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Thermodynamic relationships on complex formation. Part 6. Considerations on thermodynamic properties for mixed ligand complex equilibria

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Abstract

The organization of ΔG, ΔH and ΔS according to stepwise coordination or displacement reactions for the complex formation equilibria of Ag(I) or Cd(II) in aqueous solution shows the intervention of specific factors in the overall formation parameters which cannot be accounted for by linear models.

NOMENCLATURE

A, B, L	ligands
M	metal ion
n, a, b	coordination number
N	maximum coordination number
Sub	complex substratum
Tu	thiourea
Ts	thiosulphate ion
Tcy	thiocyanate ion
Nt	nitrite ion

Charges are omitted for simplicity.

INTRODUCTION

In the presence of two different ligands A and B, metal ions M having a maximum coordination number $N \geqslant 2$ form mixed ligand complexes $M_mA_aB_b$ ($m \geqslant 1$; $a \geqslant 1$ and $b \geqslant 1$).

In solution, single ligand complexes that are not exhaustively coordinated are also mixed ligand complexes, the second ligand being the solvent coordinated in the inner coordination sphere.

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Single-ligand mononuclear complexes MA_a $(1 \leqslant a \leqslant N)$ are usually considered to lie in between the solvated ion and the highest-coordinated complex MA_N and, further, they can in general be considered to lie in between one complex with a lower and one complex with a higher coordination number ($MA_{a'}$, MA_a, $MA_{a''}$; $a' < a < a'' \leqslant N$).

Similarly, mixed-ligand complexes lie in between corresponding single-ligand complexes at the same coordination level: the mixed complex $M_mA_aB_b$ $(a + b = n = \text{constant})$ lies in between M_mA_n and M_mB_n. This amounts to considering the formation of $M_mA_aB_b$ as occurring either by means of successive stepwise substitution of b ligands A in M_mA_n with as many ligands B ($M_mA_n + bB \rightarrow M_mA_aB_b + bA$) or by means of successive stepwise substitution of a ligands B with as many A in M_mB_n ($M_mB_n + aA \rightarrow M_mA_aB_b + aB$).

Provided the starting complex (M_mA_n or M_mB_n) is transformed step by step to the final complex (M_mA_n or M_mB_n respectively) then the properties are also modified in the same way on passing through a series of intermediate compounds, $M_mA_{n-1}B$, $M_mA_{n-2}B_2, \ldots, M_mA_2B_{n-2}$, M_mA_1 B_{n-1}.

With the assumptions of the linear dependence of property Y on the number of substitutions and that the two single ligand complexes M_mA_n and M_mB_n are reference compounds, the actual values for the mixed complexes are given by eqn. (1) which in some ways follows the model for the "ideal" behaviour for colligative properties of solutions.

$$\begin{aligned} Y_{M_mA_aB_b} &= Y_{M_mA_n} + \Delta Y b/n \\ &= Y_{M_mB_n} + \Delta Y' a/n \qquad (1) \\ \Delta Y = -\Delta Y' &= Y_{M_mB_n} - Y_{M_mA_n} \end{aligned}$$

Although the two models are similar in their formalism, they differ considerably from each other, one being a function of a discrete variable—the number of substitutions—and hence undifferentiable, the other a function of a continuous variable.

EXPERIMENTAL EVIDENCE

During long-running investigations on complex formation in aqueous solutions in systems containing two or three different ligands, the free energy, enthalpy and entropy changes for mixed mononuclear $(m = 1)$ complex equilibria of Ag(I) [1–6] and Cd(II) [7, 8] have been obtained. The whole set of data is homogeneous for temperature $(\theta = 25°\text{C})$ and ionic strength ($\mu = 1$ for KNO_3) and is suitable for being analyzed according to the above outlines. In the present article the free energy, enthalpy and entropy changes for the overall and/or stepwise complex equilibria shown in eqn. (2) are considered.

