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# The thermodynamics of lanthanide aminopolycarboxylate complexation [1]

Gregory R. Choppin

*Department of Chemistry, Florida State University, Tallahassee, FL 32306-3006, USA*

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## Abstract

The complexation by aminopolycarboxylate ligands has been a major area of interest in lanthanide chemistry for almost five decades. The number of donor sites and the variety of structures available in these ligands has provided opportunities to study a number of parameters in lanthanide complexation. It can be shown that the entropy changes are related to the number of carboxylate donors while the enthalpy changes depend on both carboxylate and nitrogen donors. The $\Delta H$–$\Delta S$ compensation indicates the importance of hydration effects on these terms, in contrast to the $\Delta G$ of formation which reflects, predominantly, the cation–ligand interactions. Variation of the length of the alkyl chains has shown that 5-membered rings are strongly favored and that the O–Ln–N rings are more sensitive to size than those of N–Ln–N.

## INTRODUCTION

Prior to 1940, the lanthanides were indeed "rare earths" in that the difficulty of their separation prevented sufficient amounts of pure samples being available for detailed studies of their chemical behavior. However, this problem was overcome when aminocarboxylate ligands were used with cation exchange resin to separate the individual lanthanides [1]. EDTA was found to be much more effective [2, 3], but the low solubility of the LnEDTA complexes led to the consideration of elution with ligands such as NTA, HEDTA, and MEDTA (see Table 1). The development of efficient commercial ion exchange separation of lanthanides using aminocarboxylate ligands created the "rare earth" industry and lanthanides are currently used in such diverse fields as nuclear medicine (for example, in MRI and in immunoassay), optical sensing (for example, in television tubes), industrial catalysis, organic synthesis, and high temperature superconductivity.

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[1] Presented at the 14th National Conference on Calorimetry and Thermal Analysis, Udine, Italy, 13–17 December 1992.

TABLE 1

Aminocarboxylic acids

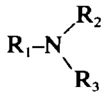
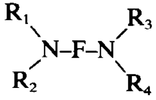
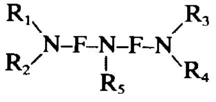
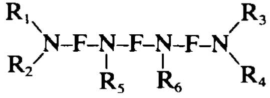
| | | | |
|---|---|---|---|
| I |  | (a) | $R_1 = H$, $R_{2\text{-}3} = CH_2CO_2H$<br>Iminodiacetic acid, IDA |
| | | (b) | $R_{1\text{-}3} = CH_2CO_2H$<br>Nitrilotriacetic acid, NTA |
| II |  | (a) | $R_{1,3} = H$, $R_{2,4} = CH_2CO_2H$, $F = C_2H_4$<br>N,N′-Ethylenediaminediacetic acid, EDDA |
| | | (b) | $R_1 = CH_3$, $R_{2\text{-}4} = CH_2CO_2H$, $F = C_2H_4$<br>N-Methylethylenediaminetriacetic acid, MEDTA |
| | | (c) | $R_1 = C_2H_5OH$, $R_{2\text{-}4} = CH_2CO_2H$, $F = C_2H_4$<br>N-Hydroxyethylethylenediaminetriacetic acid, HEDTA |
| | | (d) | $R_{1\text{-}4} = CH_2CO_2H$, $F = C_2H_4$<br>Ethylenediaminetetraacetic acid, EDTA |
| | | (e) | $R_{1\text{-}4} = CH_2CO_2H$, $F = C_6H_{10}$<br>Trans-1,2,diaminocyclohexanetetraacetic acid, DCTA |
| | | (f) | $R_{1\text{-}4} = CH_2CO_2H$, $F = C_3H_6$<br>1,3-Trimethylenediaminetetraacetic acid, TMDTA |
| | | (g) | $R_{1\text{-}4} = CH_2CO_2H$, $F = C_4H_8$<br>1,4-Tetramethylenediaminetetraacetic acid, TMEDTA |
| | | (h) | $R_{1,3} = CH_2CO_2H$, $R_{2,4} = C_2H_4CO_2H$, $F = C_2H_4$<br>Ethylenediamine-N,N′-dipropionic$_2$-N,N′-diacetic acid, EDPDA |
| III |  | (a) | $R_{1\text{-}5} = CH_2CO_2H$, $F = C_2H_4$<br>Diethylenetriaminepentaacetic acid, DTPA |
| | | (b) | $R_{1,5,3} = CH_2CO_2H$, $R_{2,4} = CH_2CONHCH_3$, $F = C_2H_4$<br>Diethylenetriaminepentaacetic acid bis(methylamide), BMA |
| | | (c) | $R_{2,4} = CH_3$, $R_{1,3,5} = CH_2CO_2H$, $F = C_2H_5$<br>N,N″-dimethyl-diethylenetriaminetriacetic acid, BME |
| IV |  | (a) | $R_{1\text{-}6} = CH_2CO_2H$, $F = C_2H_4$<br>Tetraethylenetetraaminehexaacetic acid, TTHA |

