Inorganica Chimica Acta, 126 (1987) 131–135)

A Kinetic Investigation of Lanthanide(III) Complex Formation with Picolinic Acid

T. E. ERIKSEN§, I. GRENTHE≠ and I. PUIGDOMENECH*,≠

The Royal Institute of Technology, Departments of Nuclear and Inorganic Chemistry, S-100 44 Stockholm 70, Sweden

(Received June 7, 1986; revised September 1, 1986)

Abstract

The kinetics of formation of 1:1 lanthanide picolinate complexes has been studied at 20 °C in aqueous solutions containing 0.5 M tert-butanol using the radiation induced pH-jump technique. Forward rates of reaction have values in the range 4.9×10^8 M^{-1} s^{-1} for La^{3+} to 15×10^8 M^{-1} s^{-1} for Dy^{3+}. A dissociative interchange mechanism with a chelate ring closure as rate-controlling step is considered for the interpretation of the data. Rates of formation for the lanthanide picolinate complexes are compared with rates of formation of mixed complexes between picolinate and lanthanide–EDTA and with lanthanide systems containing ligands with carboxylate groups.

Introduction

The chemistry of lanthanide(III) complex formation in aqueous solution has been the subject of extensive research [1–3]. In order to achieve a clear understanding of the nature of the different contributions to complex formation (e.g., ligand geometry, size of central ion, solvent effects, etc.), kinetic data should be considered. Ultra-sound absorption studies of lanthanide sulfates and nitrates [4, 5] indicate a Diebler–Eigen [6] multistep dissociative mechanism with rates of water exchange, k_{ex}, in the range $0.6-8.0 \times 10^8$ s^{-1}, in fair agreement with k_{ex} values determined by oxygen-17 NMR (*i.e.*, 11.0×10^8 s^{-1} and 2.4×10^8 s^{-1} for Gd^{3+} and Ho^{3+}, respectively [7, 8]). For multidentate ligands like murexide, anthranilate and tartrate, the experimental values [4, 9, 10] for the overall forward rate of complex formation, $\vec{k}$, are about an order of magnitude lower than the values expected in terms of a Diebler–Eigen mechanism, a discrepancy that has been explained by the introduction of a chelation step [9, 10].

The present paper reports on a kinetic study of the complex formation between some lanthanide(III) ions and the picolinate ligand. The results are compared with data for other ligand systems and with the rates of complex formation between picolinate and lanthanide–EDTA complexes [11].

Experimental

Lanthanide(III) perchlorate solutions were prepared from the oxides (Nucor Corp., Res. Chem., 99.9%) and perchloric acid (Merck, p.a.). The metal content was determined volumetrically with EDTA [12]. A sodium perchlorate solution was prepared from sodium carbonate (Merck, p.a.) and perchloric acid. The salt concentration of this stock solution was found by weighing samples dried at 125 °C. The acid excess of all perchlorate solutions was determined using potentiometric titrations and Gran [13] plots. Picolinic acid (pyridine-2-carboxylic acid, Sigma), tert-butanol, carbon tetrachloride (all Merck, p.a.) and Methyl Red (*o*-carboxybenzene-azodimethyl-aniline, Merck) were used as received.

The proton concentration of the solutions used in the kinetic measurements was adjusted with diluted NaOH solutions (~5 mM, prepared by diluting clear 50% NaOH in nitrogen atmosphere).

Details on the radiation induced aqueous pH-jump technique are given elsewhere [14]. The pulse radiolysis set up with optical and conductometric detection systems have also been described previously [15, 16]. The solutions were irradiated with 0.2–1.5 μs long electron pulses from a 7 MeV microtron accelerator. The doses used, as determined by KSCN-dosimetry, were in the range 4–20 J kg^{-1} per pulse, giving rise to an increase in proton concentration of $1-5.5 \times 10^{-6}$ mol dm^{-3}. The time resolution of the optical measurements is limited by the electron pulse width. The recovery time of the conductivity detection system from overloading by spurious signals due to electron beam stopping by the electrodes is ~0.5 μs.

Rate constants of complex formation were obtained from kinetic data in the form $1/\tau$ *versus* F(c)

---

§Department of Nuclear Chemistry.

≠Department of Inorganic Chemistry.

*Author to whom correspondence should be addressed. This work is part of the *Ph.D. Thesis* of I.P.