The diagrams in Fig. 1 refer to one-ligand complex equilibria in aqueous solutions between Ag(I) and SCN−, SCN_2H_4, $S_2O_3^{2-}$, Cl^-, Br^-, I^-, NH_3; or between Cd(II) and SCN_2H_4, $S_2O_3^{2-}$, Cl^-, Br^-, I^-, NO_2^-. The data for AgL (L = halide or SCN^-) are pertinent to the homogeneous equilibria $Ag(I) + L \rightleftharpoons AgL$ where AgL is in solution and do not refer to solid–solution equilibria involving AgL precipitates. On the right-hand side of each diagram in Fig. 1 the highest coordinated complex found in the cited references is reported; on the left-hand side of Fig. 1 the solvated metal ion, whose complexation equilibria according to the reaction $M + 0L \rightleftharpoons M$ entails $\Delta G = \Delta H = \Delta S = 0$, regardless of the nature of acceptor or donor.

The diagrams in Fig. 2 refer to the complex with coordination level $n = 2$. The starting and ending species are simple ligand complexes. The reported transformation occurs in two successive steps (eqn. (2)), passing through a single intermediate.

$$MA_2 \xrightarrow[-A]{+B} MAB \xrightarrow[-A]{+B} MB_2 \qquad (2)$$

The whole set of available data has been systematized in subsets of reactions of the same substratum with different entering ligands.

In Fig. 3 single intermediate transformations are shown, referring to three-coordinated complexes of Ag(I). The processes on the abscissa can be schematized as in eqn. (3).

$$\text{Sub–}A_2 \xrightarrow[-A]{+B} \text{Sub–}AB \xrightarrow[-A]{+B} \text{Sub–}B_2 \qquad (3)$$

Lastly, in Fig. 4 four-step transformations (two intermediates) for complexes with coordination level $n = 3$ are shown.

COMMENTS

By mere inspection of the diagrams two obvious features are seen.

(i) The smooth pattern of the free energy changes in comparison with the articulate behaviour of ΔH or ΔS which exert each-other a sort of mutual compensation. Previous articles [9] have been devoted to this and it is not discussed here.

(ii) In spite of agreement being found in some cases between experimental and calculated (by the linear model) values, owing to the rarity of such agreement, and taking into account the fact that the different dependences on temperature of the different complexes makes those rare cases less meaningful, the agreement with the model cannot be considered as a general rule.

The divergence between calculated and experimental values originates from at least three different sources.

