The small variations observed between the two complexes are probably due to experimental uncertainties and variations in τ_r and outer-sphere contributions.

For Gd(HEDTA), R_1 at pH 10 is unchanged from those of pH 8 and 9, while the q value has decreased to 1. The possibilities are as follows: (1) the concentration difference between Tb (10 mM) and Gd (0.2–5 mM) studies favors oligomerization in the Tb case; (2) τ_r increased on oligomerization, raising R_1 as q decreased; (3) an oligomer formed that allowed several Gd(III) ions to relax some or all of the protons simultaneously, resulting in an effective increase in the magnetic moment experienced by the protons. A separate study concluded that points 2 and 3 were the most likely possibilities.[22]

The relaxivity of Gd(TTHA) decreases with increasing pH and reaches a minimum value of 2.1 (mM s)$^{-1}$ at pH 8.0. This evidence and the results from fluorescence water counting and energy transfer indicate that Gd(III) is fully coordinated by the TTHA ligand after pH 8.0 to form monomeric species. A plot of R_1 vs q values for all complexes in monomeric forms gives a straight line with an intercept of 2.2 ± 0.1 (mM s)$^{-1}$, a slope of 1.6 ± 0.1 (mM s)$^{-1}$ per water, and a correlation coefficient of 0.97 (Figure 5). The intercept value is very similar to the limiting relaxivity value of Gd(TTHA)$^{3+}$, which represents the outer-sphere relaxivity for Gd(III) complexes of amino carboxylate ligands (without the TTHA data, the intercept of the linear regression analysis was 2.2 ± 0.2). The value of the slope is the estimated contribution of each inner-sphere water to R_1 for this series of simple mononuclear Gd(III) amino carboxylate complexes.

It is noted that the luminescence temperature (27 °C) and relaxivity temperature (40 °C) were different. However, variation of temperature only changes the q number and relaxivity to a small extent. The overall linear relationship between q and R_1 still exists.

Contribution from the Chemistry Department, San Jose State University, San Jose, California 95192,
and Department of Inorganic and Analytical Chemistry, A. Jozsef University, POB 440, H-6701 Szeged, Hungary

Equilibrium Studies of Lanthanide Nitrate Complexation in Aqueous Methanol

Herbert B. Silber,*[†] Roya Bakhshandehfar,[†] Larry A. Contreras,[†] Ferenc Gaizer,[‡] Mark Gonsalves,[†] and Sabariah Ismail[†]

Received March 28, 1990

The complexation between Er(III) and Nd(III) with nitrate and perchlorate was studied by UV–vis spectroscopy. In water, no complexes are detected between the lanthanide cations and perchlorate. The addition of methanol causes complexation only between Er(III) and perchlorate. Under the same conditions, the stoichiometries of the nitrate complexes in water are different for Nd(III) and Er(III) compared to Eu(III). These differences continue as a function of solvent composition even at low water mole fractions where Eu(III) and Er(III) form complexes up to the tris complex, whereas Nd(III) only forms complexes up to the bis complex. Equilibrium constants and complexation thermodynamics are presented and used in discussing differences within the lanthanide series.

Introduction

Because of the increased utility of lanthanide ions as spectroscopic probes in biological systems, more detailed knowledge of the coordination behavior of these ions with simple counterions is needed. It is commonly believed that the chemistry of the lanthanide ions in solution is predominantly electrostatic in nature, with the chemical and physical properties determined by size differences within the series. In addition, there has been a long-standing debate about whether or not a coordination number change occurs within the lanthanide series.[1] Recent probes of the structures and reactivities of the inner solvation shells of the lanthanide cations have involved techniques such as FT-IR and FT-NMR spectroscopy.[2–4]

Ultrasonic relaxation investigations of the lanthanide nitrates in water not only can measure the extent of the interaction within the lanthanide series but also can separate the absorption into contributions from both inner- and outer-sphere complexes.[5] Repeating these measurements in aqueous methanol solutions has provided even more insights into not only the interactions between the lanthanide ion and the ligand but also the effect of solvent upon the complexation process.[6] Evidence that the ultrasonic data can predict some of the chemistry of the lanthanides in aqueous methanol comes from an examination of the data for the complexation between Er(III) and Cl^-.[7] Using the variation of the relaxation frequency for inner-sphere complexation, we predicted that below a water mole fraction, X, of 0.07 the $ErCl_2^+$ species is formed. Hamze et al. investigated the corresponding Nd(III) complex in 5% water by volume and found only the mono complex with Cl^-.[8] However, at 0% water, both $NdCl^{2+}$ and $NdCl_2^+$ were found. Although differences in the ultrasonic data were observed between Nd(III), Eu(III), and Er(III) with nitrate, in the absence of complete equilibrium studies it is impossible to give a detailed explanation for the ultrasonic differences. Hence, we initiated the equilibrium studies on lanthanide nitrate systems.