0020-1693/87/$3.50

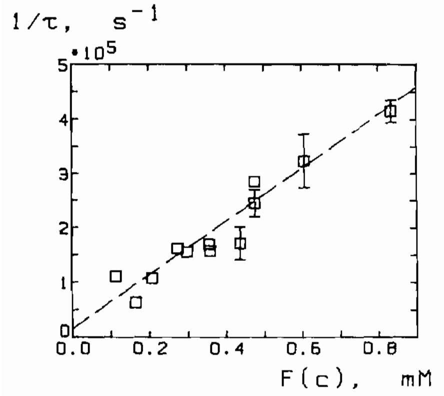


Fig. 1. Kinetic data for the lanthanum(III)–picolinate system (0.5 M tert-butanol, ~20 °C, conductometric monitoring). The dashed line corresponds to the rate constants given in Table I.

[17] plots (*c.f.* Fig. 1), assuming rapid pre-equilibration of the protolytic reactions of the ligand

$$\tau^{-1} = \vec{k}F(\mathrm{c}) + \overleftarrow{k} \tag{1}$$

$$F(\mathrm{c}) = \pi_{\mathrm{f}}\left[[\mathrm{L}^-] + [\mathrm{M}^{3+}]\,\frac{K_{\mathrm{a}}^{\mathrm{HL}} + [\mathrm{L}^-]}{K_{\mathrm{a}}^{\mathrm{HL}} + [\mathrm{H}^+] + [\mathrm{L}^-]}\right] \tag{2}$$

where L^- and M^{3+} denote the picolinate anion and lanthanide cation, respectively, [ ] denotes equilibrium concentrations, and $K_{\mathrm{a}}^{\mathrm{HL}}$ is the acid dissociation constant of the ligand. The activity coefficient product, π_{f}, was calculated from the ionic strength, I, using Davies equation

$$\log f_{\mathrm{i}} = -\mathrm{A}z_{\mathrm{i}}^2[\{\sqrt{I}/(1 + \mathrm{B}\mathring{a}\sqrt{I})\} - 0.3I] \tag{3}$$

where A = 0.56 (at 20 °C, in ~3.5% tert-butanol aqueous solutions with $\epsilon \approx 75$), B = 0.33 [18], and the ion size parameter $\mathring{a}$ was set equal to 5 Å. When the ionic strength varies during the relaxation experiment, factors of the general form

$$\left[1 + \frac{\partial \ln \pi_{\mathrm{f}}}{\partial \ln [i]}\right]$$

must be added to eqn. (2) (see for example p. 75 in ref. 19) in order to account for the change of the activity coefficients as the reactions proceed. However, numerical calculations show that for the aqueous solutions used in this study the partial derivatives can be neglected.

The range of concentrations studied was 0.1–3.0 mM for the lanthanides, and 0.05–1.5 mM for picolinic acid (in order to avoid the formation of $\mathrm{M(L)}_n^{3-n}$ complexes with $n > 1$, $[\mathrm{M}^{3+}]_{\mathrm{tot}} \geqslant 2 \times [\mathrm{L}^-]_{\mathrm{tot}}$ was used in all solutions). The pH values varied between 5.6 and 6.0. The experimental values of the relaxation times, τ, for reaction (5) were usually in the range 2–16 µs (*c.f.* Fig. 1), while for these aqueous solutions, the expected relaxation times of the fast H^+–ligand reactions are ~1 µs and could not be detected experimentally.

The kinetic data for each lanthanide cation were fitted to eqn. (1) with a standard weighted least squares procedure using the constraint

$$\log(\vec{k}/\overleftarrow{k}) = \log K_{\mathrm{ML}}$$

where the equilibrium constants, K_{ML}, were either determined potentiometrically (in 0.5 M tert-butanol and 0.1 M $\mathrm{NaClO_4}$ aqueous solutions at ~20 °C) or estimated from data available in the literature [20] (in 0.1 M $\mathrm{KNO_3}$ at 25 °C). For kinetic data collected with conductometric detection, the K_{ML} values were extrapolated to zero ionic strength using eqn. (3). Figure 1 displays the experimental data for the lanthanum(III) system together with the line corresponding to eqn. (1) with the rate constants given in Table I.