The first source is in the structure of the model itself, the connections

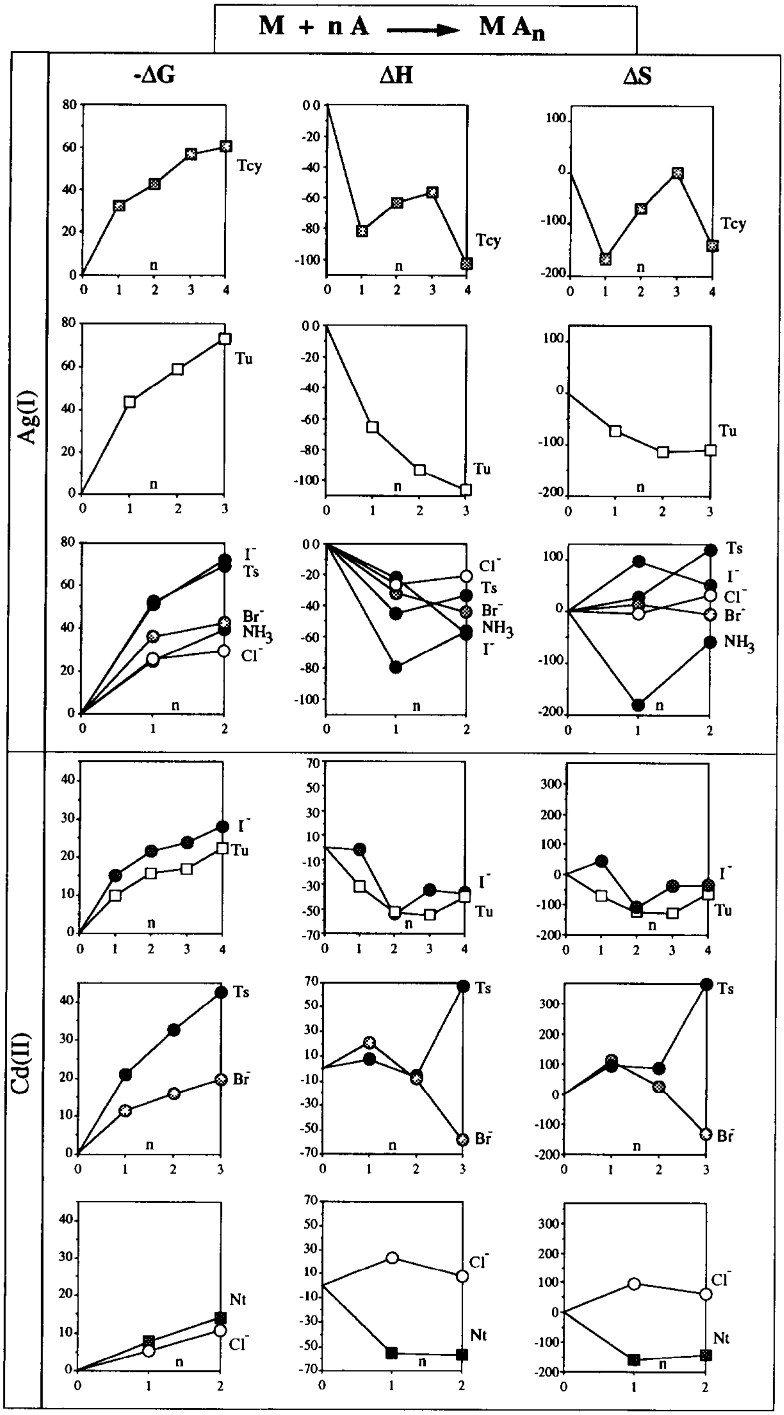

Fig. 1. Free energy, enthalpy and entropy change patterns (as kJ mol^{-1}, kJ mol^{-1} and J mol^{-1} K^{-1} respectively) for overall complex formation reactions of Ag(I) and Cd(II) with various ligands in relation to the coordination number n. (θ = 25°C, ionic strength μ = 1 for KNO_3).

