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Complexes of Tri- and Tetra-Protonated Forms of 1,4,8,12-Tetraazacyclopentadecane with Chloride, Nitrate, Iodate, and Sulfate Ions in Aqueous Media: I. Formation Constants, Thermodynamic Properties, and Bonding Mechanisms

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Abstract. Complexation stoichiometries and formation constants of tri- and tetra-protonated forms of 1,4,8,12-tetraazacyclopentadecane with NO_3^-, Cl^-, IO_3^- and SO_4^{2-} ions are determined by pH potentiometric and ^{13}C NMR spectrometric measurements. Estimates of ΔH and ΔS are obtained from the values of the temperature dependent formation constants and acid dissociation constants. All four anions form only 1 : 1 complexes with the triprotonated amine species. NO_3^- and Cl^- form 1 : 1 complexes only with the tetraprotonated amine, while IO_3^- and SO_4^{2-} form both 1 : 1 and 2 : 1 complexes. The complexation behavior is interpreted in terms of solvation and internal hydrogen bonding interactions.

Key words. Tetraazacyclopentadecane, macrocyclic polyamine, anion complexation.

1. Introduction

Protonated macrocyclic polyamines form complexes with anions in aqueous solutions. Although complexation reactions of this type have been discovered only within the last decade, numerous investigations have been reported [1, 2, 3]. In most cases, the complexation reactions involve 1 : 1 adducts of the anion with highly protonated forms of the polyamine, although some complexes involve 2 : 1 adducts [4, 5]. Anion complexes have been reported with tetra-, hexa-, and octaprotonated macrocyclic polyamine species [6]. Bonding in these complexes has usually been explained in terms of electrostatic and ionic-hydrogen bonding interactions. Solvent release mechanisms have also been cited as driving forces in these reactions [4, 5, 7].

It has generally been assumed that anions form complexes only with the highly protonated forms of large macrocyclic polyamines. These polyamines are usually at least tetra-protonated and contain six or more nitrogen atoms, although in a recent study, some of us report a sulfate complex with a 3+ polyamine species [5]. The purpose of this work is to elucidate the phenomena of polyamine-anion binding by examining a smaller member of the class of macrocyclic polyamine compounds, namely 1,4,8,12-tetraazacyclopentadecane, which will be abbreviated here as L. In the course of this work we determine anion complexing properties of H_4L^{4+} species

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with chloride, nitrate, iodate, and sulfate ions. We also find novel 1 : 1 complexes of monovalent anions with a triprotonated L species.

In order to obtain the experimental data necessary to characterize these complexation reactions and their stoichiometries we employ a pH potentiometric method which provides temperature dependent complexation constants and complexation enthalpies and entropies. These parameters provide a basis for interpretation of the complexation phenomena. A discussion of the experimental procedures and the additional experiments and calculations needed to justify the assumptions underlying this work appear in the following paper [8].

2. Experimental

2.1. pH POTENTIOMETRIC METHODOLOGY

In this work we estimate anion complexation constants for various L species. Complexation constants of protonated macrocyclic polyamine species with a variety of anions [4, 5, 7] have been obtained by using pH potentiometric methods to determine the difference between apparent acidity constants of the acid species in complexing and non-complexing media.

We illustrate this method by describing the complexation of sulfate with tri- and tetra-protonated species of hexacyclen (1,4,7,10,13,16-hexaazacyclooctadecane) [4]. This chemical system can be characterized as a monoprotic acid/base conjugate pair which we denote here by 4+/3+. The pH of this 4+/3+ buffer system depends on the acid dissociation constant and on the relative concentrations of the conjugate species. A complexing agent (SO_4^{2-}) added to the 4+/3+ solution forms complexes with both the 4+ and 3+ species. The relative concentration of the two uncomplexed species changes and therefore, the pH changes. By adding portions of a sulfate solution to the 4+/3+ buffer (a procedure which we will call 'titrating'), we generate a set of pH vs. composition data. This data together with the set of equations describing the equilibria can be analyzed by means of a nonlinear regression procedure which yields values and standard error estimates for the various equilibrium constants describing the acid-base and complexation reactions.

