Journal of Alloys and Compounds, 207/208 (1994) 465–467
JALCOM 3069

Complexation of lanthanide ions by diethylenetriamine-*N*,*N*′,*N*″-penta-*β*-propionate

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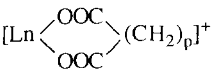
Abstract

The stability constants for the formation of the lanthanide chelates LnH_2DTPP^0 and LnH_3DTPP^+ (DTPP = diethylenetriamine-*N*,*N*′,*N*″-penta-*β*-propionate) have been measured in solutions of 0.50 M ($NaClO_4$) ionic strength by pH measurement. The similar stabilities of the two complexes indicate that both species involve similar binding sites of the ligand. The similarity in their entropy and enthalpy values also support such a model. Fluorescence data indicate that the primary coordination sphere of the Eu^{III} ion in both complexes contains 5.5 ± 0.5 water molecules compared to the value of 8.8 ± 0.5 for the free Eu^{III}(aq) ion. This is consistent with binding of the lanthanide ion *via* three donor sites of DTPP.

1. Introduction

An important question in lanthanide complexation is the effect of ring size on the thermodynamic changes for complexation by different classes of chelating ligands. In the homologous series of



$$[\mathrm{Ln}\langle{}^{\mathrm{OOC}}_{\mathrm{OOC}}\rangle(\mathrm{CH_2})_p]^+$$

(p = 0–4), as the size of the chelate ring (n) increases from 5 to 7, a sharp decrease in log β_{101} values results [1].
Further increases in ring size to $n = 8$ and 9 do not result in further decrease in log β_{101} below that for $n = 7$. Luminescence lifetime measurements of these Eu^{3+} complexes were used to determine the residual hydration of the Eu^{III} in the complexes [2]. The results indicated that malonate ($n = 6$) acts as bidentate ligand whereas the residual hydration in the succinate ($n = 7$), glutarate ($n = 8$) and adipate ($n = 9$) were interpreted as reflecting an equilibrium between mono- and bidentate ligation [2].

A decrease in stability with increased ring size is observed also in complexation by mixed donor ligands; *viz.* polyaminocarboxylates [3–6]. The values of log β_{101} for the formation of $LnENDPDA^-$ (ENDPDA = ethylenediamine-*N*,*N*′-diacetate-*N*,*N*′-di-*β*-propionate), $LnTMDTA^-$ (TMDTA = trimethylenediaminetetraacetate) and $LnTMEDTA^-$ (TMEDTA = tetramethylenediaminetetraacetate) were lower than those for complexation with ethylenediaminetetraacetate (EDTA) (in which $n = 5$ for all rings). This was attributed to the presence of two six-membered N–Ln–O rings in $LnENDPDA^-$, a six-membered N–Ln–N ring in $LnTMDTA^-$, and a seven-membered N–Ln–N ring in $LnTMEDTA^-$.

The present paper reports a study of a lanthanide aminopolycarboxylate system in which all N–Ln–O rings are six-membered. The ligand is diethylenetriamine-*N*,*N*′,*N*″-penta-*β*-propionate (DTPP).

2. Experimental details

Lanthanide perchlorate solutions were prepared and standardized as described previously [7]. A pure, recrystallized sample of DTPP was provided by C. Musikas (CEA, France). The protonation constants were determined by direct pH titration of the ligand acid (*ca.* 2–3 mM) with standard base. The pH range covered allowed for the accurate measurement of only the first seven protonation constants. The stability constants were determined by titrating equimolar mixtures of metal + ligand using sodium hydroxide (0.05 M) as the titrant. Metal hydroxide formation occurred at values of pH > 7; *i.e.* after the addition of three equivalents of base. A Corning 130 pH meter fitted with a combination glass-calomel electrode was used. All solutions were thermostated at 25.0 °C and had a final ionic strength of 0.5 M ($NaClO_4$). Correction for the hydrogen ion activity was made using an activity coefficient of 1.585 for H^+ [3].

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SSDI 0925-8388(93)03069-U

The heats of protonation of the free ligand and the heats of complexation of the lanthanum, gadolinium, terbium and dysprosium ions were measured by calorimetric titration. The measurements were obtained using an adiabatic calorimeter designed in this laboratory [8] and interfaced to a PC [9] to perform all the routines of the stepwise calorimetric titration. The heats of dilution were obtained for each system by substituting 0.5 M $NaClO_4$ solution, first for the titrant, and subsequently for the titrand.