The system Gd^{3+}/picolinate was also studied in the presence of 0.1 M $\mathrm{NaClO_4}$ as inert electrolyte. The measurement of changes in conductivity to monitor the relaxation process is not possible at such high concentration levels with the pulsed dc technique used. The acid-base indicator Methyl Red was used to measure pH changes as a function of time. In that case the concentration variable F(c) in eqn. (1) is given by [17]

$$F(\mathrm{c}) = [\mathrm{L}^-] + \frac{[\mathrm{M}^{3+}]}{1 + \alpha} \tag{4}$$

TABLE I. Rate Constants for the Complex Formation between Lanthanide(III) Cations and Picolinate. Values obtained by the pulse radiolytic pH-jump method at ~20 °C, and 0.5 M tert-butanol

Metal cation	Detection system and ionic strength	$(\vec{k} \pm \sigma) \times 10^{-8}$ $(\mathrm{M^{-1}\,s^{-1}})$	$(\overleftarrow{k} \pm \sigma) \times 10^{-4}$ $(\mathrm{s^{-1}})$	$\log K_{\mathrm{ML}}$
La^{3+}	Conduct. ($I \simeq 0$)	4.9 ± 0.6	1.5 ± 1.9	4.51
Nd^{3+}	Conduct. ($I \simeq 0$)	8.4 ± 1.9	1.3 ± 5.6	4.83
Gd^{3+}	Conduct. ($I \simeq 0$)	9.8 ± 2.4	1.0 ± 8	5.01
	Optical ($I = 0.1$)	5.3 ± 0.9	2.6 ± 3	4.30
Dy^{3+}	Conduct. ($I \simeq 0$)	14.9 ± 1.7	1.2 ± 1.9	5.11
Lu^{3+}	Conduct. ($I \simeq 0$)	7.6 ± 1.3	0.3 ± 2.8	5.36

$$\alpha = [H^+] \Bigg/ \left(K_a^{HL} + [L^-] \; \frac{K_a^{HI} + [H^+]}{K_a^{HI} + [H^+] + [Ind^-]} \right)$$

where Ind^- denotes the Methyl Red anion, and K_a^{HI} is the acid dissociation constant of the pH indicator.

The slower reaction

$$Gd^{3+} + Ind^- \rightleftharpoons Gd(Ind)^{2+}$$

contributed to the relaxation curves [14] which now describe the sum of two exponential functions. Both relaxation times could be determined (as described in pp. 146–147 of ref. 17). The slower relaxation times obtained had values expected from the rate constants of the $Gd(Ind)^{2+}$ reaction [14].

Equations (2) and (4) were evaluated with the HALTAFALL computer program [21, 22] (locally modified to include activity coefficient corrections according to eqn. (3)) from the known total concentrations, pH, and equilibrium constants corrected to the actual ionic strength.

Results and Discussion

The rate constants obtained for complex formation between lanthanide cations and picolinate are given in Table I. The salt effect on the $\vec{k}$ value for a 0.1 M ionic medium in the Gd^{3+}-picolinate system, calculated using eqn. (3), was found to be 0.24, which agrees, within the experimental uncertainty, with the experimental difference (*c.f.* Table I).

The observed kinetic parameters for the overall reaction

$$M^{3+} + Pic^- \underset{\overleftarrow{k}}{\overset{\vec{k}}{\rightleftharpoons}} M(Pic)^{2+} \qquad (5)$$

may be correlated [4, 5] to the stepwise Diebler–Eigen [6] mechanism

$$M(H_2O)_n{}^{3+} + Pic^- \underset{K_{os}}{\rightleftharpoons} [M(H_2O)_n(Pic)]^{2+}$$

$$[M(H_2O)_n(Pic)]^{2+} \underset{k_{43}}{\overset{k_{34}}{\rightleftharpoons}} M(H_2O)_{n-1}(Pic)^{2+} + H_2O \qquad (6)$$

with the relationship

$$\vec{k} = K_{os}k_{34}$$

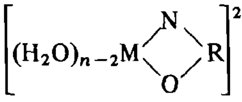
where K_{os} is the equilibrium constant for the fast outer-sphere association (which is usually estimated with either the Fuoss or Bjerrum equations [23, 24]). The rate constant for cation desolvation, k_{34}, should be equal to the rate constant for water exchange, k_{ex}.

