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Simple Relations between Enthalpies of Complexation, Stability Constants and Metal Cation Radii

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For the formation of 1:1 complexes between a given ligand and several metal ions, two new relationships are reported:

$\Delta H_1 = b_2r^{-2} + b_4r^{-4}$

and

$\log K_1 = d_2r^{-2} + d_4r^{-4}$,

where ΔH_1, $\log K_1$ *and* r *are the enthalpies of complexation, stability constants and cation radii respectively. The parameters in these equations are determined for a number of O and N donor ligands. The form of the equations is justified.*

Introduction

Various attempts have been made to relate stability constants of metal ion–ligand complexes, and enthalpies of complexation, to properties of the cations [1–4]. Multiparametric correlations of these quantities have also been reported [5–7]. The present work describes two new relations between (a) enthalpies of complexation and cation radii, and (b) stability constants and cation radii. These equations are based on an analysis of the various factors affecting the magnitudes of the thermodynamic functions of complexation. The analysis was applied to the formation in aqueous solution of the 1:1 complexes between pyridine and Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}, and between ammonia and the same metal ions. Earlier work on the theoretical calculation of stability constants involving organic ligands appears to have been limited to anionic ligands [8].

The Models and the Calculations

The models and the methods of calculation will be described very briefly, as it is beyond the scope of this paper to give details. The metal ions are regarded as charged conducting spheres, pyridine as an isotropically polarizable sphere with a permanent off-set dipole, and ammonia is given its standard geometry [9]. The model for pyridine is calibrated in the manner done for water in a study of hydration of alkali metal cations [10].

The thermodynamic functions for the complex formation reactions in solution are related to the corresponding quantities for the gas phase reaction and the various hydration and vaporization functions by Cycle I.

$$\begin{tikzcd}
M(H_2O)_6^{2+}(g) & +\ L(g) \arrow[r, "\Delta Y_{gpc}"] & M(H_2O)_5L^{2+}(g) \arrow[d, "\Delta Y''_{h(C)}"] & +\ H_2O(g \arrow[d, "-\Delta Y_{vap}"] \\
M(H_2O)_6^{2+}(aq) \arrow[u, "-\Delta Y'_{h(C)}"] & +\ L(aq) \arrow[u, "-\Delta Y_{h(L)}"] \arrow[r, "\Delta Y_{soln}"] & M(H_2O)_5L^{2+}(aq) & +\ H_2O(a
\end{tikzcd}$$

Cycle I

where ΔY is ΔH, ΔS or ΔG of the process indicated by the subscripts, *viz.*, soln: complex formation in solution; gpc: gas phase complexation; h(C): transfer of $M(H_2O)_6^{2+}$ (g) or $M(H_2O)_5L^{2+}$ (g) to aqueous solution; vap: vaporization; h(L): hydration of the ligand L.

The enthalpy changes ΔH_{gpc} are given by:

$$\Delta H_{gpc} = \Delta E + \frac{h}{2}\Delta\sum_i \nu_i + RT^2\left[\frac{\partial \ln q'}{\partial T}\right]_P + RTV\left[\frac{\partial \ln q'}{\partial V}\right]_T, \qquad (1)$$

where ΔE is the change in potential energy at absolute zero, $h/2\Delta\sum_i\nu_i$ is the change in zero point vibrational energy, and q' is the ratio of the products of the translational, rotational and vibrational partition functions for the products and the reactants. ΔE is computed from the ion–dipole, ion–induced dipole and London attractions, as well as the lateral and the inverse twelfth repulsions. For pyridine, the repul-

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TABLE I. Relative Enthalpies, Free Energies and Stability Constants for the Pyridine Complexes.

	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
ΔH_1(rel)	1	–	–	1.125	1.250	1.084
ΔH_{calc}(rel)	1	1.155	1.168	1.255	1.280	1.149
$\log K_1$(rel)	1	–	–	1.145	1.322	1.118
ΔG_{calc}(rel)	1	1.143	1.154	1.234	1.251	1.143

sion constants were obtained by minimising ΔE with respect to the ion–ligand distance. For ammonia, the repulsion constants were determined independently [11] and then scaled to fit the calculated enthalpy of hydration of the Ni(II) ion to the experimental [12] enthalpy. Crystal field stabilization energies were taken into account as was the Jahn–Teller stabilization of the copper(II) complexes. The partition functions and entropy changes are obtained by standard statistical mechanical methods. Other terms considered are Born charging, cavitation and formation of the structure breaking regions around the complexes in aqueous solution. Water is treated by the appropriate model according to whether pyridine or ammonia complexes are considered.

