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A spectroscopic investigation of temperature effects on solution complexation in the Eu^{3+}–acetate system

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Abstract

Europium–acetate complexation was studied using luminescence spectroscopy as a function of temperature between 8 and 59°C. The $^5D_0 \rightarrow {}^7F_0$ luminescence transition of Eu^{3+} was used to identify the presence of 1:1, 1:2, and 1:3 complexes with acetate in $NaClO_4$ media. The results indicate an increase in complexation for all three species with increasing temperature. An estimate of the stability quotient β_1 for $Eu(Ac)^{2+}$ at 25°C was obtained by observing changes in the intensity of its $^5D_0 \rightarrow {}^7F_0$ transition as the acetate concentration was varied. A value of log $\beta_1 = 1.94 \pm 0.13$ was obtained, consistent with reported stability quotients measured by other techniques. Although overall complexation increases with temperature, little change was observed in the distributions of the 1:1, 1:2, and 1:3 complexes at constant ligand-to-metal ratios.

Keywords: Europium–acetate complexation; Luminescence spectroscopy; Temperature

1. Introduction

The solution chemistry of the trivalent f-elements is of interest to a wide range of scientists, including economic geologists, biologists/biochemists, and nuclear/radiochemists. For example, geologists are interested in the mobility of the rare earth elements (REEs) in groundwater systems, which can serve as natural tracers of diagenetic processes in sedimentary formations [1–5]. Lanthanides are frequently used as optical probes for biological studies of spectroscopically inactive, but biologically important metal ions such as Ca^{2+} [6], and serve as shift reagents in diagnostic applications such as magnetic resonance imaging [7]. Finally, the separation of trivalent actinides from nuclear processing solutions (e.g. Ref. [8]), and predicting the risks imposed by release of isotopes of Am^{3+} and Cm^{3+} to the environment (e.g. Ref. [9]) both rely on a fundamental knowledge of the solution thermodynamics and species formed in various systems.

Stability quotients that describe the solution complexation of the trivalent f-elements have been measured by a variety of methods. Approaches include potentiometry, spectrophotometry, ion exchange, and solvent extraction. Potentiometry, ion exchange, and solvent extraction are considered indirect methods for studying chemical equilibria because assumptions must be made concerning speciation in the system of study. These assumptions are incorporated into mathematical fitting of the experimental data. Spectrophotometric methods are usually more direct because individual species can frequently be resolved. Luminescence spectroscopy and lifetime measurements have been demonstrated to be useful direct probes for observing the speciation of Eu^{3+} in solution [6].

Carboxylic acids are important complexors of the trivalent f-elements due to the electrostatic behavior of these metals, and the hard-donor nature of the carboxylate oxygen groups. Acetate is one of the simplest carboxylate ligands. Critical evaluations of available data on the trivalent lanthanide complexes with acetate include publications by Smith and Martell [10], and Wood [11]. A summary of reported values is provided in Table 1.

Most measurements of stability quotients have been conducted under ambient conditions. The effect of temperature on solution complexation has recently received attention because of problems in the processing of high level radioactive waste and its disposal, and interest in the geochemistry of natural hydrothermal systems. Grenthe [12] reported enthalpy measurements for the formation of

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Table 1
Stability constants reported for acetate complexes with the rare earth elements

Metal	log β_1	log β_2	log β_3	Comments
Nd^{3+}	1.92±0.04	3.02±0.05	3.58±0.08	$T=25$°C, $I=2.0$ M, [10]
Nd^{3+}	2.76	4.54	nd	$T=25$°C, $I=0$, [21]
Nd^{3+}	2.62±0.2	4.63±0.2	nd	$T=25$°C, $I=0$, [17]
Nd^{3+}	1.9±0.2	3.2±0.2	nd	$T=20$°C, $I=2.2$ M, [18]
Eu^{3+}	1.94±0.13	nd	nd	This work

the 1:1 and 1:2 acetate complexes, which can be used to predict the effect of temperature on equilibria over small temperature ranges. Reported enthalpy values were small and positive, suggesting that complexation should increase with temperature. In the absence of experimental data over large temperature ranges, Shock and Koretsky [13] estimated stability constants for REE–acetate complexes using a modification of the Helgeson–Kirkham–Flowers (H-K-F) equation.