The acid-base behavior of L is much more complicated than that of hexacyclen. H_4L^{4+} is a weak tetraprotic acid. In a solution of ionic strength 0.5 M containing no complexing agents, the first and second pK values lie near 3.5 and 5.0 at 25°C, the third and fourth near 10. Since the pH values of all the solutions used in this work are below 6.0, the presence of the two basic species, HL^+ and L, can be ignored. However, because pK_2 is not far from pK_1, the H_4L^{4+}, H_3L^{3+}, and H_2L^{2+} species along with their possible anion complexes must all be included in the description of the solution equilibria. We have found that the equations required to describe these equilibria are as follows:

$$H_4L^{4+} = H_3L^{3+} + H^+ \tag{1}$$

$$K_1 = \frac{[H^+][H_3L^{3+}]}{[H_4L^{4+}]} \tag{1a}$$

$$H_3L^{3+} = H_2L^{2+} + H^+ \tag{2}$$

$$K_2 = \frac{[H^+][H_2L^{2+}]}{[H_3L^{3+}]} \qquad (2a)$$

$$H_3L^{3+} + X^{n-} = H_3LX^{3-n} \qquad (3)$$

$$K_{3X} = \frac{[H_3LX^{3-n}]}{[H_3L^{3+}][X^{n-}]} \qquad (3a)$$

$$H_4L^{4+} + X^{n-} = H_4LX^{4-n} \qquad (4)$$

$$K_{4X} = \frac{[H_4LX^{4-n}]}{[H_4L^{4+}][X^{n-}]} \qquad (4a)$$

$$H_4L^{4+} + 2X^{n-1} = H_4LX_2^{4-2n} \qquad (5)$$

$$K_{4X2} = \frac{[H_4LX_2^{4-2n}]}{[H_4L^{4+}][X^{n-}]^2} \qquad (5a)$$

In these equations, X^{n-} represents chloride, nitrate, iodate, or sulfate ions. The equilibrium constant expressions, along with mass and charge balance equations relevant to each solution, constitute a set of model equations. This model of the complexation behavior of L depends on several assumptions. First, H_2L^{2+} forms no complexes with the anions present in the solutions; second, protonated L species do not form complexes with the iodide ions used to set the ionic strength of the solutions; third, protonated L species do not form complexes involving two different types of anions; fourth, the hydroxide ion concentrations are negligible; and fifth, the solution volumes are additive.

Analysis of pH vs. composition data provides values for the complexation and acidity constants. However, the simple experimental method described for hexacyclen involving a single titration experiment is no longer sufficient. We must modify the experiment by obtaining pH vs. composition data for two separate buffer mixtures, whose initial pH values are approximately equal to pK_1 and pK_2 for L, respectively. The two data sets are analyzed simultaneously using nonlinear regression to provide values for complexation constants and acidity constants.

2.2. COMPLEXATION OF PROTONATED L SPECIES WITH CHLORIDE

In a typical experiment, a 40 mL solution containing 0.20 mmol L and 0.68 mmol HCl (2.0 mF H_4L^{4+} and 3.0 mF H_3L^{3+}) was adjusted to ionic strength 0.5 M with solid KI. (We will show below that the protonated L species do not form complexes with iodide.) This solution was titrated with 0.50 F KCl added in 3–5 mL portions. Seven pH vs. volume values were obtained. A second 40 mL mixture containing 0.19 mmol L and 0.48 mmol HCl (3.0 mF H_2L^{2+} and 2.0 mF H_3L^{3+}) and adjusted to an ionic strength of 0.5 M with solid KI was also titrated with 0.50 F KCl to provide seven more pH vs. volume data points. In each titration, the pH increased by approximately 0.1 pH unit after the addition of 25 mL of the KCl solution.

The model for this system consists of seven equations. Equations 1a, 2a, 3a and 4a describe two acid dissociations of H_4L^{4+} and the formation of 1 : 1 complexes of chloride with H^4L^{4+} and with H_3L^{3+}. The charge and mass balance equations are

$$4[H_4L^{4+}] + 3[H_3L^{3+}] + 3[H_4LCl^{3+}] + 2[H_2L^{2+}] + 2[H_3LCl^{2+}] + [K^+] + [H^+] = [I^-] + [Cl^-] \tag{6a}$$

$$F_{Cl} = [Cl^-] + [H_4LCl^{3+}] + [H_3LCl^{2+}] \tag{6b}$$

$$F_L = [H_4L^{4+}] + [H_3L^{3+}] + [H_4LCl^{3+}] + [H_3LCl^{2+}] + [H_2L^{2+}] \tag{6c}$$