Complexation between lanthanide ions and nitrate in water has been detected by techniques such as difference spectroscopy,[9,10] UV–vis absorption spectroscopy,[11,12] solvent extraction,[13–15] lu-

---

[†] San Jose State University.
[‡] A. Jozsef University.

(1) See, for example: Spedding F. H.; Pikal, M. I.; Ayers, B. O. *J. Phys. Chem.* **1966**, *70*, 2430.
(2) Cossy, C.; Helm, L.; Meier, P.; Merbach, A. E. *Inorg. Chem.* **1988**, *27*, 1973.
(3) Fratiello, A.; Kubo-Anderson, V.; Bolinger, T.; Cordero, C.; DeMerit, B.; Flores, T.; Matejka, D.; Perrigan, R. D. *J. Solution Chem.* **1989**, *18*, 313.
(4) Fratiello, A.; Kubo-Anderson, V.; Bolinger, T.; Cordero, C.; Demerit, B.; Flores, T.; Matejka, D.; Perrigan, R. D. *J. Magn. Reson.* **1989**, *83* 358.
(5) Silber, H. B.; Scheinin, N.; Atkinson, G.; Grecsek, J. J. *J. Chem. Soc. Faraday Trans. I* **1972**, *68* 1200.
(6) Silber, H. B.; Campbell, R. L. *J. Less-Common Met.* **1989**, *149*, 265. Reprinted in *Rare Earths 1988*; Silber H. B., Morss, L. R., DeLong, L. E., Eds.; Elsevier Sequoia S.A.: Lausanne, Switzerland, 1989; Vol. II, pp 265–269.
(7) Reidler, J.; Silber, H. B. *J. Phys. Chem.* **1974**, *78*, 424.
(8) Hamze, M.; Meullemeestre, J.; Schwing, M. J.; Vierling, F. *J. Less-Common Met.* **1986**, *118*, 153.
(9) Coward, N. A.; Kiser, R. W. *J. Phys. Chem.* **1966**, *70*, 213.
(10) Anagnostopoulos, A.; Sakellaridis, P. O. *J. Inorg. Nucl. Chem.* **1970**, *32*, 1740.
(11) Silber, H. B.; Gaizer, F.; Pham, T.; Strozier, M. *J. Less-Common Met.* **1986**, *126*, 315.
(12) Silber, H. B.; Strozier, M. S. *Inorg. Chim. Acta.* **1987**, *128*, 267.
(13) Choppin, G. R.; Strazik, W. F. *Inorg. Chem.* **1965**, *4*, 1250.
(14) Henrie, D. E.; Fellows, R. L.; Choppin, G. R. *Coord. Chem. Rev.* **1976**, *18*, 199.
(15) Peppard, D. F.; Mason, G. W.; Hucher, I. *J. Inorg. Nucl. Chem.* **1962**, *24*, 881.

0020-1669/90/1329-4473$02.50/0 © 1990 American Chemical Society

minescence,[16] and ultrasound.[17] Although differences in the magnitudes of the equilibrium constants exist in water, considering the variety of techniques, conditions and assumptions, the results are all within a relatively narrow range. Only for Eu was there a second complex found.

Fewer studies have been carried out in aqueous organic solvents.[8,12] During the course of this investigation, Majdan and Sadowski published a spectroscopic study in 90% methanol, finding two complexes: $Nd(MeOH)_xNO_3^{2+}$ with $K_1 = 3.6$ and $Nd(MeOH)_x(NO_3)_2^+$ with $K_2 = 1$.[18] Details were not given about the temperatures, extinction coefficients, or method of the data fit.