TABLE 2

Average number of coordinated water molecules *h* and total coordination number for Eu(III) and Tb(III) in aminocarboxylate complexes [9]

| Ligand | $CN_L$ [a] | *h* [b] | $CN_T$ [c] | Ligand | $CN_L$ [a] | *h* [b] | $CN_T$ [c] |
|---|---|---|---|---|---|---|---|
| NTA | 4 | 4.5 | 8.5 | TMDTA | 6 | 2.4 | 8.4 |
| MEDTA | 5 | 3.6 | 8.6 | DCTA | 6 | 2.3 | 8.3 |
| HEDTA | 6 | 3.1 | 9.1 | DTPA | 8 | 1.1 | 9.1 |
| EDTA | 6 | 2.6 | 8.6 | BMA | 8 | 1.2 | 9.2 |
| EDPDA | 6 | 2.5 | 8.5 | TTHA | 10 | 0 | ≤10 |

[a] $CN_L$ is the total number of donor sites on the ligand. [b] The uncertainty in these values is approx. ±0.5. [c] $CN_T$ is the total coordination number ($CN_2$ + h).

The early studies reflected confusion about the coordination number of the aminopolycarboxylate ligands when complexed with the lanthanides. Changes in coordination number across the cationic series from La to Lu were proposed for HEDTA [4] and EDTA [3, 5]. For example, for EDTA, hexadentation (2 nitrogens and 4 oxygens) was proposed for La–Sm and pentadentation (2 nitrogens, 3 oxygens) for Tb–Lu. The debate over the ligand coordination number was resolved by NMR spectroscopy which confirmed hexadentation for EDTA for all the lanthanides (from La to Lu) [6, 7]. The NMR spectra also showed that the Ln–O bonds were shorter lived than the Ln–N bonds.

Further insight into the nature of lanthanide–aminopolycarboxylate complexation was provided by measurements of the Eu and Tb fluorescent lifetimes of the complexes. These measurements provided the values of the residual inner sphere hydration of the complexed cation and, hence the total coordination number of the lanthanides [8, 9]. The data in Table 2 [4] show that the total coordination number for Eu(III) is approx. $8.6 \pm 0.2$, implying for EuEDTA an equilibrium between EuEDTA · $2H_2O$ and EuEDTA · $3H_2O$. The values of $CN_T$ in Table 2 support hexadenate chelation by EDTA, EDPDA, DCTA, and TMDTA. DTPA and DTPA–BMA could be either hepta- or octadentate; these ligand are probably octadentate with the middle carboxylate somewhat more weakly bound (longer Ln–O average distances). The DTPA–BMA ligand (see Table 1) appears to bind through the carbonyl oxygen of the amide groups, from NMR spectral data [10]. The hydration data of the lanthanides has been reviewed recently [11] and supports a model of a variation in the hydration number of the $Ln^{3+}_{aq}$ cations [12–14] resulting in different numbers of $H_2O$ molecules being lost in the formation of the complexes.

## THERMODYNAMICS OF COMPLEXATION

Analysis of the thermodynamic parameters of complexation of lanthanides with aminocarboxylate ligands has been quite helpful in understanding lanthanide coordination chemistry. Figure 1 shows that a linear correlation exists between $\log \beta_{101}$ ($\beta_1$ is the stability constant for 1:1 complexation) and $\sum \mathrm{p}K_a$ for ligands which have only 5-membered chelate rings [14]. The correlation of $\log \beta_{101}$ with $\sum \mathrm{p}K_a$ for these complexes is an indication that the bonding between the lanthanides and the ligand is strongly ionic for both the Ln–O and Ln–N bonds.

