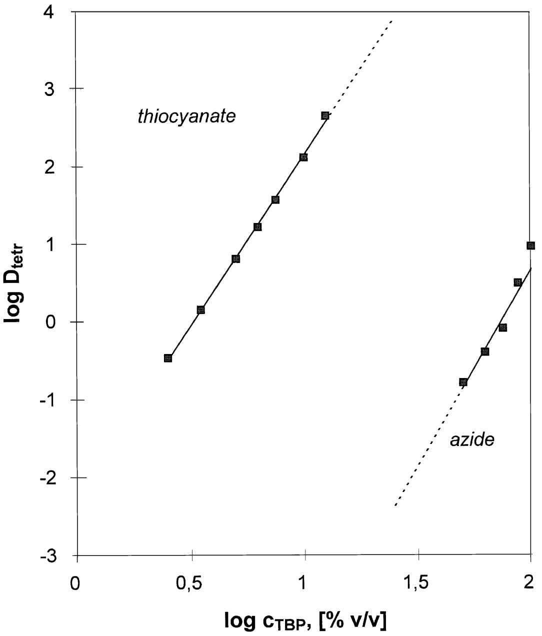

Fig. 5. The distribution ratios of the tetrahedral $[Co(NCS)_4]^{2-}$ and $[Co(N_3)_4]^{2-}$ complexes, D_{tetr}, as a function of TBP concentration in heptane. Concentration of NaN_3 and NaNCS = 4.0 M.

4. Conclusions

Studies on intensity of the hypersensitive transition band of Nd(III) as a function of the ligand have shown that the cyanate, azide and thiocyanate (at higher concentration) ions form inner-sphere complexes with lanthanide ions. That is contrary to our previous assumption [4] that from the pseudohalide ligands only NCS^- and $NCSe^-$ form inner-sphere complexes. The tendency to form inner-sphere complexes increases in the order:

$$NCSe^- < NCS^- < N_3^- < NCO^-.$$

This conclusion is supported by a study of the luminescence lifetimes of Eu(III) in cyanate complexes. It follows from this study that already in 0.6 M NaCNO solution there are two cyanate ligands in the inner coordination sphere of Eu(III) ion. The decrease in the luminescence lifetimes of Eu(III) in azide complexes can also be explained by formation of inner-sphere complexes, assuming that the N_3^- ligand is even a better quencher than the water molecule.

As demonstrated by spectral results, lanthanides form inner-sphere complexes with NCO^- and N_3^- anions more readily than with the NCS^- anion, a much better extraction with TBP of lanthanides from thiocyanates must originate in much higher transfer (partition) constant of the

$Ln(NCS)_3$ complex. This conclusion has been indirectly confirmed by the study of extraction of the tetrahedral complexes of Co(II) with N_3^- and NCS^- ligands, which shows that N_3^- metal-bonded ligands interact with water molecules much stronger than NCS^- metal-bonded ligands.

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