Thermodynamic relationships of complex formation. Part 5. Isoequilibrium relationships in soft–soft interactions in hard solvents

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Abstract

The inspection of the $\Delta H - \Delta S$ patterns for reactions between Ag(I) complex substrata and various entering ligands discloses linear interplay between the two parameters. The actual ΔH (ΔS) values demonstrate that soft–hard interactions can produce favourable enthalpy changes coupled to unfavourable entropy changes, and confirm that soft–soft interactions can yield unfavourable enthalpy changes coupled to favourable entropy changes. These results, together with the already published enthalpy–entropy interplays, which show negative values of both ΔH and ΔS for hard–hard interactions in aqueous solution, demonstrate that in this solvent soft–soft (hard–hard) interactions do not necessarily produce $\Delta H < 0$ ($\Delta H > 0$) coupled to $\Delta S < 0$ ($\Delta S > 0$) because their values also descend from the role of the solvent molecules in the specific reaction. The coordinated solvent produces a sort of 'shielding' or 'levelling' of the acceptor and donor abilities.

INTRODUCTION

Chemical reactions can be viewed as the reorganization of a system where 'chemically active' parts come into contact [1] in some way. Solvation, which is always actual in solution for at least one of the participants in the reaction, together with changes in the solvation states between reac-

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tants and products, implies that the solvent medium has a well defined role, which often becames the driving force for reactions in solution.

Although it is rather hard to conceive of an 'inert' solvent [2–5], it is essentially true that the intervention of a solvent is qualitatively and quantitatively different in connection with both its nature and the actual chemical reaction.

The overall macroscopic parameters characterizing a chemical process (namely ΔG, ΔH, ΔS, ΔV, ...) can be considered the outcomes of partial contributions related to the steps into which the process is in reality or for convenience dissected. Some of these contributions derive mainly from the nature of the reactants and products; others are linked mainly with solute–solvent interactions and with the number of solvent molecules involved in the chemical reaction.

In a series of related reactions, both parts of the contributions can vary, but there are reactions where some (any one) of them remain unaltered and the others modify along the series in a more or less systematic way. The two types of behaviour imply mutual correspondence among the contributions of the various parameters which refer to the same transformation [6–9]. When part of the range of parameters is constant throughout the series, the above-mentioned correspondences are restricted to the variable part, and in simple cases they conform to linear relationships. In such a case one can refer to the 'residual part' and the 'proportional part' of two mutually related parameters whose meanings are strictly linked to the selected coordinates for the representation of the reaction series [8,9].

Investigations on complex formation between Ag(I) and thiourea (Tu), thiosulphate (Ts), thioacetamide (Ta), thiocyanate (Tcy), chloride, bromide, iodide and ammonia in aqueous solution and a constant ionic medium (1 M KNO_3) [10–14] in three ligand systems have been performed in the laboratory of one of the authors over a long period. Single ligand and mixed ligand mononuclear complexes have been identified at different coordination levels. The thermodynamic parameters ΔH and ΔS for their formation have been deduced from the dependence of the chemical affinities on temperature. The data refer to a number of related Ag(I) complexes that allow the evaluation of the free energy enthalpy and entropy changes for a large number of ligand coordination and/or displacement reaction series.

In previous contributions [13,14], ΔH–ΔS patterns for the overall and stepwise Ag(I) complexing reactions have been reported and compensating linear enthalpy–entropy interplays have been identified. Reactions which can have no element in common have been simultaneously included in these diagrams. By adequately selecting the series of reactions it is possible to extract information on the qualitative and quantitative origin of the compensating enthalpy–entropy phenomenon.

The present paper shows the analysis of the ΔH–ΔS data for a series of coordination reactions between single ligands and Ag(I) complex substrata

in aqueous solution with the aim of characterizing possible interconnections between the thermodynamic parameters and identifying the isoequilibrium conditions.