The complex patterns for $\Delta H_{101}$ and $\Delta S_{101}$ with $Z$ are complementary, which led to the suggestion [15, 16] that the variations in $\Delta S_{101}$ and $\Delta H_{101}$ with $Z$ are dominated by the dehydration which occurs upon complexation. This would lead to $|\Delta H_h| > |\Delta H_r|$ and $|\Delta S_h| > |\Delta S_r|$, where r represents ionic reaction and h dehydration. The values of $\Delta H_h$ and $\Delta S_h$ must be positive, leading to positive values of $\Delta H_{101}$ and $\Delta S_{101}$ for systems in which the above relationship is dominant. In fact, the experimental values for most simple complexes of the lanthanides have such positive values. Moreover, a "compensation effect" [15] exists such that $\Delta H_h \simeq T\Delta S_h$ leading to $\Delta G_h \approx 0$. Thus

$$\Delta G_{101} = (\Delta H_h + \Delta H_r) - T(\Delta S_h + \Delta S_r) \approx \Delta G_r$$

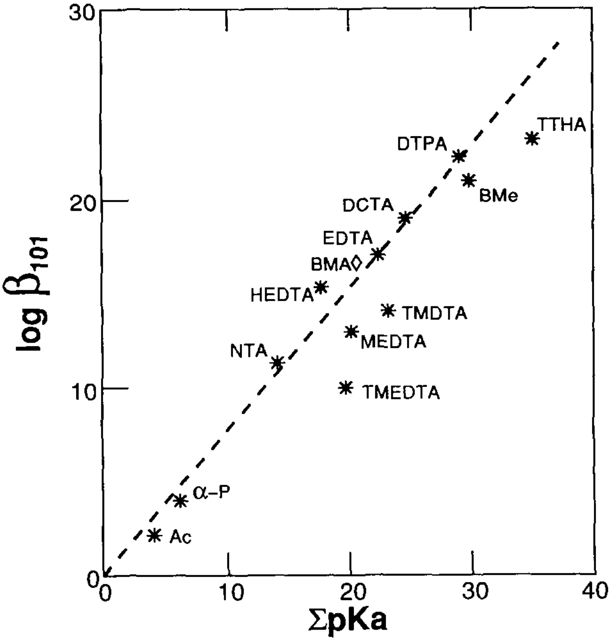


Fig. 1. Correlation of $\log \beta_{101}$ for Sm complexes and the total ligand acidity, $\sum \mathrm{p}K_a$. Ac = acetate, $\alpha$-P = $\alpha$-picolinate.

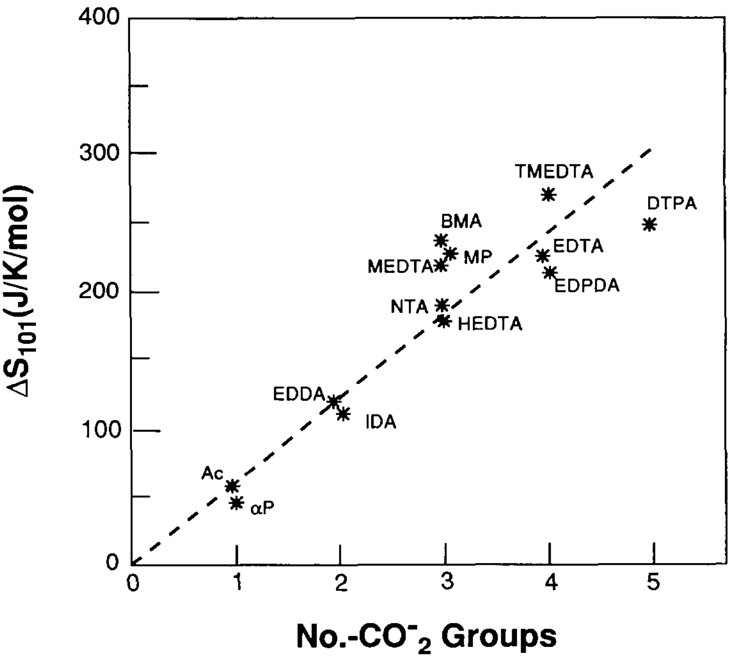


Fig. 2. Correlation of $\Delta S_{101}$ and the number of carboxylate groups for Sm(III) aminocarboxylate complexation.

The conclusion from this discussion is that the free energy change is most reflective of the metal–ligand bonding interactions.

