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Thermodynamic relationships of complex formation. Part II. Enthalpy–entropy interdependence in hard–hard interactions in aqueous solution

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Abstract

Thermodynamic data for hard–hard interactions in stepwise complex formation in aqueous solution between UO_2(II), Th(IV) or tervalent cations and carboxylate ligands are inspected for the occurrence of enthalpy–entropy relationships. Such relationships are found in the first complexation of UO_2(II) and in all the stepwise complex formations between Ln(III) (Ln = lanthanide) and acetate, propionate, isobutyrate, lactate, or α-hydroxyisobutyrate. Weaker correlations occur in the Th(IV) complex formation and in the Ln(III)–glycolate systems.

The enthalpy–entropy susceptibilities are different for the various complexation reactions.

The thermodynamic parameters are the macroscopic results of many contributions, as they are the steps into which a chemical process can be dissected as a matter of fact or convenience.

In solution, complex formation derives from solvent mediated acceptor–donor interactions, and it follows immediately that these interactions can be resolved into two parts (at least): (i) one for which the solvent is responsible (or mainly responsible), and (ii) a second due (or mainly due) to the interactions between the two partners [1]. The two parts are not independent and it would be a serious error to consider them in isolation, for they are strictly connected [2,3], although in different ways, according to the particular substratum, ligand and solvent medium.

The changes in thermodynamic parameters for such interactions can be split into two parts, to each of which the same origin as for the related interaction can be ascribed. Thus, for reactions in solution, the dissection of ΔG, ΔH and ΔS into a contribution due (or mainly due) to the solvent role and a contribution due (or mainly due) to the reagents is allowed. The first of these, related to the cratic part [4] of the reaction, was named "external"

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by Hepler [5–7], who distinguished it from the other which he named "internal" ($\Delta G = \Delta G_{\text{Ext}} + \Delta G_{\text{Int}}$, and similarly for ΔH and ΔS).

Changes in the cratic part of the reaction produce changes in the corresponding part of ΔG, ΔH and ΔS simultaneously while the other part remains unaltered (or almost unaltered). The changes in ΔG, ΔH and ΔS are thus correlated. The simplest (but not the sole) way by which they are connected is a reciprocal linear dependence. In such cases, the present author prefers to use the terms "proportional" and "residual" [1]. In a series of related reactions (homologous reactions), the "proportional part" is the part of one parameter which is related to the corresponding part of another parameter simply by means of a proportionality coefficient ($\Delta G = \Delta G_{\text{Res}} + \Delta G_{\text{Prop}}$, and likewise for ΔH and ΔS. $\Delta G_{\text{Prop}} \propto \Delta H_{\text{Prop}}, \ldots$). The other part constitutes the "residual part".

Researches on complex formation between substituted thioureas and Ag(I) (in H_2O and CH_3OH) [8,9] or Hg(II) (in H_2O) [10] have revealed linear ΔH vs. ΔS relationships. In these systems, the alkyl substituents modify the solvation state of reagents and products while the metal ion-to-ligand interactions remain unaffected (or almost unaffected) because of the binding mechanism between the soft Ag(I) or Hg(II) ions and sulphur donor ligands (σ bond and π back-bond), and the ΔH vs. ΔS relationships arise from changes in the cratic part of the considered homologous reactions.

As far as Ag(I) and Hg(II) are concerned, for each of these ions two linear and parallel trends have been identified. The first is the one connected with the reaction $M + L = ML$ (here and subsequently, charges are omitted for simplicity). The other one embraces at the same time the second and third stepwise complex formation $ML_{n-1} + L = ML_n$ ($n = 2$ or 3). The experimentally evaluated isoequilibrium temperatures from the relationships $\Delta H = \Delta H_I + \tau \Delta S$ ($\Delta H_I = \Delta H_{\text{Intercept}}$) are within the investigated temperature range [for Ag(I) systems $T_{\text{iso}} = 309$ K (36 °C) in H_2O and $T_{\text{iso}} = 293$ K (20 °C) in CH_3OH. For Hg(II) systems $T_{\text{iso}} = 293$ K (20 °C) in H_2O].

The above mentioned reactions are characteristic for soft–soft interactions [11,12]. This contribution is devoted to the analysis of thermodynamic data for complexing reactions in aqueous solution between $4f$ or $5f$ metal ion and oxygen donor ligands. Both the acceptors and donors are hard in nature and interact with each other in different ways than those of Ag(I) or Hg(II) with sulphur donor ligands.