Recently, Deberdt et al. [14,15], Ding et al. [16], and Wood [17] have used indirect methods to report the effect of temperature on the 1:1 and 1:2 complexes with the REEs to temperatures in excess of 200°C. In experimental studies over such wide temperature ranges, significant increases in the stability constants are observed that are greater than that predicted by Shock and Koretsky. Also, data fitting required only consideration of the 1:1 and 1:2 complexes. Wruck et al. [18] used laser-induced photoacoustic spectroscopy to study the effect of temperature on the stability quotients of the 1:1 and 1:2 Nd–acetate complexes from 20–70°C, and observed increased formation of the 1:2 complex as temperature was increased. Their estimates of enthalpy for the 1:1 and 1:2 complexes using a van't Hoff extrapolation of the experimental stability constants were consistent with the enthalpy values reported by Grenthe [12].

The objective of this study was to directly investigate speciation in the Eu^{3+}–acetate system, and establish a methodology for estimating stability constants from Eu^{3+} luminescence spectra. Luminescence spectroscopy was used to observe changes in the speciation of the Eu^{3+}–acetate system over the temperature range of 8 to 59°C. Our results are consistent with recent studies of the temperature dependence for the trivalent–acetate system; in addition our spectroscopic data suggest that formation of the 1:3 complex is small yet significant. Most importantly, this study indicates that although overall complexation increases with temperature, changes in the distribution of the 1:1, 1:2, and 1:3 complexes for a given ligand:metal ratio are insignificant.

2. Materials and methods

2.1. Solution preparation, data collection, and processing

Stock solutions of europium (Eu^{3+}) and acetate (Ac^-) were prepared by dissolving europium oxide (Aldrich) and sodium acetate (Aldrich) in dilute $HClO_4$ (spectroscopic grade) with distilled deionized water. Temperature was controlled to ±0.5°C using a NESLAB RTE-111 circulating water bath. Solution pH was adjusted to ~5.5 with NaOH and $HClO_4$. pH was measured using an Accumet® Model 50 meter and combination pH electrode.

Luminescence spectra were obtained by exciting the $^7F_0 \rightarrow {}^5D_2$ transition of Eu^{3+} with the 465.8 nm line of an argon ion laser (Lexel 95). The sample luminescence was dispersed by a 1-m single monochromator (SPEX 1704) with a grating blazed at 500 nm (1200 grooves/mm) and detected with a cooled photomultiplier tube (Hamamatsu R928) and a photon counting system (Ortec 944).

For stability constant determinations, emission spectra of 0.1 M Eu^{3+} solutions in a 1 M $NaClO_4$ medium at variable Ac^- concentrations (0.025–0.7 M) were measured individually. In the variable temperature experiments, luminescence spectra of a solution containing 0.1 M Eu^{3+} and 0.3 M Ac^- (pH 5.5, $I=1$ M $NaClO_4$) were recorded at fixed temperature ranging from 8 to 59°C.

All data analysis, plotting, and fitting routines were completed using IGOR Pro©, version 3.14 by WaveMetrics.

2.2. Luminescence spectra

Temperature dependent $^5D_0 \rightarrow {}^7F_{0-2}$ luminescence spectra for Eu^{3+} in the presence of acetate are shown in Fig. 1.

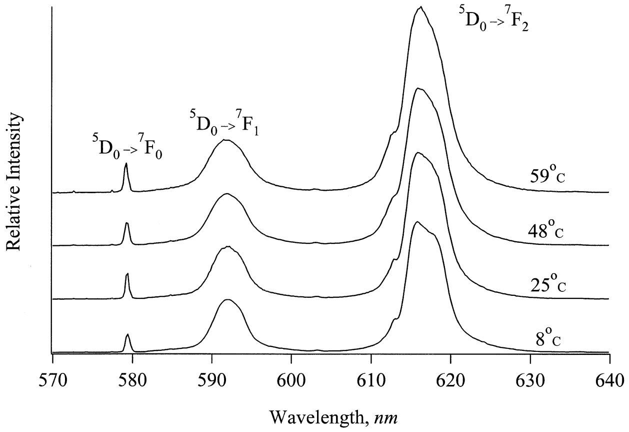

Fig. 1. $^5D_0 \rightarrow {}^7F_{0-2}$ luminescence transitions of Eu^{3+} in an aqueous acetate solution as a function of temperature range of 8 to 59°C. All spectra are normalized so that the $^5D_0 \rightarrow {}^7F_1$ peak intensity corresponds to one intensity unit.