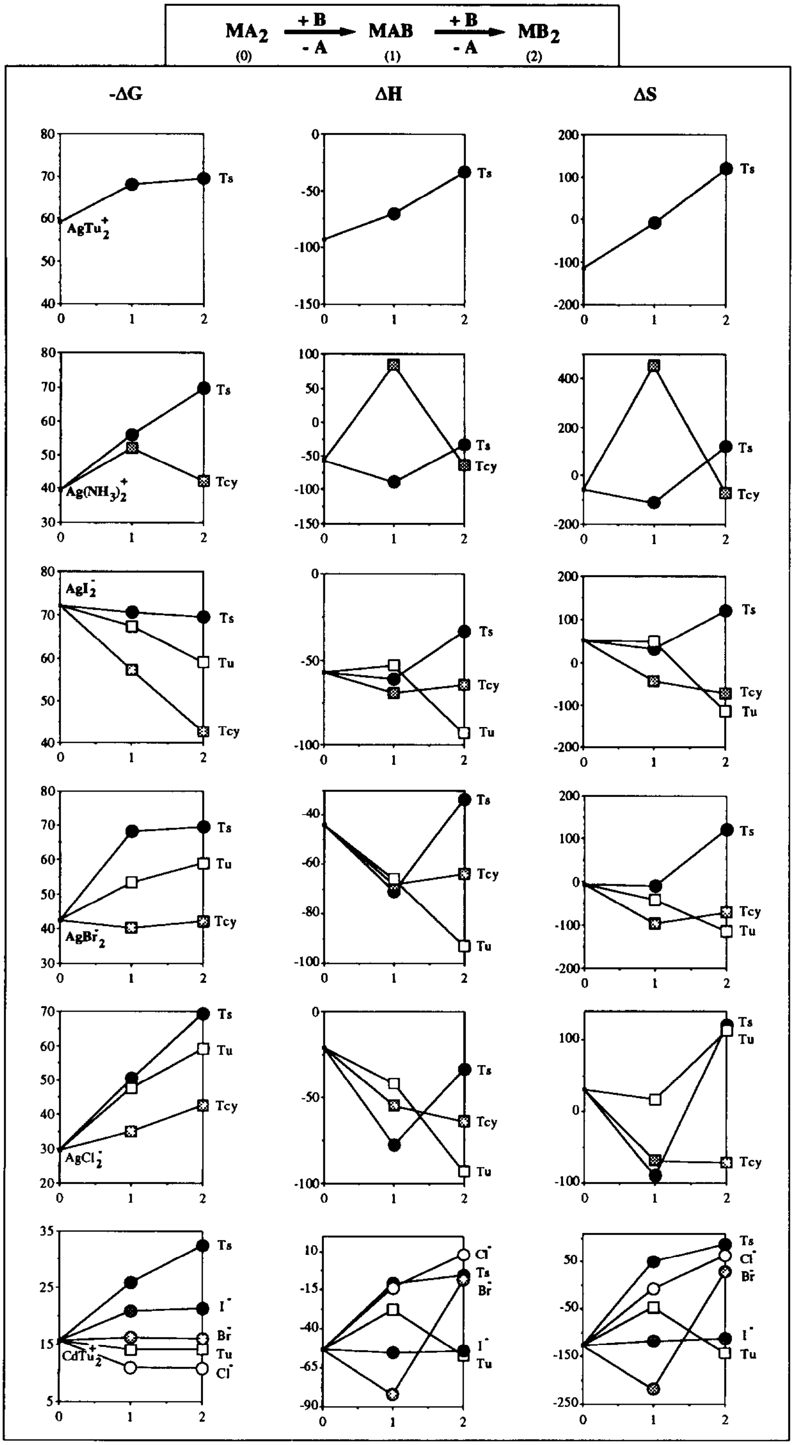

Fig. 2. Free energy, enthalpy and entorpy change patterns (as kJ mol^{-1}, kJ mol^{-1} and J $\mathrm{mol}^{-1}\,\mathrm{K}^{-1}$ respectively) for two-step ligand displacement reactions of dicoordinated complex Ag(I) or Cd(II) substrata with various entering ligands. ($\theta = 25°\mathrm{C}$, ionic strength $\mu = 1$ for KNO_3).

among the various terms of the series being "forced" along the pathway. implicit in the model. For linear models, the changes of the dependent and independent variables are mutually proportional; in other words, the whole change ΔY is uniformly distributed over the whole corresponding ΔX range.

The second source is related to the terms of the series used as the basis for quantifying the assumed model. The (subjective) selection of the extremes of the diagrams (MA_n and MB_n in Figs. 1–4) leads to a well defined ranked sequence between estimated and experimental values. Different selections lead to different sequences.

A third source is the fact that each complex is an individual entity upon which exclusive factors intervene which often are totally absent in others