In the literature quite a lot of thermodynamic data concerning the complex formation between tervalent rare earth ions and carboxylate ligands is reported. Most reports refer to the same temperature and ionic strength engendered by the same background electrolyte.

The systems for which data are analyzed in this work have been investigated at one temperature by pH-metric measurements for the speciation and free energy data. The complex formation enthalpy changes were obtained by direct calorimetry. As free energy data at only one temperature are available, a detailed statistical analysis for the occurrence of single intersection points in Van't Hoff space is not possible, although suggested by some authors [13,14], so that ΔH–ΔS point patterns are inspected for the reactions which may be reciprocally related in some way. The two thermodynamic parameters ΔH and ΔS are independent, for ΔH is obtained by direct calorimetry and ΔS comes from linear combination of two independently obtained values (ΔG is obtained by potentiometry). Moreover, the linearity condition in Van't Hoff space (which implies the invariance of ΔH and ΔS with temperature) and the occurrence of a single intersection point are biunivocally interconnected with linear trends between any two of the parameters of the Gibbs equation (ΔG–ΔH, ΔG–ΔS, ΔH–ΔS). Whichever event occurs in Van't Hoff space, this is linearly mapped in the other, and vice versa.

This contribution deals with the occurrence of enthalpy–entropy relationships in the stepwise complex formation between $UO_2(II)$ [16,18–21], Th(IV) [16–18,20,22] or tervalent rare earth $4f$ ions [23–25] and carboxylate ligands. The homologous series which can be constructed are (i) the stepwise complexation of the same metal ion with a set of related ligands, or (ii) the reactions of related metal ions (those of the $4f$ series) with the same ligand. It is interesting to have data for the same complexing reaction but in various solvents.

In Fig. 1, ΔH–ΔS patterns for stepwise complex formation of $UO_2(II)$ with carboxylate ligands are shown. Data refer to 25 °C and ionic strength $\mu = 1$ for $NaClO_4$.

From the point distribution in Fig. 1A it can be inferred that the ligands, e.g. glycolate, chloroacetate, thioglycolate, aspartate, hydrogen-succinate, β-chloropropionate, acetate, thiodiacetate and succinate, in the reaction $M + L = ML$ are strictly connected by a linear enthalpy–entropy relationship [$\Delta H = -0.384(0.19) + 0.156(0.01) \times \Delta S$; $R = 0.988$: figures in parentheses are standard deviations]. Out of the trend for more favourable ΔH and ΔS are malonate, iminodiacetate, oxydiacetate and, to a less extent, glycolate.

The data for the second and third stepwise complex formation $ML_{n-1} + L = ML_n$ ($n = 2$ or 3) do not show any definite trend, but they can be grouped in two separate clusters with their baricentres lying approximately on the trend defined by the first complex formation. Also in the second stepwise complexation, malonate is distinguished sharply and in the same direction.

For Th(IV) stepwise complex formation, enthalpy–entropy changes are not so highly correlated as in the previous case [comparison between $UO_2(II)$ and Th(IV) series is legitimate because the same set of ligands is concerned], but the stepwise reactions $ThL_{n-1} + L = ThL_n$ ($n = 1$–4) lie roughly on a trend with a weak positive correlation coefficient (see Fig. 2 A–C). As for $UO_2(II)$ complexes, so also for Th(IV) complexes with malonate, oxydiacetate and glycolate are out of trend for lower ΔH and higher ΔS (see Fig. 2).