The spectra represent a superposition of contributions from all Eu^{3+} species present in the solution. Each of the three emission bands is helpful in understanding the coordination environment of Eu^{3+}. The $^5D_0 \rightarrow {}^7F_1$ transition is a magnetic dipole transition, the energy and intensity of which are insensitive to changes in speciation. As a result, it is frequently used as an internal intensity standard for other transitions. The intensity of the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition is highly sensitive to distortions from spherical symmetry. Complexation reduces the spherical symmetry of the aquo Eu^{3+} ion and leads to a pronounced increase of the intensity of this transition.

The $^5D_0 \rightarrow {}^7F_0$ transition is non-degenerate and cannot be split by a crystal field. Its energy is also sensitive to the extent of nearest neighbor bonding covalency. The energy of the $^5D_0 \rightarrow {}^7F_0$ transition decreases with increasing covalency and exhibits a red shift with increasing coordination by a given ligand [19,20]. Consequently, every chemical species has a distinct $^5D_0 \rightarrow {}^7F_0$ transition energy and the number of peaks in the $^5D_0 \rightarrow {}^7F_0$ spectral region can be used to determine the number of species present in a mixture.

Fig. 2 shows high resolution luminescence spectra of the $^5D_0 \rightarrow {}^7F_0$ transition for 1.12:1 and 3.37:1 Ac^-:Eu^{3+} aqueous solutions. Spectra have been normalized to the $^5D_0 \rightarrow {}^7F_1$ intensity in each case, and are deconvoluted into components of equal bandwidth to identify the contributing species. The $^5D_0 \rightarrow {}^7F_0$ transition of the uncomplexed, aqueous Eu^{3+} ion is known to occur at 578.8 nm with an extremely low intensity [19]. Increasing Ac^- complexation is expected to shift the transition energy to progressively longer wavelengths. We accordingly assign the peaks at 579.2 nm, 579.45 nm and 579.75 nm to complexes of Eu^{3+} with one, two and three Ac^-, respectively, as indicated in Fig. 2. The weak feature on the short wavelength side of the spectrum is an artifact due to an extraneous plasma line from the laser excitation source. Upon increasing the ratio of Ac^-/Eu^{3+} from 1.12 to 3.37, the spectra clearly indicate the formation of higher order complexes.