The Goldschmidt crystal radii [13] of the ions are used, except for Cu(II), for which an apparent axial radius of 100 pm and an apparent equatorial radius of 75 pm are employed. For the ions, the polarizabilities [14, 15], ionization potentials [16] and d-orbital splittings [17–20] are obtained from the literature. Jørgensen's factorization [21] and the rule of average environment [22] are employed to estimate the crystal field stabilization energies of the complexes. For the pyridine complexes, the properties of water and pyridine are as far as possible the experimental values [10, 23–26]. For the ammonia complexes, atomic polarizabilities [27, 28], experimental ionization potentials [24] and moments of inertia computed from the standard geometries [9] are used. *Ab initio* STO-3G [29] electron populations are employed. Experimental enthalpies and entropies of hydration [30] of the ligands are used.

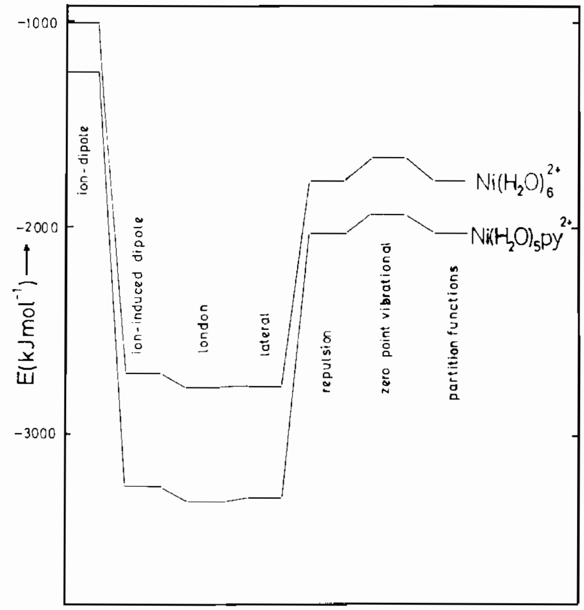

Fig. 1. Components of ΔH_{gpc} for $Ni(H_2O)_6^{2+}$ and $Ni(H_2O)_5$-py^{2+}.

Results and Discussion

Solution Phase Complexation Reactions of Pyridine and Ammonia with the Cations

The calculated free energies and enthalpies agree with the Irving–Williams series for the pyridine complexes. Taking the values for the Mn(II) complex as unity, a plot of the relative experimental enthalpy changes ΔH_1(rel) [31] against the relative calculated enthalpy changes ΔH_{calc}(rel) for the Mn(II), Ni(II), Cu(II) and Zn(II) complexes is a straight line:

$$\Delta H_1(\text{rel}) = 0.251 + 0.738\ \Delta H_{calc}(\text{rel}), \tag{2}$$

correlation coefficient = 0.903. Similarly, for the stability constants:

$$\log K_1(\text{rel}) = -0.0157 + 1.004\ \Delta G_{calc}(\text{rel}), \tag{3}$$

correlation coefficient = 0.868. Correcting the experimental stability constants to zero ionic strength would be expected to influence equation (3) only slightly. The numerical results are given in Table I. The relative importance of the components of ΔH_{gpc} are shown in Fig. 1 for $Ni(H_2O)_5py^{2+}$ and $Ni(H_2O)_6^{2+}$, and Fig. 2 shows the variation of the components of ΔE with cation–ligand distance.

For the monoammine complexes, the order of stabilities is the same as the Irving–Williams series

TABLE II. Parameters for the Relations between Enthalpies, Stability Constants and Cation Radii.