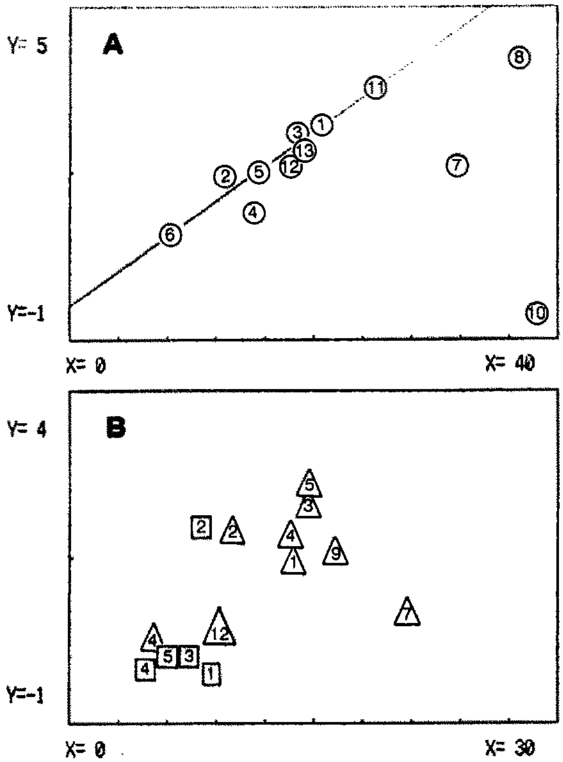

Fig. 1. ΔH vs. ΔS (in kcal mol^{-1} and kcal mol^{-1} K^{-1} respectively) relationships for the stepwise complex formation ($ML_{n-1} + L = ML_n$) between $UO_2(II)$ and carboxylate ligands in aqueous solution at 25 °C and ionic strength $\mu = 1$ for $NaClO_4$. Ordinate ΔH; abscissa ΔS. standard deviations are reported in parentheses. A: $UO_2(II) + L = UO_2L$; $\Delta H = -0.384(0.19) + 0.156(0.01) \times \Delta S$; $R = 0.988$; B: $UO_2L + L = UO_2L_2$; $\Delta H = -1.04(0.56) + 0.205(0.05) \times \Delta S$; $R = 0.77$. Ligands: 1 = acetate; 2 = chloroacetate; 3 = β-cloropropionate; 4 = glycolate; 5 = thioglycolate; 6 = glycine; 7 = malonate; 8 = succinate; 9 = oxydiacetate; 10 = iminodiacetate, 11 = thiodiacetate; 12 = aspartate, 13 = hydrogen succinate.

The series of reactions represented in the previous figure and in Fig. 2 each originate from the same central ion with a set of interrelated ligands for gradual substitutions (see the sequence at the foot of Fig. 1).

The following figures, Figs. 3 and 4, show enthalpy–entropy relationships in stepwise complex formation where the metal ion, but not the ligand, is changed. As they are 4*f* tervalent metal ions, it can be supposed that the series is homologous in spite of the discontinuity of elements met with in some complexing reactions [25]. The data for the rare earth complex formation were analyzed in the way described in order to have an opposite situation (invariant ligand and variable central ion) to that referred to in Figs. 1 and 2 [also opposite to those in Ag(I) or Hg(II) complex formation] and because the original data, as reported by the various authors, allow immediately such a kind of analysis. In a subsequent paper the reactions of the same lanthanide ion with different related ligands will be considered.