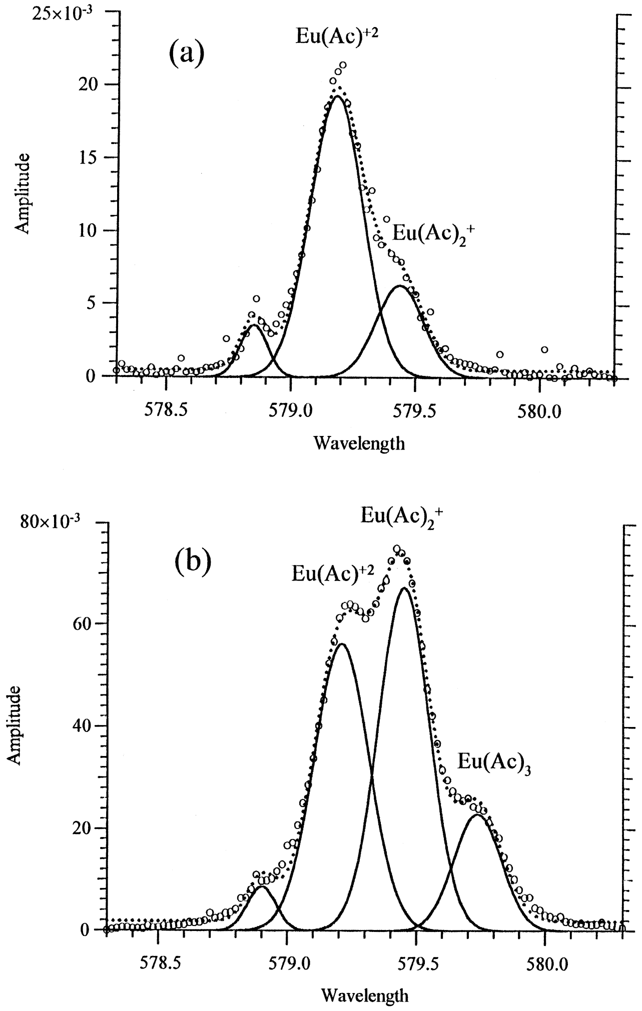

Fig. 2. High-resolution $^5D_0 \rightarrow {}^7F_0$ luminescence spectra of Eu^{3+} (0.1 M) in aqueous acetate solution at 25°C with (a) $[Ac^-] = 0.112$ M and (b) $[Ac^-] = 0.337$ M. Experimental data shown as open circles (○), results of deconvolution shown as solid lines (—), and calculated spectra based on peak deconvolution are indicated by a dotted line (····).

2.3. Spectroscopic estimation of stability quotients

We have completed spectral studies of Eu^{3+} in aqueous acetate solutions over a range of Ac^-:Eu^{3+} ratios extending up to 7:1. Changes in the relative intensity of the deconvoluted $^5D_0 \rightarrow {}^7F_0$ transition directly reflect relative changes in the distribution of individual Eu^{3+}: Ac^- complexes as the ligand:metal ratio is varied. Although quantum yields of the individual $^5D_0 \rightarrow {}^7F_0$ transitions for each complex species are unknown, we can use a proportional relationship for the transition intensity of the 1:1 Eu:Ac^- species to estimate a stability quotient at low Ac^-:Eu^{3+} ratios.

At low ligand:metal ratios, we assume that $Eu(Ac)^{2+}$ is the dominant species, and we restrict our consideration to the following equilibrium:

$$Eu^{3+} + Ac^- \leftrightarrow Eu(Ac)^{2+} \tag{1}$$

with stability quotient β_1 given by:

$$\beta_1 = \frac{[Eu(Ac)^{2+}]}{[Eu^{3+}][Ac^-]} = \frac{[Eu(Ac)^{2+}]}{\{[Eu^{3+}]_t - [Eu(Ac)^{2+}]\}\{[Ac^-]_t - [Eu(Ac)^{2+}]\}} \tag{2}$$

where the subscript t denotes the total concentration of a given component. If $[Eu(Ac)^{2+}] = \kappa I$, where I is the measured $^5D_0 \rightarrow {}^7F_0$ transition intensity for $Eu(Ac)^{2+}$ (i.e.