TABLE II. Rate Constants for the Chelate Ring Closure/Opening of 1:1 Complexes between Lanthanide(III) Cations and Picolinate

Metal cation	$\log(K_{34}/M^{-1})$ $(I \to 0)$	$\log(k_{45}/s^{-1})$	$\log(k_{54}/s^{-1})$
La^{3+}	1.20	6.15 ± 0.05	4.2 ± 0.4
Nd^{3+}	1.41	6.2 ± 0.1	4.1 ± 0.8
Gd^{3+}	1.34	6.3 ± 0.1	4.0 ± 1
Dy^{3+}	1.21	6.62 ± 0.05	4.1 ± 0.5
Lu^{3+}	1.23	6.3 ± 0.1	3.5 ± 1

The calculated value for K_{os} using Fuoss [25] equation is 22 ± 4 M^{-1} at 20 °C (for metal–ligand distances of 5–12 Å), which together with the $\vec{k}$ values in Table I gives k_{ex} in the range 2.2–6.8 × 10^7 s^{-1}. However, k_{ex} values for lanthanide(III) cations are in the range 0.8–11 × 10^8 s^{-1} [4, 5, 7–9], and therefore the rate determining step must be the formation of a chelate ring

$$[(H_2O)_{n-1}M{-}O{-}R{-}N]^{2+} \underset{k_{54}}{\overset{k_{45}}{\rightleftharpoons}}$$



$$+ H_2O \qquad (7)$$

(here *O–R–N* represents the bidentate picolinate ligand). In this case we have

$$\vec{k} = K_{os}\frac{k_{34}k_{45}}{k_{43} + k_{45}} \; ; \quad \overleftarrow{k} = \frac{k_{43}k_{54}}{k_{43} + k_{45}}$$

and if the assumption is made that $k_{43} \gg k_{45}$, then

$$\vec{k} = K_{os}K_{34}k_{45} \; ; \quad \overleftarrow{k} = k_{54} \qquad (8)$$

Values for the equilibrium constant of coordination of the carboxylic group, K_{34}, were estimated from the lanthanide(III)–acetate formation constants [26], and the equilibrium constant for outer-sphere association between acetate and lanthanide cations. The rate constants obtained for ring opening/closure, k_{45} and k_{54}, are given in Table II. As values for $\log k_{43}$ are [9] about 7.8, the assumptions made in eqns. (8) are consistent with the results obtained.

The rate constant for ring closure will depend on the strength of the lanthanide–water bond after the carboxylate group is coordinated to the aqueous metal cation. An examination of the kinetic data available in the literature for ligands containing carboxylate groups, *i.e.*, tartrate [10], anthranilate [27] (for these two systems, k_{45} and k_{54} were calculated as outlined above), malonate [9] and dipicolinate [28], as well as for the mixed complex formation between lanthanide EDTA and picolinate [11] or 5-sulfosalicylate [29], reveals values of $\log k_{45}$ between ~8 and ~4 (for dipicolinate and tartrate, respectively). The values presented here for the picolinate system, *c.f.* Table II, are of the

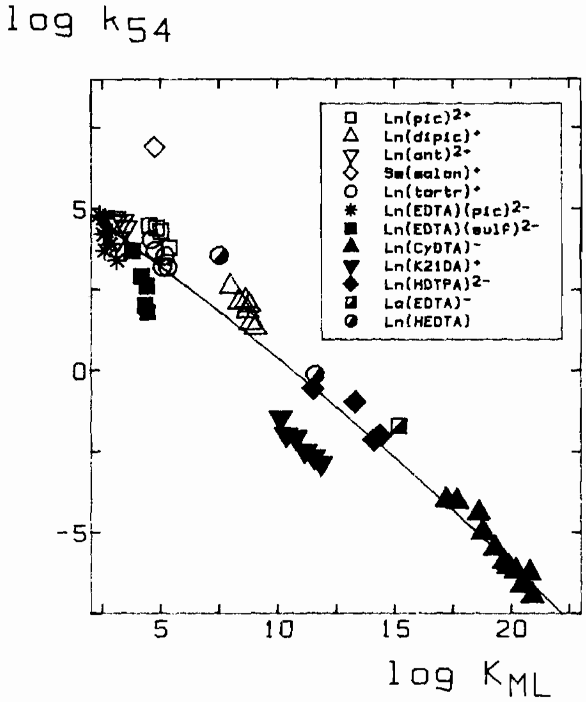


Fig. 2. Rate constants for the lanthanide chelate ring opening step, k_{54}, as a function of the formation equilibrium constant, K_{ML}, for several ligands with carboxylate groups. The line corresponds to eqn. (9) with $W^r = -39$ kJ/mol, $\Delta G_0{}^{\ddagger} = +79$ kJ/mol and $k_{54} = (kT/h)\exp(-\Delta G^{\ddagger}/RT)$.

same order of magnitude as those for malonate and anthranilate, as well as those for the mixed complexes formed between lanthanide EDTA and picolinate.

