

## Thermodynamic Properties of Rare Earth Complexes

### IV. Discussion of Factors of Importance for Complex Formation in Aqueous Solution

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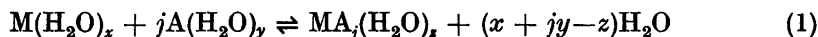
The experimental values of  $\Delta\mathcal{H}_i^\circ$  and  $\Delta\mathcal{S}_i^\circ$  for the formation of rare earth carboxylate complexes in aqueous solution have been discussed. The large similarity between the variation of  $\Delta\mathcal{H}_i^\circ$  and of  $\Delta\mathcal{S}_i^\circ$  through the lanthanide series for the investigated complexes is probably connected with the hydration of the central ion. A very simple model where the cloud of water molecules surrounding the metal ion is more or less broken, as the complexes are formed, will describe qualitatively both the change in enthalpy and entropy when going from one lanthanide to another and the change in enthalpy and entropy for consecutive complex formation reactions.

During the last twentyfive years a large number of investigations of thermodynamic properties of various metal complexes have been published. In most of these investigations only the change in free energy for the various complex formation reactions was determined. The purpose of these measurements was in most cases only to decide, *via* the stability constants, which species actually existed in the solutions. The free energy changes have very often been correlated with properties of the metal ion and/or the ligand.<sup>1</sup> Knowledge of the enthalpy and entropy changes for complex formation reactions will enable us to make the same correlations for these properties and thus presumably increase our knowledge of the factors of importance for the formation of complexes in solution. The enthalpy change is assumed to depend mainly on the difference in bond energy between the coordinated water and the ligand. Coordinated water should be taken in a wide sense so that the enthalpy changes, caused by changes in the solvent layers beyond the first one on replacement of water of hydration by ligands also are included. This means that the structure of the hydrogen bonds surrounding the solute species will be important for the magnitude of the enthalpy change. The entropy is concerned with the various modes of motion of molecules and atoms, with

the restrictions on their movements and also with the change in the number of particles in the system if molar units are used. These factors are in the first place concerned with the forces acting between the ions and the water molecules in the hydrate shell and the forces between the ions and the ligands, that is, with the factors determining the enthalpy changes accompanying complex formation.

The following discussion is based on the model for hydration of metal ions given by Eley and Evans<sup>2</sup> and on the similar model for complex formation reactions proposed by Duncan.<sup>3</sup> These models are approximate but by studying the variation of the enthalpy and entropy for a series of similar complexes one can hope that most of the errors will cancel. One such series of similar complexes is formed by the trivalent lanthanide ions, all with the same configuration of the outer electron shells. The lanthanide ions form a unique series for a study of the influence of the size of the central ion on complex formation reactions. The fact that the 4-f orbitals are well screened from the influence of external fields from the ligands means that bond effects caused by the lack of spherical symmetry of this electron shell (ligand field effects) are small. Furthermore all rare earths form, with a given ligand, the same type of complexes.

In the preceding communications<sup>4-6</sup> of this series the changes in free energy, enthalpy and entropy for a series of complex formation reactions of the type:



have been reported. For the sake of brevity charges have been omitted in the formula. M is one of the trivalent rare earth ions and A a carboxylate ion, acetate, glycolate, thioglycolate, diglycolate or dipicolinate. The experimental values of  $\Delta\mathcal{G}_i^\circ$ ,  $\Delta\mathcal{H}_i^\circ$ , and  $\Delta\mathcal{S}_i^\circ$  (for the notation see Ref. <sup>5</sup>, p. 2488) for the various systems are tabulated in Tables 3 and 5 in Part II and in Tables 3, 6, and 8 in Part III of this series. This material will be discussed and compared with enthalpy and entropy data previously reported for the rare earth EDTA<sup>7</sup> and HEDTA<sup>8</sup> complexes. First a summary of the experimental findings:

1. For all the systems investigated there is a regular increase in stability ( $-\Delta\mathcal{G}_i^\circ$ ) of the complexes from lanthanum through europium. For the heavy rare earths there may be a decrease in stability, *e.g.* for the first acetate complexes, an increase in stability, *e.g.* for the EDTA complexes, or an essential constancy with occasional maxima or minima in stability, *e.g.* for the first glycolate, diglycolate and dipicolinate complexes. The stability of the yttrium complexes is in general of the magnitude expected from its ionic radius. Due to the shape of the  $\Delta\mathcal{S}_i^\circ$  versus atomic number curve there are in some cases, *e.g.* for the diglycolate complexes, two possible positions for the yttrium complexes. One is the position expected from the ionic radius, the other position is among the lighter rare earths. However, if  $\Delta\mathcal{H}_i^\circ$  and  $\Delta\mathcal{S}_i^\circ$  are also considered there is no doubt that yttrium has the position expected from its ionic radius.