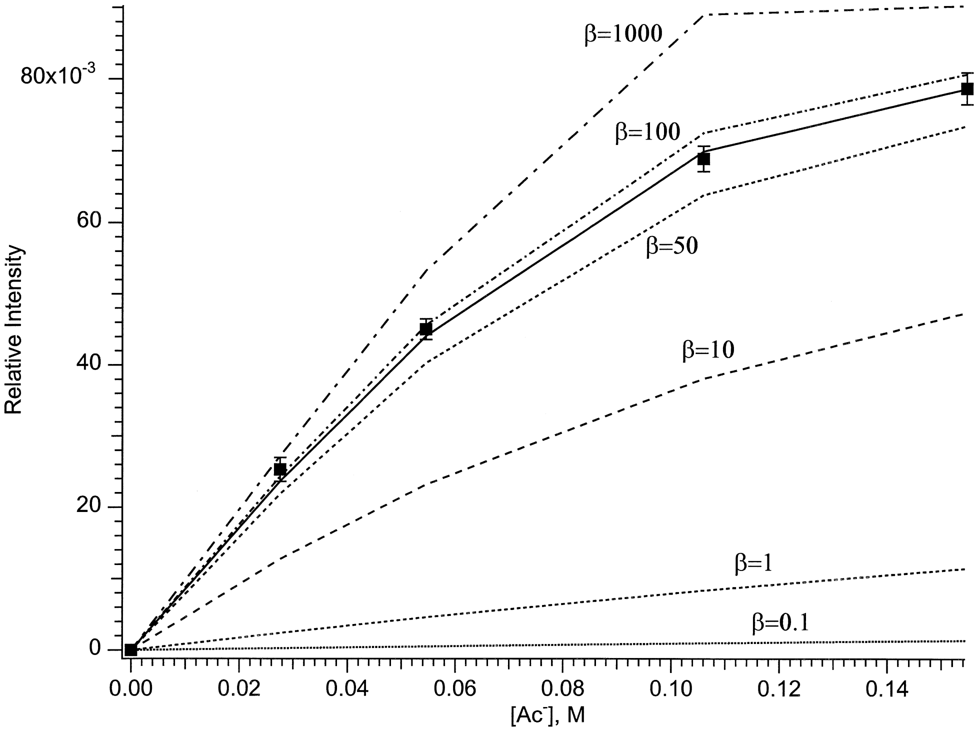

Fig. 3. Normalized $^5D_0 \rightarrow {}^7F_0$ intensity of $Eu(Ac)^{2+}$ as a function of $[Ac^-]$. $[Eu]_t = 0.1$ M. Dashed curves depict Eq. (4) for various values of β_1 using an estimated value of κ (see text for more detail).

the 579.2 nm feature shown in Fig. 2) and κ is a proportionality constant, then:

$$\beta_1 = \frac{\kappa I}{\{[Eu^{3+}]_t - \kappa I\}\{[Ac^-]_t - \kappa I\}} \tag{3}$$

which can be solved to obtain I:

$$I = \frac{Q - \sqrt{Q^2 - 4[Eu^{3+}]_t[Ac^-]_t\beta_1^2}}{2\kappa\beta_1} \tag{4}$$

where:

$$Q = \beta_1[Eu^{3+}]_t + \beta_1[Ac^-]_t + 1. \tag{5}$$

Eq. (4) was fit to changes in the $^5D_0 \rightarrow {}^7F_0$ transition intensity for $Eu(Ac)^{2+}$ as a function of initial Ac^- concentration, as shown in Fig. 3.

3. Results and discussion

3.1. Stability quotient determination

In a pH 5.5 solution of Eu^{3+}, increasing the acetate concentration from 0 to 0.7 M resulted in a significant increase in the intensity of the $^5D_0 \rightarrow {}^7F_2$ hypersensitive transition (data not shown), as well as an overall shift in the $^5D_0 \rightarrow {}^7F_0$ transition to longer wavelengths (Fig. 2). In addition, changes in the shape of the $^5D_0 \rightarrow {}^7F_0$ transition as Ac^- was increased suggested the formation of higher order acetate complexes. Using the methodology described above, an estimate of 87.1 ± 0.13 ($\kappa = 0.1411$) was obtained for β_1, consistent with values reported by others (Table 1). Perhaps this result is fortuitous since the quantum yields of the individual species are unknown. Once this problem is resolved, however, we are confident that our method for estimating stability constants will allow estimation of complexation constants for all species present.

3.2. Temperature effect on speciation

Fig. 1 shows the luminescence spectra obtained from a 1:3 ratio of Eu^{3+}–acetate as temperature was increased from 8 to 59°C. The relative intensities of the $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_0$ transitions increase with increasing temperatures, suggesting greater Eu^{3+}–acetate complexation. In addition, high-resolution spectra of $^5D_0 \rightarrow {}^7F_0$ transition from 8 to 59°C are shown in Fig. 4. Similar to the data analysis shown in Fig. 2, deconvolution of $^5D_0 \rightarrow {}^7F_0$ transition indicates that a small fraction of the 1:3 complex is present at all temperatures. Previous studies of the temperature dependence of acetate complexation for the trivalent f-elements using indirect methods have not considered the formation of the 1:3 complex. Although its contribution to overall complexation appears relatively small in the system studied herein, we anticipate that further evaluation of this transition will allow estimation of its contribution to total complexation.

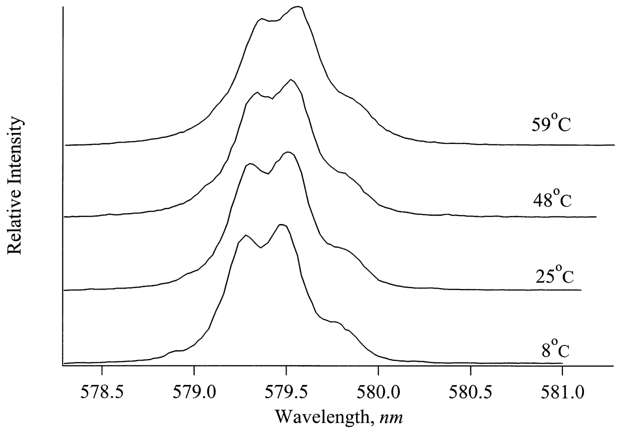

Fig. 4. High-resolution luminescence spectra of the $^5D_0 \rightarrow ^7F_0$ transition as a function of temperature with $[Ac^-] = 0.337$ M and $[Eu^{3+}] = 0.1$ M.