On the other hand, the rate of chelate ring opening is more affected by the strength of the bond between the lanthanide cation and the second coordinating group of the ligand. Figure 2 shows a survey of chelate ring opening rate constants for ligands containing carboxylate groups. Data for cyclohexylenediaminetetraacetate (CyDTA) [30, 31], 1,7-diaza-4,10,13-trioxacyclopentadecane-N,N'-diacetate (K-21DA) [32, 33], diethylenetriaminepentaacetate (DTPA) [34, 35] and ethylenediaminetetraacetate (EDTA) [36] are also included. As seen, with the notable exception of the malonate system, values of log k_{54} generally decrease with increasing strength of the metal–ligand bond as expressed by log K_{ML}, with a 'Brønsted' slope [37] of ~0.6, indicating that for the chelate ring opening reaction (7) there is some degree of bond formation to the entering water molecule in the transition state (a fact that is not in contradiction with a dissociative interchange mechanism for reaction (6)). Using a modified Marcus equation [37, 38]

$$\Delta G^{\ddagger} = W^r + \Delta G_0{}^{\ddagger}\left(1 + \frac{\Delta G}{4\Delta G_0{}^{\ddagger}}\right)^2 \qquad (9)$$

with the data in Fig. 2, we obtain values of $W^r = -39 \pm 30$ kJ/mol and $\Delta G_0{}^{\ddagger} = 79 \pm 30$ kJ/mol (where W^r is the energy required to bring the reactants together in the precursor configuration (including solvation energies) and $\Delta G_0{}^{\ddagger}$ is the intrinsic energy barrier (the free energy of activation when the free energy change at equilibrium, ΔG, is zero)). It must be noted, however, that eqn. (9) is deduced [37] assuming both that $W^r = W^p$ (where W^p is the energy required to make the successor configuration from the final products [37]) and that W^r and $\Delta G_0{}^{\ddagger}$ are constant, which might not necessarily be true for all cases shown in Fig. 2. As expected from considering reaction (7), the W^r term is small as compared with the intrinsic energy barrier.

The discrepancy of the samarium malonate data from the general trend in Fig. 2 might be real or an artifact resulting from an erroneous value of the equilibrium constant, as the K_{ML} used in the calculations for that system [9] is not quite in agreement with more recent thermodynamic data [39]. The formation of acid complexes [40] of type $M(HL)^{2+}$ at $\log[H^+] \geqslant -3$ might also have influenced the malonate study. It has already been shown [10, 30] that for a given ligand, $\bar{k}$ decreases with the inverse of the lanthanide ionic radii, *i.e.*, it decreases with the strength of the predominantly ionic metal–ligand bond.

Supplementary Material

Tables of experimental relaxation times, τ, calculated $F(c)$ (*c.f.* eqns. (2) and (4)) and chemical compositions of each aqueous solution studied in this investigation, have been stored with the Editor-in-Chief in Padua.

Acknowledgement

The financial support of the Swedish Natural Science Research Council is gratefully acknowledged.

References

1 D. G. Karraker, *J. Chem. Ed.*, *47*, 424 (1970).
2 G. R. Choppin, *J. Less-Common Met.*, *100*, 141 (1984).
3 G. R. Choppin, *J. Less-Common Met.*, *112*, 193 (1985).
4 N. Purdie and M. M. Farrow, *Coord. Chem. Rev.*, *11*, 189 (1973).
5 D. W. Margerum, G. R. Cayley, D. C. Weatherburn and G. K. Pagenkopf, in E. A. Martell (ed.), Coordination Chemistry', Vol. 2, ACS Monograph 174, Am. Chem. Soc., Washington D.C., 1978, pp. 1–220.
6 H. Diebler and M. Eigen, *Z. Phys. Chem. (Frankfurt am Main)*, *20*, 229 (1959).
7 R. V. Southwood-Jones, W. L. Earl, K. E. Newman and A. E. Merbach, *J. Chem. Phys.*, *73*, 5909 (1980).