The magnitude of  $-\Delta\mathcal{G}_i^\circ$  ranges from about 2 kcal·mole<sup>-1</sup> for the first acetate complexes to about 25 kcal·mole<sup>-1</sup> for the EDTA complexes. There is, except for the EDTA complexes, no regular variation with the ionic radius of the change in free energy. However, the variation of  $\Delta\mathcal{G}_i^\circ$  within the rare earth series shows, for all systems except the EDTA ones, large similarities,

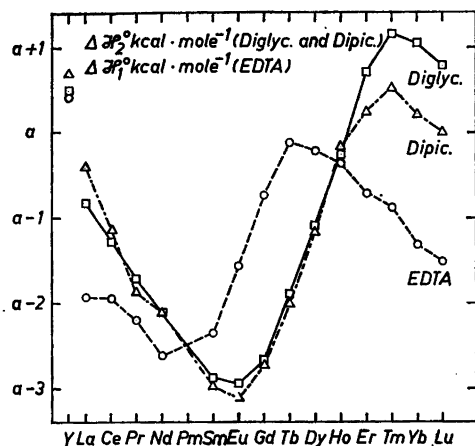


Fig. 1.  $\Delta \mathcal{H}_1^\circ$  for the formation of rare earth EDTA complexes and  $\Delta \mathcal{H}_2^\circ$  for the formation of the corresponding diglycolate and dipicolinate complexes.  $a$  has a value of 0, -6, and -1 for the diglycolate, dipicolinate and EDTA systems, respectively.

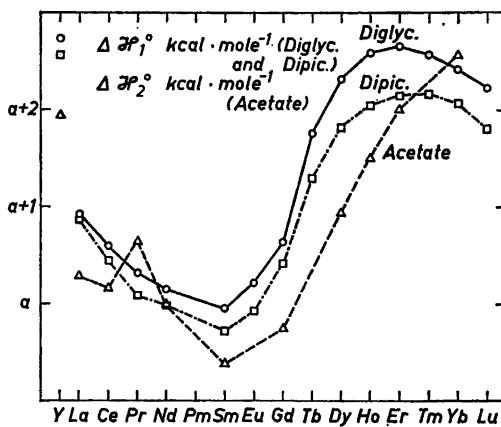


Fig. 2.  $\Delta \mathcal{H}_1^\circ$  for the formation of rare earth diglycolate and dipicolinate complexes and  $\Delta \mathcal{H}_2^\circ$  for the formation of rare earth acetate complexes.  $a$  has for the various systems a value of -1, -4, and +3.5 respectively.

despite the large differences in stability. These similarities are specially pronounced for the diglycolate and the dipicolinate systems.

2. The stability of the rare earth carboxylate complexes is due mostly to the large increase in entropy for the system when the complex is formed. The variation of the stability constants for a certain complex within the rare earth series is due both to enthalpy and entropy effects. Neither the enthalpy nor the entropy changes vary in a simple way with the ionic radius; e.g.  $\Delta \mathcal{H}_1^\circ$  and  $\Delta \mathcal{S}_1^\circ$  usually form a double series (cf. Figs. 1-3). In these cases there are also

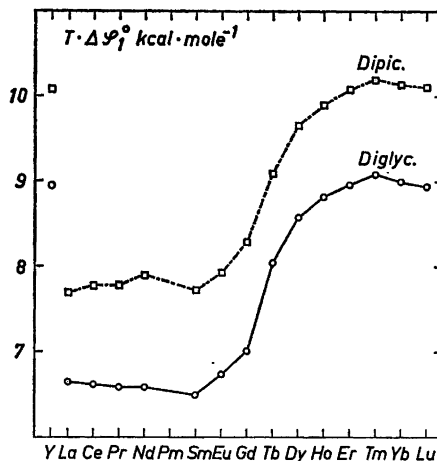


Fig. 3.  $T \cdot \Delta \mathcal{S}_1^\circ$  for the formation of rare earth diglycolate and dipicolinate complexes.

similarities in the variation of the enthalpy and entropy terms through the lanthanide series even for complexes with large differences in enthalpy and entropy. This point is for the entropy term illustrated in Figs. 1—6 in Part II of this series and for the enthalpy term in Figs. 1 and 2 in this communication.

3. On addition of the first and second ligands there is an increased entropy and a decreased enthalpy contribution for the heavy rare earths as compared to the light ones; *cf.* Figs. 1 and 4 in Part II. When ligands beyond the first one are added, the enthalpy and entropy contributions to the free energy change will increase, respectively decrease. A qualitative relationship has thus been established between the enthalpy and entropy changes in the sense that the more exothermic the complex formation reaction is, the less positive is the corresponding entropy change.