The plot (Fig. 2) of $\Delta S_{101}$ for Sm complexation against the number of ligand carboxylate groups shows that $\Delta S_{101}$ is a direct function of the number of coordinated carboxylate groups, except for cases where steric rigidity, etc., may introduce an extra entropy effect, e.g. in LnDCTA. The slope of the correlation line for the Sm complexes in Fig. 2 is $59 \pm 7$ J $K^{-1}$ $mol^{-1}$ (correlation coefficient, 0.85) which is the value of $\Delta S_{101}$ for $SmAc^{2+}$ formation. The correlation in Fig. 2 plus the slope value indicate that it is the binding of the carboxylates which causes the dehydration of the lanthanide cation. From the "compensation" argument, if $\Delta S_{101} \simeq n\Delta S_{Ac}$ where $n$ is the number of carboxylate groups and $\Delta S_{Ac}$ is $\Delta S_{101}$ for $LnAc^{2+}$, we can assume that the contribution to $\Delta H_{101}$ or carboxylate interaction is $\approx n\Delta H_{Ac}$. However, the Ln–N bonding must also contribute to $\Delta H_{101}$. Assuming that no further dehydration occurs upon formation of the Ln–N bonds, this Ln–N enthalpy contribution, $\delta\Delta H(N)$, should be directly related to the basicity of the N donors as measured by the sum of their $pK_a$ values. The value of $\delta\Delta H(N)$ can be calculated from $(\Delta H_{101} - n\Delta H_{Ac})$. The correlation of $\delta\Delta H(N)$ with $\sum pK_a(N)$ is shown in Fig. 3 (correlation coefficient 0.88). The values for MEDTA, TMEDTA, and EDPDA are lower than expected, indicating weaker Ln–N bonding in the 6-membered rings in TMEDTA and EDPDA; in LnMEDTA, one end

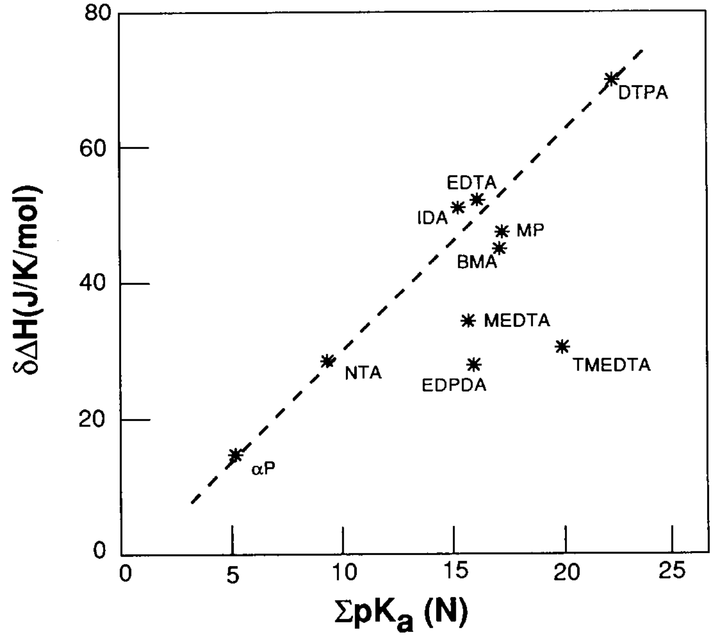


Fig. 3. Correlation of $\delta\Delta H$(N), the enthalpy for Sm–N binding in aminocarboxylate complexes. with $\sum$ p$K_a$(N).

of the ligand has only one N–Ln–O ring which must also weaken the Ln–N bonding.

## RING SIZE

In Fig. 1, the log $\beta_{101}$ values for the TMDTA and TMEDTA complexes which have 6- and 7-membered N–Ln–N rings, respectively, are much smaller than the LnEDTA values. For many different types of complexes, the order of complexing strength of lanthanides relative to ring size is $5>6>7$. The EuEDPDA complex has a 5-membered N–Ln–N ring but two of the four O–Ln–N rings are 6-membered. As we see in Fig. 1, this also reduces the complexation strength, but the presence of two such 6-membered rings does not reduce it as much as the expansion to 6 members of the single N–Ln–N ring in LnTMDTA. This agrees with the NMR data which indicated that the Ln–N bonds are longer-lived and are more significant in the strength of the complexes.

The rate constants for the acid-catalyzed decomposition follow the sequence [17, 18] TMEDTA > TMDTA > EDPDA > EDTA > DCTA. This pattern further reflects the order of stability of the chelate rings of 7, 6, and 5 members (TMEDTA, TMDTA, and EDTA) and the more important role of the N–Ln–N ring in the complex stability compared to the N–Ln–O rings (TMDTA vs. EDPDA). The kinetic stability of the DCTA complexes is due to the steric effects of the cyclohexyl ring: the more bulky and/or more rigid ligand results in slower decomposition.

## CONCLUSION

The coordination number of the aminopolycarboxylate ligands is a constant for all metals of the lanthanide series, e.g. hexadentate for EDTA. The $\Delta S_{101}$ value primarily reflects the dehydration of the metal ion, while $\Delta G_{101}$ reflects the metal–ligand bonding interactions. The variation of log $\beta_{101}$ with $\sum pK_a$ of the ligands supports a strongly ionic nature for the bonding. Five-membered chelate rings provide greater stability than larger rings. The Ln–N interactions are stronger than the Ln–O interactions, and play larger roles in metal–ligand stability.

## ACKNOWLEDGEMENT

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