The investigated series of reactions are generated according to the following criteria:

(1) Reactions of one substratum (sub), which is invariant along the series), with various entering ligands (Sub + $L_{(i)}$ = Sub–$L_{(i)}$). Each substratum will generate its own series which will be made up of as many terms as there are investigated ligands. The general features of the series will reflect the influence of the substratum on the acceptor–donor interactions with the considered ligands.

(2) Reactions of one ligand with a set of variously coordinated substrata in terms of both the nature or number of ligands. As many series as investigated ligands can be generated. The comparison between the various series will reflect the influence of the incoming ligand on the donor–acceptor interactions of the considered substrata.

SERIES OF REACTIONS OF SINGLE SUBSTRATA WITH VARIOUS LIGANDS

Figure 1(A–C) reproduces the ΔH–ΔS behaviour in the stepwise complexing reaction series of Ag(I), AgTu$^+$ and AgTu$_2^+$ respectively. The reaction series of the other substrata also exhibit linear behaviour and will not be reproduced here. In Table 1 are given (i) the parameters of the linear regression ΔH–ΔS ($\Delta H = \Delta H_{res} + \tau\,\Delta S$) obtained by least squares, (ii) the correlation coefficients, and (iii) the number of points on which the regression is based. By means of these data one can judge the reliability of the values of the various parameters.

Each series of reactions of the same substratum with different ligands (Sub + $L_{(i)}$ = Sub–$L_{(i)}$) shows a single linear ΔH–ΔS trend for which the descriptors ΔH_{res} and τ vary according to the nature of the substratum. Owing to the heterogeneity of the incoming ligands in terms of donor atoms, hardness–softness, the pair of parameters ΔH_{res} and τ can be considered as characteristics of the substratum regardless of the coordinating properties of the incoming ligands. On such a basis, mono- or dicoordinated Ag(I) substrata differ from solvated Ag(I) by their less exothermic ΔH_{res} of about 20 kJ mol^{-1}. ΔH_{res} represents the enthalpy change for a real or hypothetical isoentropic ($\Delta S = 0$) reaction belonging to the trend. The free energy change for such a reaction is independent both of temperature ($\partial(\Delta G)/\partial T = 0$) and the susceptivities $\partial(\Delta H)/\partial(\Delta S) = \tau$. The differences in ΔH_{res} can be interpreted as the outcome in the actual solvent of the stabilization of the central ion in consequence of substitution of coordinated solvent molecules by ligands of higher affinity.