Fluorescence measurements were made with solutions in which the metal:ligand ratio was 1:1 and the pcH was *ca.* 5.3. A pulsed laser beam at 395 nm (energy = 3 mJ and pulse width in the nanosecond range) was used. The emission was analyzed by a LeCroy 6103 amplifier fitted with a Hamamatsu R955 photomultiplier tube and a LeCroy TR 8828C transient recorder. The whole system was interfaced to a PC computer through a LeCroy 8901A GPIB [2].

3. Results and discussion

The protonation constants of the DTPP anion were computed using the program Superquad on a VAX computer and the protonation thermodynamic parameters were obtained using the Delta-h program written in this laboratory. A summary of the results is given in Table 1. The first three equilibrium constants associated with nitrogen protonation are in close agreement with the analogous constants for DTPA. By contrast, $\log K_n$ values with $n > 4$ are significantly larger for DTPP than for DTPA. Lengthening of the chain between the nitrogen and the carboxylate reduces the effect of the nitrogen on the carboxylate basicity.

The hydrolysis of the lanthanides interfered sufficiently with the complexation with DTPP that all titrations had to be performed below pH 7. In the acid pH range, the species formed in significant concentrations were LnH_2DTPP^0 and LnH_3DTPP^+. The respective $K_{1(21)}$ and $K_{1(31)}$ constants associated with the reactions

$$Ln^{3+} + H_iDTPP^{i-5} \longleftrightarrow LnH_iDTPP^{i-2}$$

$$K_{1(i1)} = [LnH_iDTPP]/[Ln][H_iDTPP] \quad (i = 2 \text{ or } 3)$$

are shown in Table 2. The respective thermodynamic parameters for the complexation of lanthanum, gadolinium, terbium and dysprosium ions are listed in Table 3. Unfortunately, the formation of protonated complexes prevents comparison with the DTPA complexes for which analogous complexes are unprotonated.

TABLE 1. Thermodynamics of stepwise protonation of DTPP ($I = 0.50$ M ($NaClO_4$); $T = 298$ K)

n	$\log K_n$	$-\Delta H_n$ (kJ mol^{-1})	ΔS_n (J K^{-1} mol^{-1})
1	9.61 ± 0.01	26.0 ± 2.0	97 ± 7
2	8.78 ± 0.01	22.4 ± 1.2	93 ± 4
3	4.94 ± 0.01	8.0 ± 0.3	68 ± 1
4	4.23 ± 0.02	2.9 ± 0.3	71 ± 2
5	3.79–0.02	10.0 ± 1.2	39 ± 4
6	3.24 ± 0.02		
7	2.79 ± 0.03		

The luminescence decay measurements for Eu^{3+}, Eu^{3+} + DTPA and Eu^{3+} + DTPP indicated that the average number of coordinated water molecules are 8.8 ± 0.5, 1.2 ± 0.5 and 5.5 ± 0.5, respectively. In the DTPA system (pcH > 2), the Eu^{3+} was present only as $EuDTPA^{2-}$; the presence of *ca.* one H_2O in the primary coordination sphere of the complexed Eu^{3+} indicates that DTPA most likely acts as an octadentate ligand. In the DTPP system, at pcH 5.3, Eu^{3+} is present as $EuH_2DTPP^0 + EuH_3DTPP^+$ in a molar ratio of *ca.* 4:1. If we assume EuH_2DTPP^0 and EuH_3DTPP^+ differ by one water molecule, the observed value of 5.5 at the 4:1 molar ratio results in value of $n_{H2O} = 5.3 \pm 0.5$ for EuH_2DTPP^0 and 6.3 ± 0.5 for EuH_3DTPP^+. Within the experimental uncertainties, these values suggest that the H_2DTPP^{3-} ligand is coordinated to europium

TABLE 2. Stability constants of lanthanide–DTPP complexes ($I = 0.50$ M ($NaClO_4$); $T = 298$ K)

Ln^{3+}	$\log K_{1(21)}$	$\log K_{1(31)}$
La	4.11 ± 0.07	3.71 ± 0.05
Pr	4.08–0.05	3.93 ± 0.03
Nd	4.08–0.03	3.85–0.02
Sm	4.28 ± 0.04	4.08–0.03
Eu	4.27 ± 0.04	4.05 ± 0.03
Gd	3.90 ± 0.01	3.61 ± 0.01
Tb	3.94 ± 0.01	3.47–0.02
Dy	3.92 ± 0.04	3.47 ± 0.05
Ho	3.72 ± 0.02	3.49 ± 0.02
Er	3.70 ± 0.02	3.49 ± 0.02
Tm	3.66 ± 0.02	3.45 ± 0.02
Yb	3.68 ± 0.04	3.51 ± 0.02
Lu	3.79 ± 0.02	3.50 ± 0.02
Y	3.59 ± 0.06	3.57 ± 0.04