In these equations F_x represents the analytical concentration of X^{n-}. The Levenberg–Marquardt nonlinear regression algorithm [9, 10, 11] was used to obtain values for the acid dissociation and complexation equilibrium constants. In this algorithm, initial guesses of the equilibrium constants are used in the model to determine hypothetical values of the pH, pH_{calc}. The values of the equilibrium constants are then varied systematically until a minimum value of the χ^2 statistic defined by

$$\chi^2 = \sum \frac{1}{\sigma^2} (pH_{obs} - pH_{calc})^2 \tag{7}$$

is obtained. In this equation, σ is an *a priori* estimate of the uncertainty in each pH measurement. In all the experiments, we take $\sigma = 0.002$ pH units, a conservative estimate. This choice is discussed more fully in the following paper [8].

Values of the parameters obtained in this way constitute best-fit estimates in the least-squares sense. Calculated χ^2 values should approximate the number of degrees of freedom of the system. In the present example, where 14 data points lead to four parameter values (pK_1, pK_2, K_{3Cl} and K_{4Cl}), this number is 10. Estimates of the standard errors are derived by standard statistical methods. The optimized values of the parameters and their standard error estimates are given in Table 1.

We note at this point that a satisfactory fit of a model of the equilibria to the experimental data was possible only if all seven species were included. The omission of either H_3LCl^{2+} or H_4LCl^{3+} led to values of χ^2 that were too large by several orders of magnitude.

2.3. COMPLEXATION OF PROTONATED L SPECIES WITH NITRATE

The experimental procedures proving the pH vs. composition data for determining the complexation with nitrate parallel those employed with chloride. However, there is one complication. The buffer mixtures involving L were prepared by pretitration with HCl. Consequently, each solution contained chloride which forms complexes with the H_4L^{4+} and H_3L^{3+} species. The model describing the titrations with KNO_3 consists of equations 1a and 2a describing the acid-base equilibria, equations 3a and 4a with $X^{n-} = NO_3^-$, and equations 3a and 4a with $X^{n-} = Cl^-$. Three mass balance equations include equation 6b and the following two equations:

$$F_{NO_3} = [NO_3^-] + [H_3L(NO_3)^{2+}] + [H_4L[NO_3)^{3+}] \tag{8a}$$

$$F_L = [H_4L^{4+}] + [H_3L^{3+}] + [H_4LCl^{3+}] + [H_3LCl^{2+}] + [H_4L(NO_3)^{3+}] + [H_2L(NO_3)^{2+}] \tag{8b}$$

Table I. Complexation constants for H_4L^{4+} and H_3L^{3+} with chloride, nitrate, iodate, and sulfate ions at various temperatures and ionic strengths.

Chloride Complexes

t, °C	Ionic Strength, M	K_{4Cl}	K_{3Cl}	χ^2	d.f.
14.7	0.5	1.43 ± 0.05[a]	0.65 ± 0.03	9.0	12
	0.5	1.55 ± 0.06[a]	0.66 ± 0.04	1.1	8
25.0	0.5	1.87 ± 0.06	0.72 ± 0.03	9.0	13
	0.5	1.94 ± 0.06	0.74 ± 0.03	4.7	8
	0.37	2.02 ± 0.08	0.79 ± 0.04	0.8	10
	0.25	2.53 ± 0.11	0.90 ± 0.06	0.2	10
	0.12	3.59 ± 0.22	1.07 ± 0.11	0.7	10
35.0	0.5	2.30 ± 0.06	0.86 ± 0.03	10.6	12
	0.5	2.35 ± 0.06	0.86 ± 0.03	12.3	12
	0.25	3.57 ± 0.13	1.18 ± 0.06	1.2	8
45.1	0.5	2.46 ± 0.06	0.82 ± 0.03	5.3	12
55.2	0.5	3.57 ± 0.17	1.04 ± 0.06	5.7	6
	0.5	3.50 ± 0.15	0.99 ± 0.04	7.4	8