8 C. Cossy, L. Helm and A. E. Merbach, *Proc. International Rare Earth Conference*, Zürich, Switzerland, March 3–8 (1985).

9 M. M. Farrow and N. Purdie, *Inorg. Chem., 13*, 2111 (1974).

10 S. S. Yun and J. L. Bear, *J. Inorg. Nucl. Chem., 38*, 1041 (1976).

11 C. G. Ekström, L. Nilsson, I. A. Duncan and I. Grenthe, *Inorg. Chim. Acta, 40*, 91 (1980).

12 S. J. Lyle and Md. M. Rahman, *Talanta, 10*, 1177 (1963).

13 F. J. C. Rossotti and H. Rossotti, *J. Chem. Educ., 42*, 375 (1965).

14 T. E. Eriksen, I. Grenthe and I. Puigdomènech, *Inorg. Chim. Acta*, in press.

15 T. E. Eriksen, *Chem. Scripta, 7*, 193 (1975).

16 T. E. Eriksen, J. Lind and T. Reitberger, *Chem. Scripta, 10*, 5 (1976).

17 C. F. Bernasconi, 'Relaxation Kinetics', Academic Press, New York, 1976, pp. 32, 205–207.

18 H. C. Helgeson and D. H. Kirkham, *Am. J. Sci., 274*, 1199 (1974).

19 M. Eigen and L. De Maeyer, in G. G. Hammes (ed.), 'Techniques of Chemistry', Vol. VI, Part II, 3rd edn., Wiley-Interscience, New York, 1974, pp. 63–146.

20 J. E. Powell and J. W. Ingemanson, *Inorg. Chem., 7*, 2459 (1968).

21 R. Ekelund, L. G. Sillén and O. Wahlberg, *Acta Chem. Scand., 24*, 3073 (1970).

22 B. Warnqvist and N. Ingri, *Talanta, 18*, 457 (1971).

23 J. O'M. Bockris and A. K. N. Reddy, 'Modern Electrochemistry', Vol. 1, Plenum, New York, 1977, pp. 251–265.

24 J. E. Prue, *J. Chem. Educ., 46*, 12 (1969).

25 R. M. Fuoss, *J. Am. Chem. Soc., 80*, 5059 (1958).

26 R. S. Kolat and J. E. Powell, *Inorg. Chem., 1*, 293 (1962).

27 H. B. Silber, R. D. Farina and J. H. Swinehart, *Inorg. Chem., 8*, 819 (1969).

28 C. G. Ekström, 'Kinetisk Undersokning av Lantanoidernas Dipikolinatkomplex', Thesis, University of Lund, Lund, Sweden, 1978.

29 C. G. Ekström, L. Nilsson and I. Grenthe, *Inorg. Chim. Acta, 48*, 145 (1981).

30 G. A. Nyssen and D. W. Mergerum, *Inorg. Chem., 9*, 1814 (1970).

31 T. Moeller and T. M. Hseu, *J. Inorg. Nucl. Chem., 24*, 1635 (1962).

32 C. A. Chang, V. O. Ochaya and V. C. Sekhar, *J. Chem. Soc., Chem. Commun.*, 1724 (1985).

33 V. C. Sekhar and C. A. Chang, *Inorg. Chem., 25*, 2061 (1986).

34 E. Brücher and G. Laurenczy, *J. Inorg. Nucl. Chem., 43*, 2089 (1981).

35 T. Moeller and L. C. Thompson, *J. Inorg. Nucl. Chem., 24*, 499 (1962).

36 T. Ryhl, *Acta Chem. Scand., 26*, 3955 (1972).

37 M. M. Kreevoy and D. G. Truhlar, in C. F. Bernasconi (ed.), 'Techniques of Chemistry', Vol. VI, Part I, 4th edn., Wiley-Interscience, New York, 1986, pp. 13–95.

38 A. O. Cohen and R. A. Marcus, *J. Phys. Chem., 72*, 4249 (1968).

39 G. Degischer and G. R. Choppin, *J. Inorg. Nucl. Chem., 34*, 2823 (1972).

40 I. Dellien and I. Grenthe, *Acta Chem. Scand., 25*, 1387 (1971).