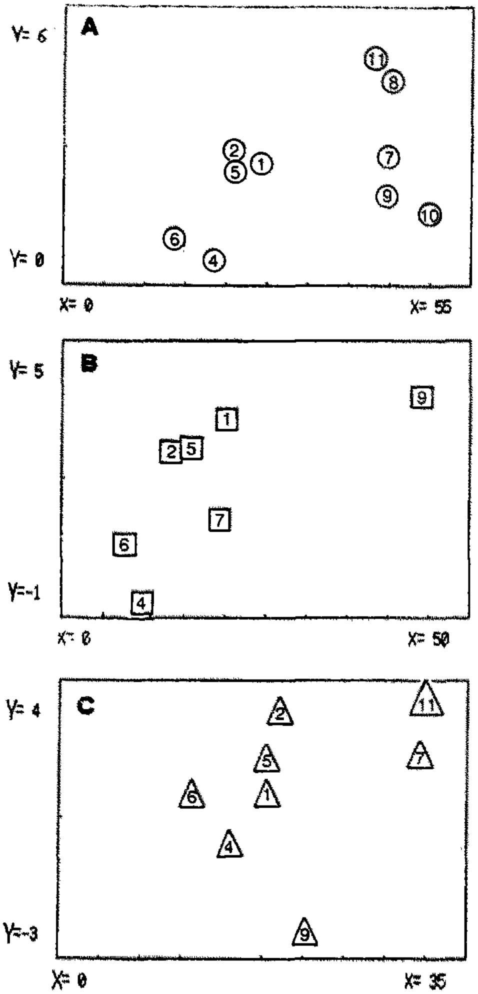

Fig. 2. ΔH vs. ΔS (in kcal mol^{-1} and kcal mol^{-1} K^{-1} respectively) relationships for the stepwise complex formation ($ML_{n-1} + L = ML_n$) between Th(IV) and carboxylate ligands in aqueous solution at 25 °C and ionic strength $\mu = 1$ for $NaClO_4$. Ordinate ΔH; abscissa ΔS. Standard deviations are reported in parentheses. A: (○) Th(IV) + L = ThL; $\Delta H = -0.694(0.55) + 0.135(0.02) \times \Delta S$; $R = 0.967$; B: (□) $ThL + L = ThL_2$; $\Delta H = -0.133(0.94) + 0.093(0.04) \times \Delta S$; $R = 0.694$; C: (△) $ThL_2 + L = ThL_3$; $\Delta H = -0.420(1.20) + 0.108(0.06) \times \Delta S$; $R = 0.694$. Ligands: see Fig. 1.

Figure 3A–C refers to the lanthanide complex formation reactions with acetate, propionate and isobutyrate which are monodentate ligands. The ΔH–ΔS patterns indicate as many linear trends as the number of successive complexes in each system. As far as the reaction M + L = ML is concerned, the data for an isoentropic reaction ($\Delta S = 0$) show more favourable enthalpy changes according to the sequence $CH_3COO^- < CH_3CH_2COO^- < (CH_3)_2CHCOO^-$.

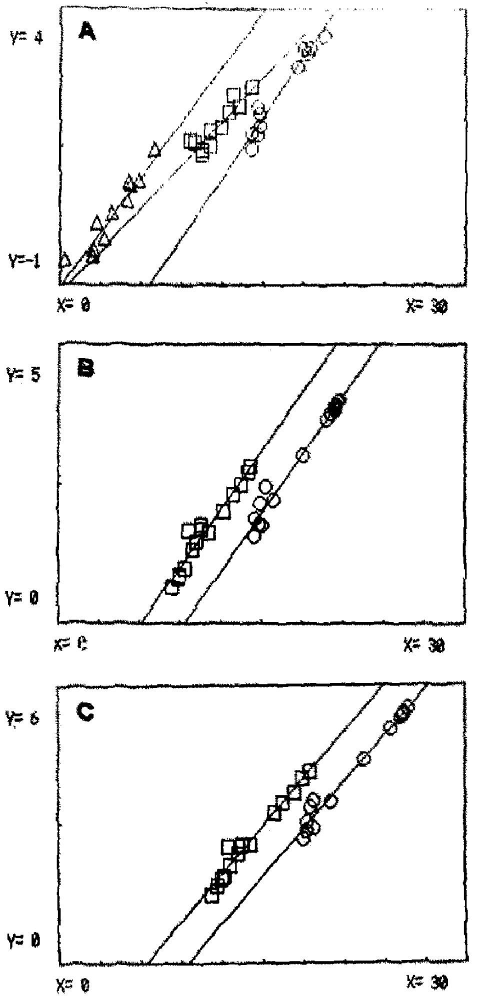

Fig. 3. ΔH vs. ΔS (in kcal mol^{-1} and kcal mol^{-1} K^{-1} respectively) relationships for the stepwise complex formation ($ML_{n-1} + L = ML_n$) between 4*f* tervalent cations and the carboxylate ligands acetate (A), propionate (B) and isobutyrate (C) at 25 °C and ionic strength $\mu = 2$ for $NaClO_4$. Ordinate ΔH; abscissa ΔS. (○) $M + L = ML$; (□) $ML + L = ML_2$; (△) $ML_2 + L = ML_3$. Acetate: $\Delta H = -3.40(0.42) + 0.360(0.026) \times \Delta S$; $R = 0.977$; propionate: $\Delta H = -3.28(0.28) + 0.350(0.015) \times \Delta S$; $R = 0.987$; isobutyrate: $\Delta H = -3.20(0.28) + 0.336(0.01) \times \Delta S$; $R = 0.991$. (□) Acetate: $\Delta H = -1.18(0.46) + 0.261(0.04) \times \Delta S$; $R = 0.912$; propionate: $\Delta H = -2.13(0.26) + 0.348(0.02) \times \Delta S$; $R = 0.971$; isobutyrate: $\Delta H = -2.19(0.24) + 0.340(0.02) \times \Delta S$; $R = 0.980$. (△) Acetate: $\Delta H = -0.94(0.16) + 0.324(0.04) \times \Delta S$; $R = 0.948$.