Nitrate Complexes

t, °C	Ionic Strength, M	K_{4NO3}	K_{3NO3}	χ^2	d.f.
14.7	0.5[b]	0.56 ± 0.04	0.28 ± 0.03	3.4	10
25.0	0.5[b]	0.43 ± 0.04	0.31 ± 0.02	0.5	14
	0.5	0.39 ± 0.04	0.23 ± 0.03	0.5	8
	0.25	0.49 ± 0.08	0.26 ± 0.05	0.6	10
35.0	0.5	0.54 ± 0.05	0.25 ± 0.03	0.6	8
45.1	0.5	0.74 ± 0.05	0.24 ± 0.03	4.5	10
55.2	0.5	0.82 ± 0.06	0.33 ± 0.03	4.6	8

Iodate Complexes

t, °C	Ionic Strength, M	K_{4IO3}	K_{3IO3}	K^c_{4IO32}	χ^2	d.f.
14.7	0.5	29.7 ± 0.6	3.46 ± 0.07	109 ± 5	8.0	13
25.0	0.5	28.8 ± 0.6	3.66 ± 0.08	100 ± 5	3.7	14
	0.25	38.8 ± 1.1	4.24 ± 0.14	162 ± 18	0.8	14
35.0	0.5	30.0 ± 0.08	3.84 ± 0.08	92 ± 2	6.2	13
	0.25	40.3 ± 1.4	4.72 ± 0.17	171 ± 25	0.8	12
45.1	0.5	27.3 ± 0.7	3.22 ± 0.10	86 ± 2	1.2	15

Sulfate Complexes

t, °C	Ionic Strength, M	K_{4SO4}	K_{3SO4}	K^c_{4SO42}	χ^2	d.f.
14.7	0.5	71.4 ± 1.7	6.9 ± 0.2	761 ± 74	11.6	15
25.0	0.5	83.5 ± 1.9	7.3 ± 0.2	871 ± 81	11.9	14
	0.5	93.7 ± 2.1	8.1 ± 0.3	880 ± 113	0.8	17
35.0	0.5	94.7 ± 2.5	7.5 ± 0.2	1023 ± 126	6.6	14
45.1	0.5	110.2 ± 2.1	9.2 ± 0.3	1159 ± 113	6.0	14
55.2	0.5	155.8 ± 4.0	9.1 ± 0.3	1871 ± 275	2.8	12
	0.5	148.2 ± 3.5	9.7 ± 0.3	1315 ± 300	3.7	16

[a] Multiple entries at the same ionic strength represent results obtained in replicate experiments usually made with different stock buffer mixtures of L. Initial L concentrations varied between about 3 mF to 6 mF.

[b] Ionic strength of L buffer mixtures made up with NaI and titrated with 0.50 F $NaNO_3$.

[c] K_{4IO32} and K_{4SO42} represent overall formation constants for $H_4L(IO_3)_2^{2+}$ and $H_4L(SO_4)_2$ complexes, respectively.

The charge balance equation is:

$$
\begin{aligned}
&[K^+] + [H^+] + 4[H_4L^{4+}] + 3[H_3L^{3+}] + 2[H_2L^{2+}] \\
&\quad + 3[H_4LCl^{3+}] + 2[H_3LCl^{2+}] + 3[H_4L[NO_3)^{3+}] \\
&\quad + 2[H_3L(NO_3)^{2+}] = [NO_3^-] + [Cl^-] + [I^-] \qquad (8c)
\end{aligned}
$$

Values of pK_1 and pK_2, the complexation constants K_{4NO3} and K_{3NO3}, and their standard errors appear in Table I. In this analysis, the chloride complexation constants for 4+ and 3+ L species were fixed parameters obtained from the KCl titration experiments in which the chloride is the sole complexing anion. The presence of the chloride complexes had only a minor effect on the calculated values of nitrate complexation constants. However, failure to include chloride complexation led to unsatisfactorily large values of χ^2.

2.4. COMPLEXATION OF PROTONATED L SPECIES WITH IODATE

The ionic strength of the L buffers used to determine the iodate complexation constants could not be adjusted to 0.5 M with iodide. Instead, NaCl was used as the background electrolyte. The model equations consist of equations 1a and 2a; 3a and 4a with $X^{-n} = \mathrm{Cl}$; and equations 3a, 4a and 5a with $X^{-n} = IO_3^-$. The appropriate mass and charge balance equations analogous to those given earlier complete the description of the model.