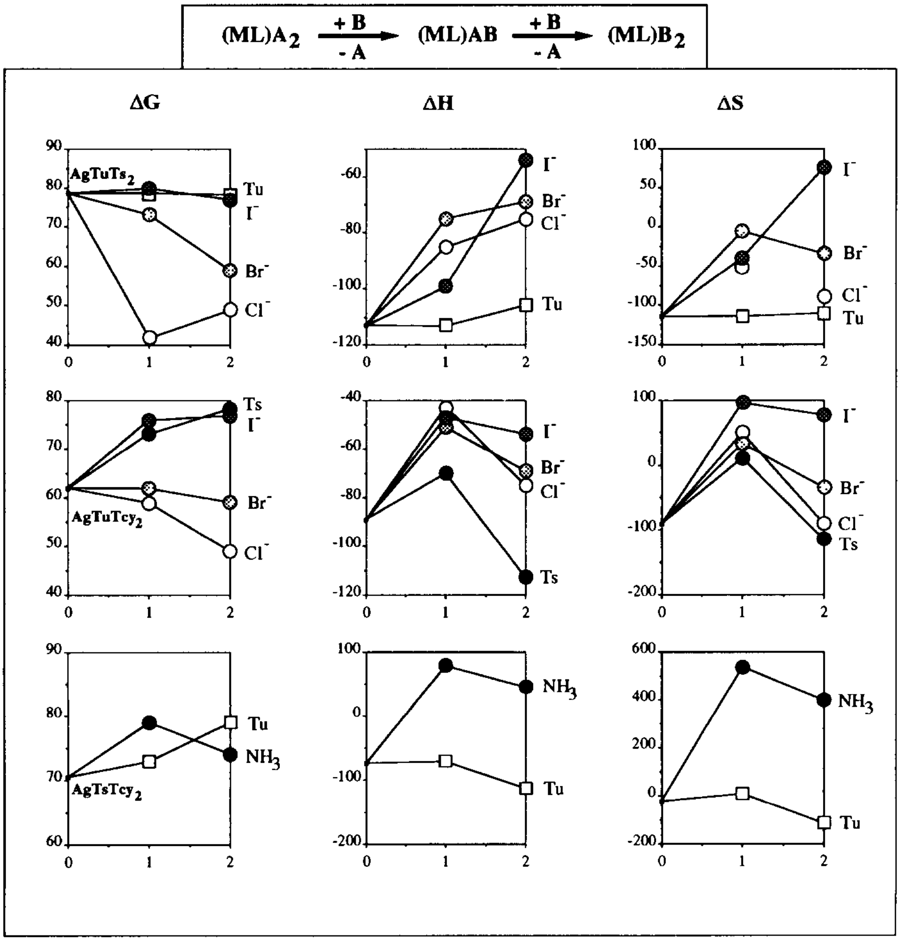

Fig. 3. Free energy, enthalpy and enthropy change patterns (as kJ mol^{-1}, kJ mol^{-1} and J mol^{-1} K^{-1} respectively) for two-step ligand displacement reactions of three-coordinated Ag(I) substrata with various ligands. ($\theta = 25°C$, ionic strength $\mu = 1$ for KNO_3).

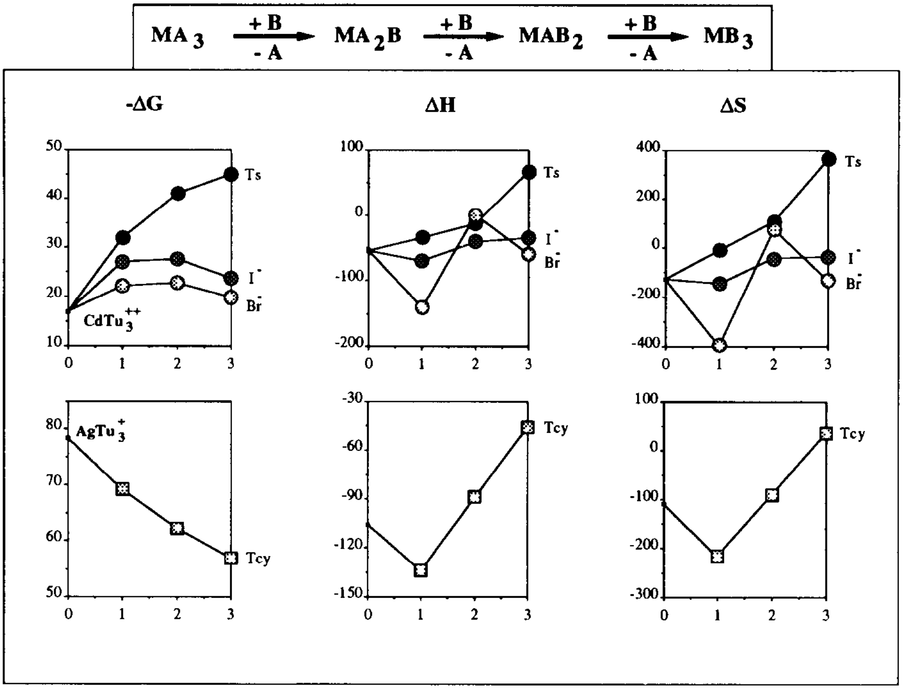

Fig. 4. Free energy, enthalpy and entropy change patterns (as kJ mol^{-1}, kJ mol^{-1} and J mol^{-1} K^{-1} respectively) for four-step ligand dispacement reactions of three-coordinated complexes.

(specific factors operate on MA_2 which are not active for MA, MA_3, MAB or any other complex). These factors cannot be identified by interpolating or extrapolating techniques, but only by means of specific investigations, hence, in principle, the properties of a complex cannot be deduced from the properties of its single separated components [9, 10].

For these reasons a suitable model for the properties of a series of complexes can be built up only a posteriori; the model will have meaning for data reduction, will be descriptive but not predictive and, of course, at this point all the terms are perfectly fitted to the model.

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