Experimental Section

The lanthanide solutions were made and standardized from Er_2O_3 (Rhone-Poulenc) and Nd_2O_3 (Molycorp). The Gilford Model 2600 UV-vis spectrometer was used as described previously.[12] Because the lanthanide absorption peaks are so sharp, it was critical to calibrate the wavelengths daily by using the internal holmium filter. For each lanthanide system, difference spectra between the lanthanide perchlorate solution and solutions that had the same lanthanide salt concentration but also had added nitrate were first run in order to establish which peaks, if any, responded to the addition of nitrate. Beer's law plots were carried out on the $Er(ClO_4)_3$ and the $Nd(ClO_4)_3$ solutions to investigate its validity at each wavelength. For $Nd(ClO_4)_3$ at each temperature, wavelength, and solvent composition, Beer's law was valid, but deviations from Beer's law were found for $Er(ClO_4)_3$. As more methanol was added, the deviations occurred at lower $Er(ClO_4)_3$ concentrations, consistent with increased complexation as the water content decreases. Since Er(III) forms a perchlorate complex, the determination of the nitrate equilibrium constants is more complicated than in the case of Nd. Because no perchlorate complexation is detected for the $Nd(ClO_4)_3$ solutions, mole ratio plots could be used to determine the ratio of nitrate to metal in the complex, but this cannot work for the Er(III) case. The wavelengths used for $Er(ClO_4)_3$ were 378.3, 379.3, and 380.3 nm, that for $Er(NO_3)_3$ was 379.3 nm, and those for Nd(III) were 521.2, 521.7, 522.2, 574.8, 575.3, and 575.8 nm. The use of wavelengths at and near the peaks improved the reliability of the data, especially since the peaks were so sharp. The ionic strength was maintained at 3.0 M with perchlorate.

We use a PC program developed by Gaizer[19-21] to determine the extent of complexation and the equilibrium constants using multiple wavelengths. Recently we have modified this program using the program Quick Basic to make it more user friendly and to speed up the calculation time. The program assumes the existence of one or more complexes of the type M_pL_q, with the stability constants defined as

$$\beta = [M_pL_q]/[M]^p[L]^q$$

At each wavelength it is assumed that Beer's law is valid for each chemical species and that the absorbances are additive. At the wavelengths used in this study, neither perchlorate nor nitrate absorbed. Although this program is most efficient when the free metal and the complexes absorb at different wavelengths, it can be used for the lanthanides where all species absorb at the same wavelengths, but there is a small difference in the extinction coefficients. To use this program, the stability constants and the extinction coefficients for each species are estimated and the program minimizes the square of the residuals, calculating the best β values and extinction coefficients.

Results and Discussion

Mole ratio plots provide an estimate of the complex stoichiometries, which are confirmed by using the Gaizer program, which does not give good minimums if the incorrect species are postulated to be present. Mole ratio plots, ultrasonics,[22,23] Benesi-Hildebrand plots,[24] and the Gaizer program all provide evidence for the existence of weak complexes between Er(III) and perchlorate in aqueous methanol and at a water mole fraction, X, of 0.13 $\log \beta_1 = 2.39 \pm 0.72$ and $\log \beta_2 = 2.23 \pm 1.30$ at 25 °C. At $X = 0.20$, two complexes are present, but only the $\log \beta_2$ is estimated to be -4 ± 0.1. Above $X = 0.20$, the interaction is minor and no complex exists in water.

Table I. Stability Constants for $Nd(NO_3)_3$ as a Function of Solvent and Temperature at $I = 3.0$[a]

	15 °C	20 °C	25 °C	37 °C
$X = 0.90$				
K_1	10.09 ± 1.2	16.23 ± 1.3	20.67 ± 1.2	28.86 ± 1.2
$X = 0.77$				
K_1	22.29 ± 1.2	27.08 ± 1.2	34.32 ± 1.2	63.10 ± 1.2
$X = 0.60$				
K_1	23.17 ± 1.2	30.09 ± 1.2	45.98 ± 1.3	90.16 ± 1.2
$X = 0.36$				
K_1	25.53 ± 1.7	39.28 ± 1.6	62.34 ± 1.4	166.7 ± 1.5
K_2	7.33 ± 1.4	6.49 ± 1.3	4.12 ± 1.1	2.09 ± 1.1
$X = 0.20$				
K_1	27.26 ± 1.5	45.12 ± 1.3	72.43 ± 1.8	176.3 ± 1.5
K_2	7.55 ± 1.0	7.03 ± 1.1	5.07 ± 1.1	2.48 ± 1.5
$X = 0.04$				
K_1	31.72 ± 1.3	54.85 ± 2.0	83.12 ± 1.4	210.9 ± 1.5
K_2	8.13 ± 1.0	7.94 ± 1.0	5.56 ± 1.0	3.75 ± 1.0

[a] X is the water mole fraction.