The experimental methods were similar to those already described. An H_4L^{4+}/H_3L^{3+} buffer (at an ionic strength of 0.5 M in NaCl) was titrated with 0.50 F $NaIO_3$. The iodate concentrations ranged from 0.0 to ≈0.1 F and 8–10 data points were obtained. A second titration of a H_3L^{3+}/H_2L^{2+} buffer also made up in NaCl provided an additional 8–10 pH vs. composition values in the same range of iodate concentrations.

Iodate ions have weakly basic properties which might have resulted in the formation of appreciable amounts of HIO_3. To rule out this possibility we estimated pK for HIO_3 by titrating a solution containing 10.0 mF or 20.0 mF HCl (with an ionic strength of 0.5 M in NaCl) with 0.50 F $NaIO_3$. The pK values were sufficiently low (near 0.5 at 25°C) so that the formation of HIO_3 could be considered negligible.

The set of equilibrium constants and their estimated standard errors for these iodate experiments are given in Table I. As was the case for the NO_3^- analysis, the chloride complexation constants were fixed. The values of χ^2 listed in the table are comparable or less than the appropriate number of degrees of freedom, suggesting that the model accurately describes the chemical equilibria. As in the previous cases, the number of complexes included in the model is the minimum needed to fit the data.

2.5. COMPLEXATION OF PROTONATED L SPECIES WITH SULFATE

The experimental methods used here were again essentially the same described above. H_4L^{4+}/H_3L^{3+} and H_3L^{3+}/H_2L^{2+} buffer mixtures containing small amounts of chloride were adjusted to an ionic strength of 0.5 M with KI and titrated with 0.167 F K_2SO_4. The sulfate ion concentration varied between 0.0 and 0.04 F.

Table II. Temperature dependent acidity constants for bisulfate ion in 0.50 F KI medium.

t, °C	pK_2
14.7	$1.107^a \pm 0.004$
25.0	1.253 ± 0.003
35.0	1.352 ± 0.004
45.1	1.481 ± 0.003
55.2	1.616 ± 0.002

[a] Each entry represents the average of six to eight pK values obtained from each titration experiment.

In these experiments the presence of HSO_4^- cannot be neglected. In order to obtain values for its acid dissociation constant K we titrated 0.50 F KI solutions containing 10.0 mF or 20.0 mF HCl with 0.167 F K_2SO_4. Temperature-dependent pK values are listed in Table II. Each reported uncertainty represents the standard deviation of a set of six to eight pK values. Point-by-point pK estimates were randomly scattered and trend-free. The values listed in Table II are consistent with previous estimates.

The sulfate pK values and chloride complexation constants are fixed parameters in the nonliner regression analysis of the sulfate experiments. The model comprises an equilibrium constant expression for the dissociation of HSO_4^-, Equations 1a and 2a; Equations 3a, 4a, and 5a with $X^{n-} = SO_4^{2-}$, and Equations 3a and 4a with $X^{n-} = Cl^-$. The mass and charge balance equations, which now include HSO_4^-, are analogous to those given earlier. The results of the data analysis appear in Table I. Again, the model contains the minimum number of species required to fit the data.

This model does not include complexes with HSO_4^-. Some of these are indistinguishable from such complexes as $H_3L(SO_4)^+$, $H_4L(SO_4)^{2+}$, and $H_4L(SO_4)_2$ which have already been included in the model. However, 'super acid' complexes such as $H_5L(SO_4)_2^+$ (corresponding to $H_4L(SO_4)(HSO_4)^+$) would affect the analysis. The quality of fit obtained here, as indicated by the values of χ^2, indicates that higher bisulfate complexes, if they exist at all, are unimportant in these experiments. This conclusion is confirmed by conductometric titration experiments described in the following paper [8].

2.6. ΔH* AND ΔS* FOR COMPLEXATION AND ACID DISSOCIATION REACTIONS

The temperature dependent equilibrium constants in Tables I and III provide a basis for estimating the enthalpy and entropy for the various complexation reactions. We employ the well-known thermodynamic relations

$$\Delta G = -RT\ln K, \left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S, \quad \text{and} \quad \left(\frac{\partial(\Delta G/T)}{\partial(1/T)}\right)_P = \Delta H \qquad (9)$$

to calculate ΔH^* and ΔS^* for the reactions whose equilibrium constants are shown in Tables I and III. The asterisk refers to a standard state at ionic strength 0.50 M.