In the second and third stepwise complexations, the corresponding ΔH–ΔS relationships (but related to different ligands) are almost identical.

For isoenthalpic reaction ($\Delta H = 0$) the three reaction series show very similar entropy changes for the corresponding complexation because of the slightly different ΔH–ΔS susceptibility in the three cases.

The gap separating the light lanthanide ions from the heavy ones in the reaction M + L = ML tends to disappear in the subsequent complexations $ML_{n-1} + L = ML_n$ ($n = 2$ or 3) and the tendency of the relative position of the various ions in the trend to be reversed. In fact, in the first complexation M + L = ML, the heavy lanthanides show more positive values for both ΔH and ΔS, whereas in the third complexation $ML_2 + L = ML_3$ (Fig. 3A) the relative position is on the whole overturned.

The subsequent figure, Fig. 4A–C, shows the enthalpy–entropy relationships for complex formation with glycolate, lactate and α-hydroxyisobutyrate. The connection among these ligands is the same as among acetate, propionate and isobutyrate, from which systematically they differ by the presence of an OH group on the α position in respect to the carboxylate.

The enthalpy–entropy relationships for the glycolate complexes are not so well defined as in the systems reported in Fig. 1A and Fig. 3A–C. The same can be said for the first complexation with lactate (Fig. 4B). In spite of that, positive trends are evident in Fig. 4A.

By comparing the ΔH–ΔS patterns for the glycolate complexes with the corresponding patterns for acetate and the patterns for lactate with those for propionate, fundamental differences are seen. In the case of acetate and propionate, the lower affinity (at 25 °C) of higher coordinated substrata compared with those of lower coordination (ML compared with M; ML_2 compared with ML; ML_3 compared with ML_2) derives from a negative shift of both ΔH and ΔS values. In the complexation reactions with glycolate, the enthalpy range remains practically unaltered, but the entropy range moves systematically toward more unfavourable values. In the system with lactate, the lower affinity of ML in the second stepwise complex formation compared with that of M derives from more positive ΔH and ΔS changes.

In the systems with glycolate and lactate, ΔH for isoentropic reactions systematically increases and ΔS for isoenthalpic reactions systematically decreases on increasing the coordination level of the substratum.

The gap separating the heavy lanthanides from the light ones in the reaction M + L = ML tends to disappear in the subsequent complexation and is noticebly reduced in the first complexation series with lactate and glycolate.

The system with α-hydroxyisobutyrate (Fig. 4C) is quite interesting, because the series of reactions $ML_{n-1} + L = ML_n$ ($n = 0$–2) shows sharp isoequilibrium relationships with three different ΔH–ΔS susceptibilities.

CONCLUSIONS

The distributions of the experimental points in some of the cases analyzed do not leave any doubt as to the occurrence of very strict enthalpy–entropy linear relationships, which lead to well defined isoequilibrium conditions.