TABLE 3. Thermodynamic parameters for the complexation of lanthanum, gadolinium, terbium and dysprosium by DTPP ($I = 0.50$ M ($NaClO_4$); $T = 298$ K)

Ln^{3+}	$\Delta H_{1(21)}$ (kJ mol^{-1})	$\Delta S_{1(21)}$ (J K^{-1} mol^{-1})	$\Delta H_{1(31)}$ (kJ mol^{-1})	$\Delta S_{1(31)}$ (J K^{-1} mol^{-1})
La	8.7 ± 1.0	108 ± 4	11.3 ± 1.2	109 ± 4
Gd	13.4 ± 1.3	120 ± 4	12.5 ± 1.3	111 ± 4
Tb	10.5 ± 0.8	111 ± 3	20.8–2.2	136 ± 7
Dy	16.8 ± 0.9	131 ± 3	17.7 ± 1.1	126 ± 4

by three donor sites while the H_3DTPP^{2-} anion is coordinated by two sites. Alternatively, we can assign the 5.5 ± 0.5 value to both complexes in which case both would be coordinated by three sites with the third proton associated with a site which is non-bonding in EuH_2DTPP^0.

In the EuH_2DTPP system, the binding sites could be two carboxylates and one nitrogen (the iminodicarboxylate portion of the ligand with a total donor pK_a *ca.* 12) or, less likely, two nitrogens and one carboxylate (total donor $pK_a \approx 17.4$). Based on the $\log \beta$ versus ΣpK_a correlation for europium complexation, ligands with ΣpK_a *ca.* 12 are expected to form complexes with $\log \beta$ *ca.* 8.5 whereas, those with total basicity of 17.4 would probably form complexes with $\log \beta$ *ca.* 12.5. This would suggest that the first model is much more likely. In the case of Eu-iminodiacetate ($\Sigma pK_a = 13.5$), $\log \beta = 6.5$ [10], which is two orders of magnitude more stable than EuH_2DTPPA^0. The lower stability of the EuH_2DTPP would be expected for a system with similar ΣpK_a to iminodipropionic acid.

These conclusions are supported by the observed entropy values for the various lanthanide–DTPP complexes. In an earlier report [11], we have shown that the entropy of complexation is linearly dependent on the number of binding carboxylates and is independent of the number of binding nitrogens. The slope of the correlation for Gd^{3+} complexes is 60 ± 5 J K^{-1} mol^{-1} per $-COO^-$ group. Accordingly, the analogous $\Delta S_{1(21)}$ (*ca.* 120 J K^{-1} mol^{-1}) for the present system would reflect binding of the metal ion to two carboxylate groups. The third donor would be the imino group bridging the two carboxylate arms.

The residual enthalpy ($\delta \Delta H$) associated with the metal–nitrogen donor interaction is given by

$$\delta \Delta H = \Delta H_{1(21)} - 2(\Delta H_{Ac})$$

where $2(\Delta H_{Ac})$ is the portion of enthalpy due to carboxylate complexation ($\Delta H_{Ac} \approx 6.5$ kJ mol^{-1}). For GdH_2DTPP^0, the value of $\delta \Delta H$ is 0.4 ± 1.3 kJ mol^{-1} suggesting a very weak interaction, if any, with the nitrogen donor. Under similar conditions, we have shown that the values for Ln–N interactions for the DTPA ($\Sigma pK_N = 22.3$, seven five-membered rings) and ENDPDA ($\Sigma pK_N = 16.10$, three five-membered and two six-membered rings) are −80 and −24 kJ mol^{-1}, respectively. These values, if normalized to the differences in nitrogen basicity would also indicate much weaker Ln–N interaction for chelate rings larger than 5.

The similarity of the thermodynamic parameters for LnH_2DTPP^0 and LnH_3DTPP^+ complexes support a similar mode of binding and consequently similar degrees of hydration. We can calculate that the reaction, $LnH_2DTPP^0 + H^+ \leftrightarrow LnH_3DTPP^+$, has an equilibrium value of *ca.* 4.7. This value is more consistent with the proton associated with a nitrogen donor than a carboxylate oxygen (Table 1).

Acknowledgments

The research was supported at F.S.U. by a grant from the USDOE-OBES Division of Chemical Sciences. We are grateful to Dr. C. Musikas for providing the ligand.

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