Values of ΔH_{res} for the series of coordination reactions of mono- or dicoordinated Ag(I) substrata although contained within a narrower range
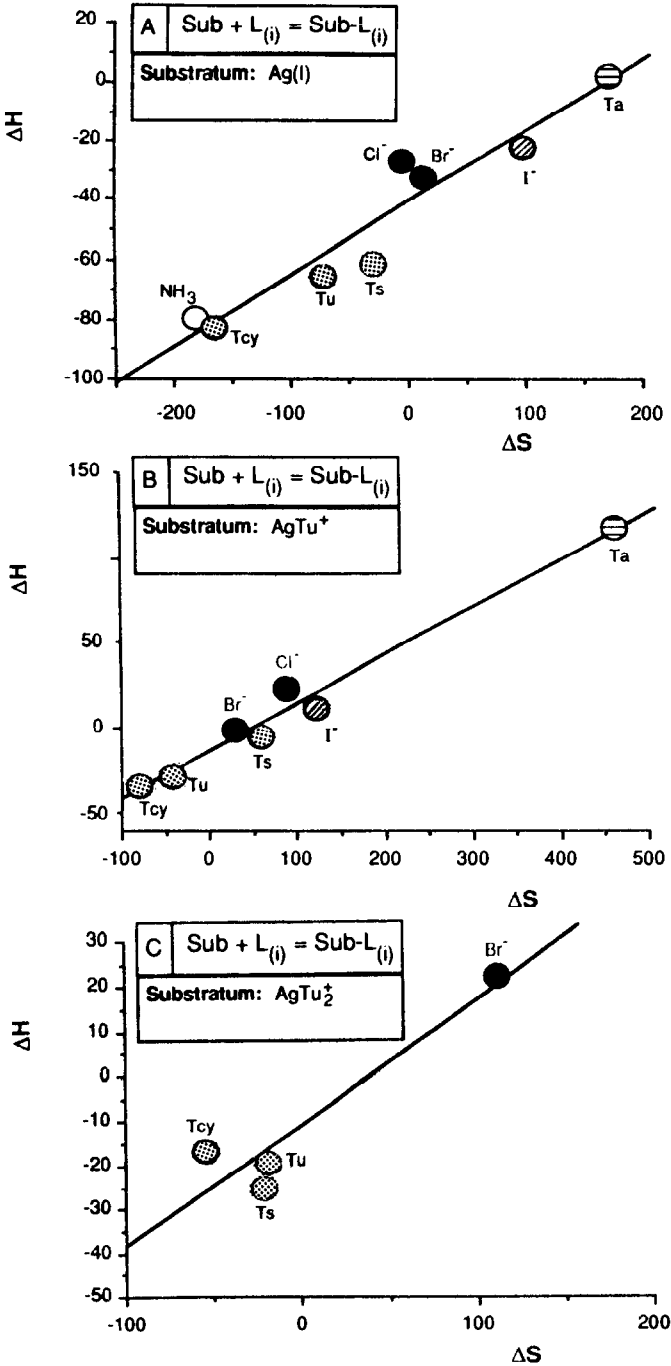
Fig. 1. ΔH versus ΔS (in kJ mol^{-1} and J mol^{-1} K^{-1} respectively) interdependences for the series of reactions between invariant Ag(I) complex substrata and various ligands (see figure) in aqueous solutions with ionic strength $\mu = 1$ for KNO$_3$. In parentheses standard deviations are reported. R = correlation coefficient. A: Sub = Ag(I); $\Delta H = -40.6(3.4) + 0.242(0.03)\,\Delta S$; $R = 0.957$. B: Sub = AgTu$^+$; $\Delta H = -13.3(3.3) + 0.280(0.02)\,\Delta S$; $R = 0.990$. C: Sub = AgTu$_2^+$; $\Delta H = -10.8(4.5) + 0.275(0.07)\,\Delta S$; $R = 0.938$.

$(-10--20 \text{ kJ mol}^{-1})$, confirm such a hypothesis. Of course exceptions can be found.

A mere inspection of ΔH (ΔS) values for the reactions reproduced in Fig. 1 ($Ag(I) + L_{(i)} = Ag(I)_{(i)}-L_{(i)}$ reveals the order

$$\Delta H_{L=NH_3} < \Delta H_{L=SCN^-} < \Delta H_{L=Tu} \approx \Delta H_{L=Ts} < 0 < \Delta H_{L=Br^-} < \Delta H_{L=I^-}$$

$$< \Delta H_{L=Ta} \qquad (1)$$

With regard to the evident trend, chloride ion appears as a probable outsider with more unfavourable changes in both enthalpy and entropy.

The positions of the various ligands in relationship (1) demonstrate the following.

(a) Soft–hard $Ag(I)-NH_3$ (!?) interactions in aqueous solution can generate favourable enthalpy and unfavourable entropy changes;

(b) Soft–soft interactions (e.g. $Ag(I)-I^-$ and $Ag(I)-Ta$) can lead to unfavourable enthalpy but favourable entropy changes;

(c) Similar ligands, such as Tu and Ta, can lead to significantly different changes in the thermodynamic parameters, whereas ligands as different in nature as NH_3-SCN^- or Tu–Ts can generate almost equal ΔH and ΔS values.