Ligand	Quantity	Coefficient of r^{-2}	Coefficient of r^{-4}	Average relative error %
ammonia	ΔH_1	1.48×10^5	-1.55×10^9	5
	$\log K_1$	-2.00×10^4	2.37×10^8	8
pyridine	ΔH_1	-1.12×10^5	2.53×10^8	2
	$\log K_1$	-9.11×10^3	1.27×10^8	4
4-methylpyridine	$\log K_1$	-1.92×10^4	1.98×10^8	2
2-aminomethylpyridine	ΔH_1	-4.00×10^4	-1.05×10^9	1
	$\log K_1$	-4.59×10^4	5.53×10^8	3
2-(methylaminomethyl)pyridine	$\log K_1$	-4.78×10^4	5.66×10^8	2
2-hydroxymethylpyridine	$\log K_1$	-1.46×10^4	1.91×10^8	1
imidazole	ΔH_1	1.48×10^5	-1.76×10^9	4
	$\log K_1$	-2.14×10^4	2.50×10^8	8
2-methylimidazole	$\log K_1$	-1.82×10^4	2.08×10^8	6
4-methylimidazole	$\log K_1$	-1.34×10^4	2.01×10^8	6
8-aminoquinoline	$\log K_1$	-6.49×10^4	5.63×10^8	4
glycine	$\log K_1$	-1.01×10^4	3.15×10^8	6
aspartic acid	$\log K_1$	-3.00×10^3	2.87×10^8	2
oxalic acid	$\log K_1$	2.62×10^4	4.49×10^7	3
succinic acid	$\log K_1$	-1.02×10^4	1.50×10^8	4

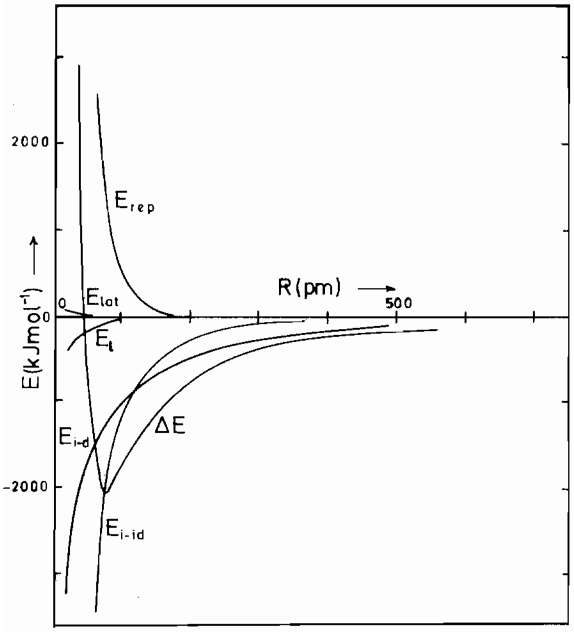

Fig. 2. Components of ΔE as functions of cation–ligand distance for $Ni(H_2O)_5py^{2+}$.

except for an inversion at Co(II) and Ni(II), this probably being due to as yet unresolved uncertainties in the repulsion energies. Such uncertainties may result from difficulties with both the repulsion equation and the determination of the repulsion constants. Some controversy surrounds the choice of repulsion formulae for ion–neutral interactions [28].

Correlations between the Thermodynamic Functions of Complexation in Solution and the Cation Radii

The ion–dipole, ion–induced dipole and inverse twelfth repulsion interactions are seen to be the dominant factors affecting the variation of enthalpies and free energies of complex formation between pyridine and the series of metal(II) ions. This suggests that the enthalpies and free energies can be expressed as functions of the cation radii. The detailed calculations showed that the repulsion terms are roughly constant at half the sums of the ion–dipole and the ion–induced dipole attractions. Taking into account the simple formulae for the two attractive terms, equations (4) and (5) are suggested:

$$\Delta H_1 = b_2 r^{-2} + b_4 r^{-4}, \tag{4}$$

and

$$\log K_1 = d_2 r^{-2} + d_4 r^{-4}. \tag{5}$$

The parameters b_2, b_4, d_2 and d_4 are determined by least squares fitting of the appropriate experimental enthalpy and stability data to the Goldschmidt cation radii. The parameters for equations (4) and (5) are collected in Table II, with enthalpies in kJ mol^{-1} and radii r in pm.

For equations such as (4) and (5) to be of value, they must be valid for extrapolation as well as for interpolation. It is expected that predictions will be successful only for metal ions in the same period and of the same charge as those for which the parameters were fitted, and which interact largely electrostatically with the ligands. Thus, using the parameters for ammonia given in Table II and the Goldschmidt radius of Ca^{2+}, $\log K_1$ for $CaNH_3^{2+}$ is calculated as 0.1. The reported experimental value is –0.2 [32]. Following Hancock and Marsicano [7] gives $\log K_1 = 1.70$ for $CrNH_3^{2+}$. Using the Pauling radius of Cr^{2+} and values from Table II gives $\log K_1 = 1.93$ for this complex. Since the Pauling radii are in general slightly smaller than the Goldschmidt radii, 1.93 is probably a little too big.

These equations have the advantage of not requiring a large data base for each ligand, while at the same time allowing reasonably accurate prediction of enthalpies and stability constants.

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