Table II. Stability Constants for $Er(NO_3)_3$ as a Function of Solvent and Temperature at $I = 3.0$[a]

	15 °C	20 °C	25 °C	37 °C
$X = 1.00$[19]				
K_1	12.59 ± 0.16	10.10 ± 0.14	8.65 ± 0.14	6.63 ± 0.12
$X = 0.89$				
K_1	18.62 ± 2.52	15.85 ± 2.09	14.13 ± 1.81	11.20 ± 1.46
K_2	2.04 ± 0.33	2.57 ± 0.32	3.02 ± 0.42	3.98 ± 0.61
$X = 0.77$				
K_1	51.17 ± 11.83	48.26 ± 12.63	46.35 ± 11.08	45.50 ± 11.80
K_2	2.09 ± 0.42	2.60 ± 0.53	3.02 ± 0.58	3.98 ± 0.77
$X = 0.53$				
K_1	52.26 ± 8.11	49.66 ± 8.56	46.00 ± 7.49	44.86 ± 9.15
K_2	4.56 ± 0.81	4.98 ± 1.03	5.65 ± 1.33	8.19 ± 1.81
$X = 0.36$ (with ClO_4^-)				
K_1	82.22 ± 18.70	79.98 ± 9.83	79.43 ± 13.04	72.78 ± 15.05
K_2	13.34 ± 1.25	15.17 ± 2.03	18.16 ± 1.87	23.10 ± 0.89
K_3	3.04 ± 0.42	2.79 ± 0.49	2.72 ± 0.32	2.44 ± 0.33
$X = 0.36$				
K_1	85.13 ± 9.84	83.18 ± 12.13	82.22 ± 12.49	75.86 ± 14.36
K_2	13.46 ± 1.53	15.49 ± 2.30	18.32 ± 2.87	22.75 ± 4.77
K_3	2.99 ± 0.38	2.69 ± 0.49	2.76 ± 0.48	2.42 ± 0.65
$X = 0.13$ (with ClO_4^-)				
K_1	125.03 ± 16.81	118.85 ± 15.98	110.15 ± 15.05	100.23 ± 13.52
K_2	28.45 ± 3.43	35.00 ± 4.73	40.83 ± 5.59	50.00 ± 6.87
K_3	18.45 ± 1.71	13.80 ± 1.27	12.27 ± 1.40	7.87 ± 1.30

[a] X is the water mole fraction.

In water, only Eu(III) forms both the 1:1 and 1:2 complexes with nitrate. The addition of methanol increases the extent of complexation for both Eu(III) and Er(III), where the ions form the tris and bis complexes, respectively. At 80% methanol and higher, Er(III) also forms the tris complex. In 93.8% methanol, Nd(III) forms the bis complex. The Gaizer program is most efficient when the metal ion remains constant and the ligand and inert electrolyte are changed. This was impossible for the perchlorate study, but can be carried out when a metal-perchlorate complex does not form. Because Er(III) complexes with per-

---

(16) Breen, P. J.; Horrocks, W. DeW. *Inorg. Chem.* **1983**, *22*, 536.
(17) Garnsey, R.; Ebdon, D. W. *J. Am. Chem. Soc.* **1969**, *91*, 50.
(18) Majdan, M.; Sadowski, P. *Monatsh. Chem.* **1988**, *119*, 295.
(19) Gaizer, F.; Mate, M. *Acta Chim. Acad. Sci. Hung.* **1980**, *103*, 335, 397.
(20) Gaizer, F.; Puskas, A. *Talanta* **1981**, *28*, 565, 925.
(21) Gaizer, F.; Silber, H. B. Submitted for publication.
(22) Silber, H. B. *FEBS Lett.* **1974**, *41*, 303.
(23) Silber H. B.; Pezzica, A. *J. Inorg. Nucl. Chem.* **1976**, *38*, 2053.
(24) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703.
(25) Silber, H. B.; Pham, T. N. In *New Frontiers in Rare Earth Science and Applications*; Guangxian, X., Jimei, X. Eds.; Science Press: Beijing, China, 1985; Vol. I.

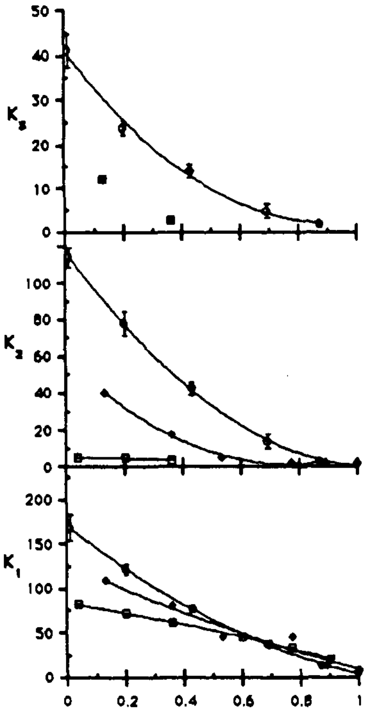

Figure 1. Variation of the association constants in aqueous methanol at 25 °C. Key: (○) Eu(III); (◇) Er(III); (□) Nd(III).

chlorate, we used $NaNO_3$ or KNO_3 as the inert electrolyte to maintain the ionic strength. Using these methods allowed us to calculate the equilibrium constants shown in Tables I and II.