In this discussion conventional free energy and entropy changes on the molar scale have been used. Both these terms consist of a unitary part characteristic of the reactants and a cratic part which depends on the change in the number of particles taking part in the reaction.<sup>9</sup> In order to compare the free energy and entropy changes for reactions with ligands of different type, *e.g.* chelate and non chelate, the unitary quantities should be used.<sup>10</sup> Unfortunately, it is not possible in most cases to determine the change in the number of particles for reactions of the type (1) because of the unknown degree of solvation both of the metal ion, the ligand and the complexes.

Comparisons between the thermodynamic quantities for different systems must be referred to a common reference state. The choice of such a reference state has been discussed in Part II of this series.

The similarity of the variation of  $\Delta\mathcal{H}_i^\circ$  and  $\Delta\mathcal{S}_i^\circ$  for a number of different complex formation reactions through the lanthanide series is an indication of the fact that this variation is caused mainly by some property of the metal ions. It is obvious that both the enthalpy and the entropy changes for reactions of the type (1) will depend on the state of the hydrated metal ions in solution and knowledge of the properties of these species is important for the present discussion. The most complete studies of the properties of the hydrated trivalent rare earths have been made by Spedding *et al.*<sup>11</sup> These authors studied the variation of properties such as mean activity coefficients, transference numbers, heats of hydration, heats of dilution, partial molar volumes and partial molar compressibilities for a number of rare earth salts. The experimental results proved that there was no simple variation of the measured properties with the crystallographic ionic radius — on the contrary a double series was observed. One possible cause of this behaviour is according to Spedding *et al.* that the configuration of the solvent molecules around the light rare earths differ from that around the heavy ones. Spedding's suggestion is based on the following simple electrostatic model: As the ionic radius in the rare earth series decreases there will be an increased polarisation of the solvent around the charged species and the solvent layer in the vicinity of the metal ion will form an ordered structure. This cloud of water molecules around the metal ion has another geometry than the bulk water. This is the iceberg concept of Frank and Evans.<sup>12</sup> The spatial extent of this cloud will depend on the radius and charge of the polarising ion, and if changes in geometric configuration were not to occur, we should expect the space of the cloud to vary in a regular way with the ionic

radius. With decreasing ionic radius there will be a possibility of a change in packing or coordination number of the solvent layer in contact with the metal ion. Such a change will, *via* hydrogen bonds, influence the structure of the solvent cloud to some distance outside the first hydration shell and thus influence the properties of the hydrated ions:

The idea of a solvent layer with a definite structure around the rare earth ions is supported by the work of Freed *et al.*<sup>13,14</sup> who found evidence for lattice vibrations coupled with the main electronic transitions in aqueous solutions of Eu.<sup>3+</sup> The idea of a change in structure of the first coordination shell somewhere in the lanthanide series is given additional support by the works of Morgan,<sup>15</sup> Brady<sup>16</sup> and Miller, Sayre and Freed.<sup>17</sup>

The ordered water structure around the metal ions will serve as an entropy source. When the complexes are formed this structure will be more or less broken down and this process is followed by an increase in entropy. The magnitude of the entropy change will mainly depend on the number of water molecules "set free" from the ordered structure. A multidentate ligand will interfere more with the hydrate shell of the metal ions than a unidentate ligand and is thus expected to give a larger entropy contribution to the stability of the complexes. This is also what is experimentally observed. In order to break down the hydrate shell of the solute species energy has to be used; this energy loss is more or less compensated by the formation of metal-ligand bonds. On addition of ligands beyond the first one the entropy changes are expected to decrease in the order  $\Delta S_1^\circ > \Delta S_2^\circ \dots$  etc. as the solute-solvent interactions are smaller for the complexes because of their decreased charge and or increased radius. A structure change in the solvent cloud somewhere in the lanthanide series will influence both the entropy and enthalpy changes for complex formation reactions. An increase in the number of water molecules "set free" will result in an increase of entropy followed by a change in enthalpy ( $\Delta \mathcal{H}_i^\circ$ ). The experimentally observed double series in the lanthanide series can thus be explained. When the central ion is more "dehydrated" these differences are expected to be smaller and should disappear when the central ion is completely dehydrated. The variations of  $\Delta H_3^\circ$  and  $\Delta S_3^\circ$  for the rare earth diglycolate and dipicolinate complexes are also more regular than the corresponding variations in  $\Delta H_1^\circ$  and  $\Delta S_1^\circ$ .