Values of ΔH_{res} for the linear trends related to the complexing reaction series of mono- or dicoordinated substrata ($Sub + L_{(i)} = Sub-L_{(i)}$); Sub = invariant mono- or dicoordinated substratum; L = variable ligand are be-
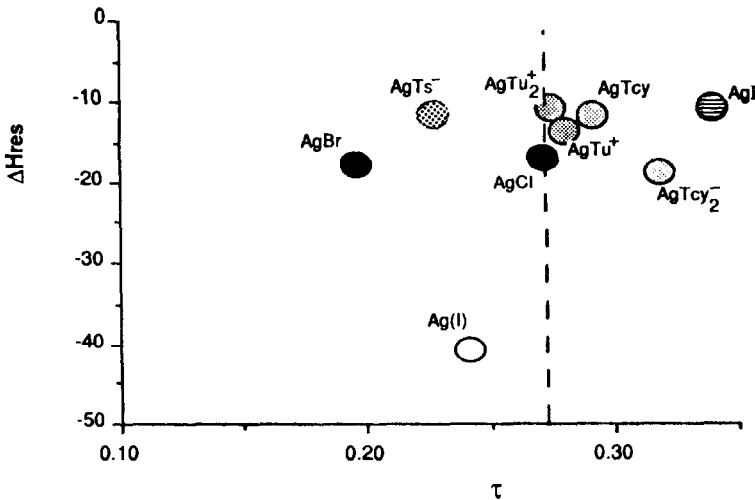

Fig. 2. ΔH_{res} versus τ pattern for the series of reactions between invariant Ag(I) mono- or dicoordinated complex substrata and various ligands in aqueous solution with ionic strength $\mu = 1$ for KNO_3. Vertical broken line indicates 0°C.

TABLE 1

Descriptor parameters of the linear $\Delta H - \Delta S$ trends ($\Delta H = \Delta H_{res} + \tau \Delta S$) found for the series of coordination reactions of single ligands with Ag(I) complex substrata in aqueous solution and ionic strength $\mu = 1$ for KNO$_3$. A: Series of reactions of single Ag(I) complex substrata with various ligands (Sub + L$_{(i)}$ = Sub–L$_{(i)}$; Sub = invariant Ag(I) complex substratum; L = variable ligand). B: Series of reactions of single ligand with various Ag(I) complex substrata (Sub$_{(i)}$ + L = Sub$_{(i)}$–L; Sub = variable Ag(I) complex substratum; L = invariant ligand). ΔH_{res}: enthalpy change for a hypothetical or real isoentropic ($\Delta S = 0$) reaction belonging to the trend. $\partial(\Delta H)/\partial(\Delta S) = \tau$: enthalpy–entropy change susceptivity with physical dimension of temperature. For linear $\Delta H - \Delta S$ trends descending from reaction series whose free energy changes linearly depend on temperature, τ is linearly related to the isoequilibrium temperature T_{iso} (K) by a scale factor. For the present case $T_{iso} = 1000\ \tau$. R is the correlation coefficient. N is the number of points (read reactions) used for the regression. Figures in parentheses are standard deviations.