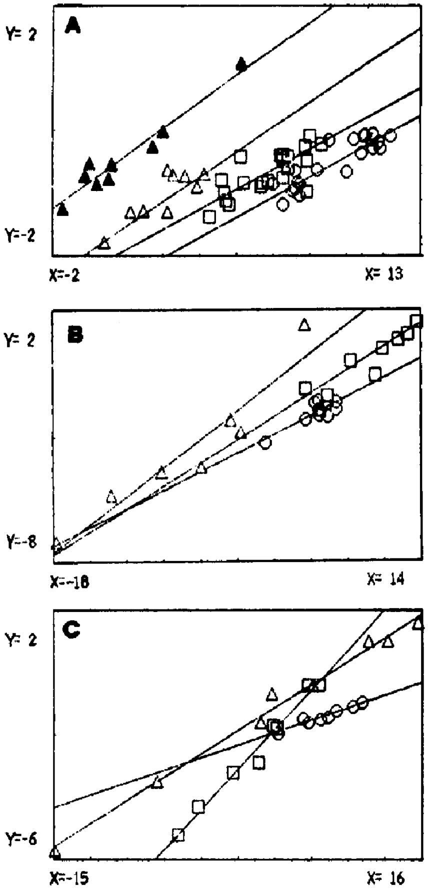

Fig. 4. ΔH vs. ΔS (in kcal mol^{-1} and kcal mol^{-1} K^{-1} respectively) relationships for the stepwise complex formation ($ML_{n-1}+L=ML_n$) between 4*f* tervalent cations and the oxycarboxylate ligands glycolate (A), lactate (B) and α-hydroxyisobutyrate (C) at 25 °C and ionic strength $\mu = 2$ for $NaClO_4$. Ordinate ΔH; abscissa ΔS. (○) $M+L=ML$; (□) $ML+L=ML_2$; (△) $ML_2+L=ML_3$; (▲) $ML_3+L=ML_4$. (○) Glycolate: $\Delta H=-2.57(0.20)+0.215(0.02)\times\Delta S$; $R=0.925$; lactate: $\Delta H=-3.21(0.27)+0.231(0.05)\times\Delta S$; $R=0.843$; α-hydroxyisobutyrate: $\Delta H=-2.41(0.11)+0.129(0.01)\times\Delta S$; $R=0.965$. (□) Glycolate: $\Delta H=-2.11(0.20)+0.213(0.03)\times\Delta S$; $R=0.854$; lactate: $\Delta H=-2.56(0.33)+0.286(0.03)\times\Delta S$; $R=0.964$; α-hydroxyisobutyrate: $\Delta H=-3.22(0.11)+0.412(0.02)\times\Delta S$; $R=0.989$. (△) Glycolate: $\Delta H=-1.67(0.17)+0.254(0.06)\times\Delta S$; $R=0.846$; lactate: $\Delta H=-1.29(0.48)+0.352(0.05)\times\Delta S$; $R=0.950$; α = hydroxyisobutyrate: $\Delta H=-1.99(0.10)+0.240(0.01)\times\Delta S$; $R=0.995$. (▲) Glycolate: $\Delta H=-0.678(0.07)+0.283(0.03)\times\Delta S$; $R=0.963$.

The systems UO_2(II)–carboxylate ligands and lanthanide ions–α-hydroxyisobutyrate in the first complexing reactions are distinguished sharply from the other ligands, for their isoequilibrium temperatures are lower than the experimental temperature (25 °C) [$T_{iso}=156$ K (-117 °C) and $T_{iso}=129$ K (-144 °C) respectively] whilst for the other systems T_{iso} values are near to or greater than 25 °C. Some consequences follow immediately from this fact.

The isoequilibrium temperatures $T_{iso} = 156$ and 129 K are not experimentally accessible in aqueous solutions. Furthermore, the affinity sequences $(-\Delta G)$ for the analyzed carboxylate ligands toward $UO_2(II)$ and the affinity sequence for tervalent $4d$ ions towards hydroxyisobutyrate do not change with temperature in H_2O. For the other systems for which T_{iso} is within the range of existence of the solvent medium, the affinity sequences undergo inversion at this point.

Owing to the ΔH–ΔS interdependence, it is nonsense to speak about enthalpy of entropy control of the reaction conforming to the trends, for in such a case ΔG can be expressed by choice as depending on the entropy $[\Delta G = \Delta H_{Int} - (T - T_{iso}) \times \Delta S \rightarrow d(\Delta G) = -(T - T_{iso}) \times d(\Delta S)$ for $T =$ const.] or enthalpy changes $\{\Delta G = T \times \Delta S_T + [(T_{iso} - T)/T_{iso}] \times \Delta H \rightarrow d(\Delta G) = [(T_{iso} - T)/T_{iso}] \times d(\Delta H)$ at $T =$ const; $\Delta S_T = \Delta H_T/T_{iso})$. Important instead are the ΔH vs. ΔS susceptibility and the residual free energy term which appear in the relationships $\Delta G = f(\Delta H)$ or $\Delta G = g(\Delta S)$. They would be analyzed in detail for their origin and meaning. In fact it is the τ parameter that determines, together with the temperature of the system, the quantitative intervention of order–disorder (ΔS) factors $[-(T - T_{iso}) \times \Delta S]$ or, if preferred, of energetic factors $\{[(T_{iso} - T)/T_{iso}] \times \Delta H\}$ on the reactions of the trend. The influence will be greater by as much as the $|T - T_{iso}|$ absolute value is greater.

The various ΔH vs. ΔS susceptibilities found in the various systems come from the solvent effect. This hypothesis is supported by the two clusters for the first coordination in Fig. 3A, B and C and by the change in the relative positions of the points on going from one trend to another in the same system.

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