By using an electrostatic model for the formation of metal complexes in solution Duncan<sup>3</sup> has shown that a linear relation is expected between the enthalpy of formation and the reciprocal ionic radius  $r$ , of the metal ions, provided no changes in structure of either complexes or hydrated metal ions occur as  $r$  is varied. The fact that  $\Delta \mathcal{H}_i^\circ$  is no linear function of the reciprocal ionic radius for the formation of rare earth carboxylate complexes is another indication of a structure change somewhere around the middle of the lanthanide series.

The very simple model outlined on the preceding pages will thus describe qualitatively both the change in enthalpy and entropy when going from one lanthanide to another and the change for consecutive complex formation reactions. In this context it must be remembered that part of the observed differences in enthalpy and entropy for consecutive complex formation reactions is due to activity terms as a result of the chosen standard states for the

various reactions (*cf.* Part II, p. 2491). For the entropy term the statistical effect of Bjerrum<sup>18</sup> must also be taken into account.

Another approach to the study of the variation in entropy for complex formation reactions has been used by Betts and Dahlinger<sup>19</sup> and by Moeller and Ferrús.<sup>8</sup> Their discussion is based on the variations of the partial molar entropies for the various complexes through the lanthanide series. The entropy change  $\Delta S_j^\circ$  for a complex formation reaction of the type (1) can be expressed as:

$$\Delta S_j^\circ = \bar{S}_{MA_j(H_2O)_x}^\circ + (x + jy - z)\bar{S}_{H_2O}^\circ - \bar{S}_{M(H_2O)_x}^\circ - j\bar{S}_{A(H_2O)_y}^\circ \quad (2)$$

where  $(x + jy - z)$  is often assumed to be zero or constant. The eqn. (2) is then rearranged as:

$$\Delta S_j^\circ + \bar{S}_{M(H_2O)_x}^\circ = \bar{S}_{MA_j(H_2O)_x}^\circ - j\bar{S}_{A(H_2O)_y}^\circ \quad (3)$$

In a series of complex formation reactions where  $j$  and  $A$  are constant eqn. (3) will give the variation of  $\bar{S}_{MA_j(H_2O)_x}^\circ$  as  $M$  is varied, provided that the values of  $\bar{S}_{M(H_2O)_x}^\circ$  are known. Very few experimental determinations of the partial molar entropies of the various trivalent rare earths are available, so the values of  $\bar{S}_{M(H_2O)_x}^\circ$  have to be calculated by the empirical relations given by Laidler<sup>20</sup> or by Powell and Latimer<sup>21</sup> instead. There are several objections to this approach:  $(x + jy - z)$  may not be constant as  $M$  is varied.  $\bar{S}_{M(H_2O)_x}^\circ$  is by the use of the empirical equations assumed to be some simple function of the crystallographic ionic radius. The available experimental values<sup>22,23</sup> of  $\bar{S}_{M(H_2O)_x}^\circ$  for the rare earths are scarce and do not fit the above-mentioned relationships very well. On the basis of Spedding's work it seems most reasonable to assume that the partial molar entropies of the hydrated rare earth ions fall into two series and do not vary in the way predicted by the Laidler or the Powell and Latimer relations. In any case, the interpretation of the entropy changes will not be facilitated by the introduction of a new and so far empirical parameter. Moeller and Ferrús have explained the variation in enthalpy and entropy for the rare earth-HEDTA complexes as due to a loss in bond strength and an increased steric hindrance, both caused by the decreasing ionic radius (*cf.* Ref.,<sup>8</sup> pp. 271—273). Betts and Dahlinger have explained a similar variation of the enthalpy and entropy changes in the EDTA series as due to a change in the coordination number (*cf.* Ref.,<sup>19</sup> pp. 97—100). In my opinion both these explanations are less probable than the one outlined before.

The importance of ligand field contributions to the stability of rare earth complexes has been discussed by several authors.<sup>24,25</sup> A loss of ligand field stabilization was thought to explain the decrease in free energy from samarium and europium to gadolinium and also the low free energy values of yttrium as compared to the elements of similar ionic radius. When the enthalpy data are examined no special loss of enthalpy is noticed for the gadolinium complexes and we can conclude that the ligand field effects are obscured by other much larger effects. The fact that no decrease in free energy is observed for curium complexes as compared to the corresponding americium complexes<sup>26,27</sup> is another indication of the fact that the "gadolinium break" is not caused by ligand field effects.

The model outlined in this discussion is certainly an oversimplification of the physical reality but by using it we are able to give a qualitative description of the variation of the enthalpy and entropy terms for the rare earth complexes. A more refined model can only be obtained when more experimental data on the structure of solutions and on the solute-solvent interactions are available.

This work has been supported by a grant from *Statens Naturvetenskapliga Forskningsråd* (Swedish Natural Science Research Council).

I wish to thank Professor Ido Leden for many valuable discussions and helpful comments on the above subject.

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Received October 14, 1963.