	ΔH_{res}	τ	t_{iso} [a]	R	N
A: Series of reactions Sub + L$_{(i)}$ = Sub–L$_{(i)}$					
Sub					
Ag(I)	−40.6(3.4)	0.242(0.03)	−31	0.957	8
AgTcy	−11.4(4.1)	0.291(0.02)	+18	0.984	7
AgCl	−16.7(5.5)	0.272(0.03)	−1	0.977	5
AgBr	−17.6(4.8)	0.196(0.07)	−77	0.843	5
AgI	−10.5(5.2)	0.340(0.05)	+167	0.977	4
AgTs$^-$	−11.3(2.4)	0.227(0.04)	−46	0.938	7
AgTu	−13.2(3.3)	0.280(0.02)	+7	0.990	7
AgTcy$_2^-$	−18.5(5.2)	0.319(0.03)	+46	0.987	5
AgTu$_2^+$	−10.8(4.5)	0.257(0.07)	+2	0.938	4
B: Series of reactions Sub$_{(i)}$ + L = Sub$_{(i)}$–L					
Sub$_{(i)}$ = monocoordinated substrata					
Ligand					
Ts	−20.2(2.1)	0.282(0.06)	+9	0.929	6
Tcy	−8.2(0.9)	0.269(0.01)	−4	0.966	6
Cl$^-$	−1.5(0.7)	0.285(0.06)	+12	0.999	5
Br$^-$	−7.3(0.9)	0.271(0.01)	−2	0.998	5
I$^-$	−21.5(0.9)	0.284(0.01)	+11	0.999	5
Tu	−17.7(0.9)	0.303(0.01)	+30	0.999	7
Ta	−17.2(2.8)	0.282(0.01)	+9	0.999	4
Sub$_{(i)}$ = dicoordinated substrata					
Ts	−18.3(1.2)	0.295(0.01)	+22	0.994	7
Tcy	−8.3(0.8)	0.277(0.00)	+4	0.999	12
Cl$^-$	−2.7(0.4)	0.277(0.00)	+4	1	5
Br$^-$	−7.9(0.9)	0.295(0.00)	+22	0.999	7
I$^-$	−5.5(3.4)	0.208(0.03)	−65	0.991	4
Tu	−16.8(0.9)	0.282(0.02)	+15	0.993	14

[a] Temperature in Celsius.

tween 0 and −10 kJ mol^{-1}. The general behaviour runs along the lines already outlined: ΔH_{res} tends towards more positive values with the thermodynamic stability of the reacting substratum for the coordination of

ligands of higher affinity (see for comparison the ΔH_{res} for the series of AgCl–AgI or AgBr–AgI with variable entering ligands).

Because the differences among the coordinated substrata are not so sharp as between Ag(I) and the complex substrata with high affinity ligands, it is fairly obvious that exceptions are to be expected in connection with specific features of the substratum (see the series of AgTcy and AgTcy$_2^-$ substrata).

The scattering of the points on the τ coordinate in Fig. 2 lends support to the assertion that the nature of the substratum of the reaction series Sub + $L_{(i)}$ = Sub–$L_{(i)}$ has a very precise role in determining the isoequilibrium temperatures of the series.

Sequences of enthalpy (entropy) changes (the sequences are not described here but they can be set up very easily by using the data reported in the literature) have elements of both similitude and dissonance with the relationship (1), but always confirm the conclusions (a), (b) and (c), above.

SERIES OF REACTIONS OF A SINGLE LIGAND WITH DIFFERENT COMPLEX SUBSTRATA

The series of reactions of single entering groups with mono- or dicoordinated substrata have been considered as two mutually distinct classes of reactions. The ΔH–ΔS behaviours in the reactions with thiourea are shown in Fig. 3 (A, B) (the behaviour of the other series is similar). Table 1 shows the calculated descriptor parameters. With the exception of iodide, the trends for the reaction series with the other ligands do not show discriminating abilities toward mono- or dicoordinated substrata. In fact, in ΔH–τ coordinates (Fig. 4) the pairs of values (ΔH_{res}, τ) related to the series of reactions $Sub_{(i)}$ + L = $Sub_{(i)}$–L ($Sub_{(i)}$ = variable mono- or dicoordinated substrata; L = invariant ligand) identify nearby points such that the patterns are a single trend or, alternatively, two indistinguishable trends.

The isoequilibrium temperatures inferred by enthalpy–entropy change susceptivities are almost uniformly distributed between 0 and 30°C, but clusters of points are observed along the ΔH coordinate (Fig. 4). According to the increasing ΔH_{res} sequence they are

(a) the series of reactions with Tu, Ta, Ts and I$^-$ (this last ligand only for the series of reactions with monocoordinates);

(b) the series of reactions with Br$^-$ or Tcy;

(c) the series of reactions with Cl$^-$.

The corresponding ΔH (ΔS) sequences for the series of reactions Sub + $L_{(i)}$ = Sub–$L_{(i)}$ (Sub = invariant; $L_{(i)}$ = variable) were influenced by the nature of the substratum (the constant term of the series), also in the present case the sequence of ΔH for the reactions belonging to one trend is not unambiguous and varies with the nature of the incoming ligand (invariant within the series).