Interestingly, although intensities of the $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_0$ transitions increase with temperature, the overall peak shape for the $^5D_0 \rightarrow ^7F_0$ transition (Fig. 4) remains fairly constant as temperature is varied. This indicates that changes in species distributions over this temperature range are relatively small, suggesting that β_1, β_2, and β_3 increase proportionally with temperature. This observation is in contrast to reports on the variation of β_1 and β_2 as a function of temperature using potentiometry [14,16,17] where β_1 increased by 0.3 log units and β_2 remained constant within experimental uncertainty between 10 and 60°C. This apparent discrepancy is not large, and is likely the result of assumptions employed in the analysis of the potentiometric data. Our study demonstrates the utility of luminescence spectroscopy for constraining the interpretation of data obtained from indirect methods.

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References

[1] M. Scherer, H. Seitz, Chem. Geol. 28 (1980) 279.
[2] J.L. Banner, G.N. Hanson, W.J. Meyers, J. Sed. Petrol. 58 (1988) 415.
[3] J.L. Banner, G.N. Hanson, W.J. Meyers, Sedimentology and geochemistry of dolostones, in: V. Shulka, P.A. Baker (Eds.), Society Econ. Paleontolog. Mineral. Spec., Publ. No. 43, 1988, p. 97.
[4] S.L. Dorobek, R.H. Filby, Bull. Can. Petrol. Geol. 36 (1988) 202.
[5] S.A. Wood, P. van Middlesworth, P. Gibson, A. Ricketts, J. Alloys Comp. 249 (1997) 136.
[6] J.-C. Bunzli, G. Choppin, Lanthanide Probes in Life, Chemical, and Earth Sciences, Elsevier, New York, 1989.
[7] A.D. Sherry, J. Alloys Comp. 249 (1997) 153.
[8] C. Musikas, Chemical separation technologies and related methods of nuclear waste management, in: G.R. Choppin, M.K. Khankhasayev (Eds.), NATO Science Series, Environmental Security, Vol. 2/53, 1999, p. 99.
[9] The National Research Council, in: The Waste Isolation Pilot Plant, National Academy Press, 1996, p. 59.
[10] R.M. Smith, A.E. Martell, Critical Stability Constants, Plenum Press, New York, 1989.
[11] S.A. Wood, J. Geol. Eng. 34 (1993) 229.
[12] I. Grenthe, Acta Chem. Scand. 18 (1964) 283.
[13] E.L. Shock, C.M. Koretsky, Geochim. Cosmochim. Acta 57 (1993) 4899.
[14] S. Deberdt, S. Castet, J.-L. Dandurand, J.-C. Harrichoury, I. Louiset, Chem. Geol. 151 (1998) 349.
[15] S. Deberdt, S. Castet, J.-L. Dandurand, J.-C. Harrichoury, Chem. Geol., in press.
[16] R. Ding, C.H. Gammons, S.A. Wood, Water–rock interaction, in: G.B. Arehart, J.R. Hulston (Eds.), Proceedings of the 9th International Symposium on Water–Rock Interaction — WRI-9, Taupo, New Zealand, Mar. 30–Apr. 3, 1998, p. 831.
[17] S.A. Wood, D.J. Wesolowski, D.A. Palmer, Geochim. Cosmochim. Acta, in press.
[18] D.A. Wruck, P. Zhao, C.E.A. Palmer, R.J. Silva, J. Solution Chem. 26 (1997) 267.
[19] P.J. Lochhead, P.R. Wamsley, K.L. Bray, Inorg. Chem. 33 (1994) 2000.
[20] G.R. Choppin, Z.M. Wang, Inorg. Chem. 36 (1997) 249.
[21] D.W. Archer, C.B. Monk, J. Chem. Soc. (A) (1964) 3117–3122.