In order to determine if the weak complex with perchlorate would effect the calculation of the stronger nitrate complexes, we repeated one set of Er measurements, using a perchlorate medium and neglecting the effect of complexation, and these are listed in Table II. At $X = 0.36$ and all four temperatures, the effect of perchlorate complexation is negligible since all of the respective equilibrium constants are each within experimental error of each other in the presence or absence of perchlorate.

We repeated the Majdan and Sadowski[18] conditions in 90% methanol and calculated a best fit of the data using the Gaizer program, followed by an alternate calculation using the Majdan and Sadowski β values.[18] The program was allowed to refine the extinction coefficients and to minimize. The standard deviation of the fit was better for our values of the two association constants. Although this does not prove that our results are the correct ones, it is consistent with that hypothesis.

The variations of equilibrium constants with solvent at 25° C are shown in Figure 1. For all three systems, the equilibrium constants increase in a regular fashion as the solvent dielectric constant decreases, a feature not found in the ultrasonic absorption studies where all three systems had a maximum in the sound absorption with solvent composition, attributed to a coordination number change accompanying complexation. Analyzing both the equilibrium and ultrasonic data, it is possible to predict which complexation step causes the coordination number change. For Er(III), the ultrasonic maximum occurs about $X = 0.4$, which is the solvent composition where the tris complex starts to appear; hence, the addition of the third complex to the inner shell of Er(III) triggers a reduced coordination number change. For Nd(III), the coordination change occurs as the bis complex forms. The maximum for Eu(III) does not correspond to any change in complex stoichiometry, and the coordination number change for this cation occurs with all of the complexes.

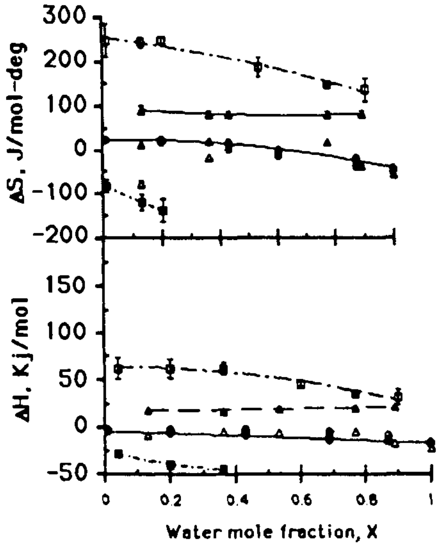

Figure 2. Complexation thermodynamics for the lanthanide nitrates as a function of solvent. Key: (○) Eu 1:1 complex; (●) Eu 1:2 complex; (⊕) Eu 1:3 complex; (□) Nd 1:1 complex; (■) Nd 1:2 complex; (△) Er 1:1 complex; (▲) Er 1:2 complex; (■) Er 1:3 complex.

Figures 2 shows the enthalpy and entropy of complexation for all of the nitrate species. Within a small range, the results are the same for all of the Er(III) and the second Eu(III) complexes, but are clearly different for the first Eu(III) complex and all of the Nd(III) ones. Earlier ultrasonic studies of the complexation in water also show differences between Nd(III) and other lanthanides.[5,23] The major difference is in the extent of outer-sphere complexes present for Nd(III), which are absent for the other lanthanides. Hence, it should not be surprising that the results are different for Nd(III) compared to the other lanthanides. Although preliminary ultrasonic data for Eu(III) with nitrate has been reported, no analysis of the relative amounts of inner versus outer complexation was possible.[26] Hence, we cannot explain why the first complex for Eu(III) is also different from the others.

These equilibrium studies not only have demonstrated that, under the same reaction conditions, different chemistries can occur within the lanthanide series with a given ligand but also have demonstrated that the extent of inner- versus outer-sphere complexation also causes differences in the complexation thermodynamics. Using these data, we have also come up with an explanation of which complexes cause sufficient steric crowding in the inner solvation shell leading to a reduced coordination number.

Acknowledgment. We thank the National Institutes of Health for partial support of this work under Minority Biomedical Research Support (MBRS) Grant RR-08192 and Minority Access to Research Careers (MARC) Grant GM08253. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the Americal Chemical Society, for partial support of this research.

---

(26) Silber, H. B. *Inorg. Chim. Acta* **1987**, *139*, 33.