REMARKS

The occurrence of linear enthalpy–entropy interdependences in series of 'homologous' reactions has been demonstrated for (i) series of coordination reactions in aqueous solution of the same central ion (Ag(I) or Hg(II)) with a set of alkyl-substituted thioureas or their subsequent stepwise coordination reactions [15–17], and (ii) series of reactions of the same
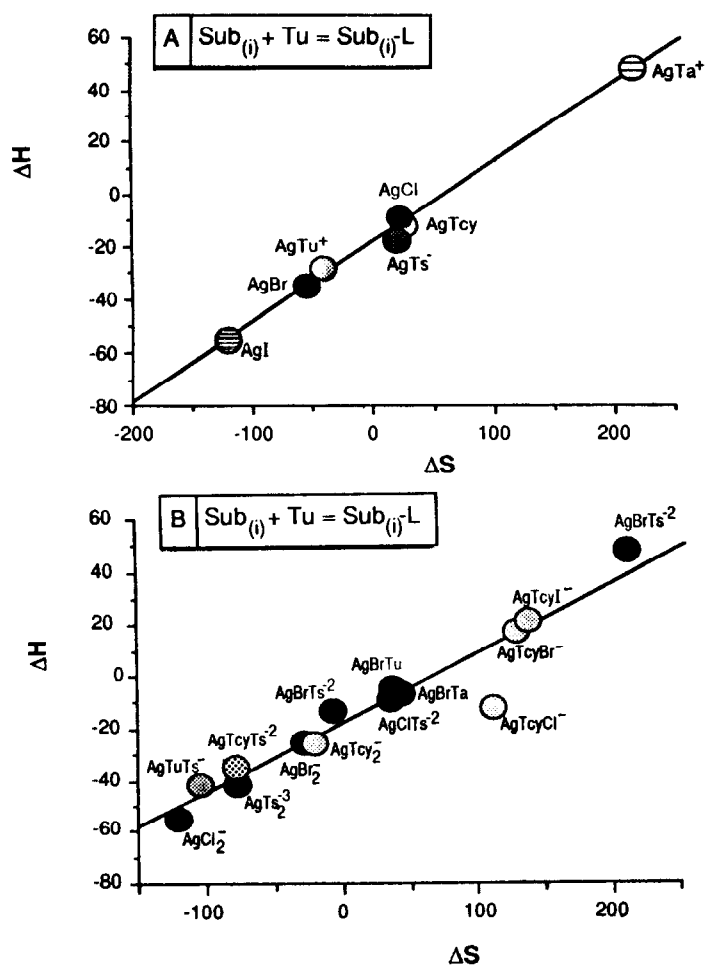

Fig. 3. ΔH versus ΔS (in kJ mol^{-1} and J mol^{-1} K^{-1} respectively) interdependences for the series of reactions between Tu invariant and various monocoordinated (A) or dicoordinated (B) Ag(I) complex substrata (see figure) in aqueous solution with ionic strength $\mu = 1$ for KNO$_3$. In parentheses, standard deviations are reported. R = correlation coefficient. A, Sub monocoordinated; $\Delta H = -17.7(0.9) + 0.303(0.01)\,\Delta S$; $R = 0.997$. B, Sub dicoordinated; $\Delta H = -16.8(0.9) + 0.282(0.01)\,\Delta S$; $R = 0.993$.
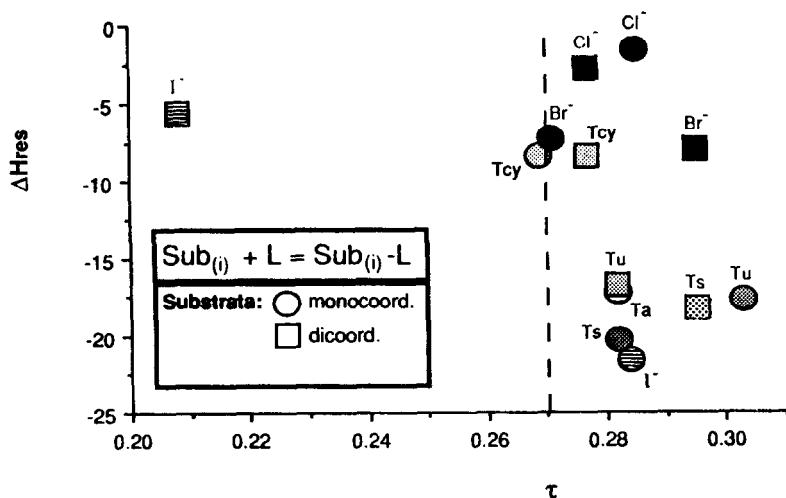
Fig. 4. ΔH_{res} versus τ pattern for the series of reactions between various Ag(I) mono- or dicoordinated complex substrata and invariant ligands in aqueous solution with ionic strength $\mu = 1$ for KNO_3. Vertical broken line indicates 0°C.

ligand (acetate, propionate, glycolate,...) with the tervalent lanthanides or their subsequent stepwise coordination reactions [8,9].

In all the cases the acceptor–donor interactions were occurring between the same acceptor and donor, and changes within the series (the way of originating the terms of the series) were due to alkyl substitutions on the base ligand, or there were gradual but systematic changes in the physico-chemical properties of the acceptor ions.

The ligands whose coordination reactions are reproduced in Fig. 1 differ greatly one from the other in the nature of the donor atoms, physical dimensions, ionic charges, hardness–softness, etc. and therefore they give rise to different gaseous donor–acceptor interactions. In spite of that, the reactions $Ag(I) + L_{(i)} = Ag(I)-L_{(i)}$ lie on a single $\Delta H-\Delta S$ curve where, in addition, coordination reactions with ligands different in nature lie near to each other (e.g. NH_3–SCN^-, Tu–$S_2O_3^-$; the first uncharged but the second negatively charged; Br^-–I^- — 'borderline' and 'soft' respectively); in contrasts, ligands similar in terms of donor atom and electronic structure (Tu and Ta, in which the thiocarbonyl sulphur act as donor) are astonishingly far apart; thiourea with negative and thioacetamide with positive changes in both enthalpy and entropy.

Similar general remarks can be made after analyzing the other complexing reactions of the other substrata, although with different relationships among the ligands.

It is largely true that in a given system different entropy levels correspond to different energy levels [18], and the enthalpy–entropy interplay for gaseous state reactions can be connected with this phenomenon. But it

seems less reliable to conclude that in solution the ΔH–ΔS interdependence can have the same origin. The most reasonable hypothesis is that the $\partial(\Delta H)/\partial(\Delta S)$ susceptivities originate from the number of solvent molecules involved in the reactions and from the energetics of the solute–solvent and solvent–solvent interactions. Moreover, the fact that such different ligands conform to the same trend can be explained by supposing that the coordinated solvent molecules exert some sort of 'shielding' or 'levelling' action on the coordinating properties of donor and acceptor determining (a) the shape of the curve and (b), together with acceptor–donor interactions, the actual ΔH_{res} value. This last hypothesis is confirmed by the sharp differences in ΔH_{res} between the series of reactions $Ag(I) + L_{(i)} = Ag(I)$–$L_{(i)}$ and the other series related to the Ag(I) complex substrata AgTu, AgTs and AgI, the interactions of which with an incoming ligand differ greatly from that with solvated Ag(I): and by the differences between the series of reactions $Sub_{(i)} + Cl^- = Sub_{(i)}$–$Cl^-$ and those with Tu, Ts, Ta or I^- as incoming ligand (invariant within the series). In both cases $\Delta(\Delta H_{res}) \approx 20$ kJ mol^{-1}.

ACKNOWLEDGEMENT

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