Table III. Temperature dependent pK_1 and pK_2 values for H_4L^{4+} at various ionic strengths.

t, °C	pK_1	pK_2	I, M
14.7	3.865[a]	5.415[a]	0.50
25.0	3.331	5.011	0.12
	3.482	5.114	0.25
	3.582	5.184	0.37
	3.648	5.229	0.50
35.0	3.276	4.933	0.25
	3.442	5.051	0.50
45.1	3.256	4.896	0.50
55.2	3.060	4.714	0.50

[a] Entries represent average values taken from several experiments. Standard deviations of replicate results were ±0.005 pH units or less.

Values of ΔH^* and ΔS^* together with corresponding values for hexacyclen appear in Table IV. Plots of ΔG^* vs. T and $\Delta G^*/T$ vs. $1/T$ are quite linear. The scatter of the data about the regression line calculated for each plot is random and consistent with the precision of the individual equilibrium constant values. The uncertainties given in Table IV are standard error estimates based on this scatter.

Table IV. Complexation and acid dissociation enthalpies and entropies for protonated L species and corresponding values for hexacyclen reactions.

	Z = 1,4,8,12-Tetraazacyclopentadecane		Z = Hexacyclen [4,5,7]	
	$I = 0.50$ M		$I = 0.22$ M	
Reaction	ΔH^*, kcal mol^{-1}	ΔS^*, cal mol^{-1} K^{-1}	ΔH^*, kcal mol^{-1}	ΔS^*, cal mol^{-1} K^{-1}
$H_4Z^{4+} + Cl^- = H_4ZCl^{3+}$	3.9 ± 0.3[a]	14.2 ± 0.8	4.9 ± 0.6	24 ± 2
$H_3Z^{3+} + Cl^- = H_3ZCl^{2+}$	2.0 ± 0.2	6.0 ± 0.8		
$H_4Z^{4+} + NO_3^- = H_4Z(NO_3)^{3+}$	3.0 ± 1.2	9 ± 4	−0.4 ± 0.6	12 ± 2
$H_3Z^{3+} + NO_3^- = H_3Z(NO_3)^{2+}$	0.5 ± 0.9	1 ± 3		
$H_4Z^{4+} + IO_3^- = H_4Z(IO_3)^{3+}$	−0.4 ± 0.3	5.4 ± 1.2	1.3 ± 0.1	17.1 ± 0.5
$H_4Z(IO_3)^{3+} + IO_3^- = H_4Z(IO_3)_2^{2+}$	−1.1 ± 0.4	−1.1 ± 1.2	−2.3 ± 0.3	−2.8 ± 1.1
$H_4Z^{4+}2IO_3^- = H_4Z(IO_3)_2^{2+}$	−1.5 ± 0.1	4.3 ± 0.1	−1.0	15
$H_3Z^{3+} + IO_3^- = H_3Z(IO_3)^{2+}$	−0.3 ± 0.7	1 ± 2		
$H_4Z^{4+} + SO_4^{2-} = H_4Z(SO_4)^{2+}$	3.4 ± 0.4	20.3 ± 1.4	5.6 ± 0.2	37.8 ± 0.6
$H_4Z(SO_4)^{2+} + SO_4^{2-} = H_4Z(SO_4)_2$	0.1 ± 0.6	4.9 ± 1.8	2.1 ± 0.8	15.6 ± 2.4
$H_4Z^{4+} + 2SO_4^{2-} = H_4Z(SO_4)_2$	3.5 ± 0.6	25.3 ± 2.2	7.7	53
$H_3Z^{3+} + SO_4^{2-} = H_3Z(SO_4)^+$	1.5 ± 0.3	9.0 ± 1.0	2.8 ± 0.9	16.7 ± 2.8
$H_4Z^{4+} = H_3Z^{3+} + H^+$	8.6 ± 0.1	12.0 ± 0.3	14.0 ± 0.1	32.0 ± 0.3
$H_3Z^{3+} = H_2Z^{2+} + H^+$	7.4 ± 0.2	1.0 ± 0.5		

[a] Uncertainties are standard error estimates derived from the scatter of points about van Hoff plots.

3. Discussion

A comparison of the present results with those obtained previously for the complexation of various monoanions and sulfate ion with protonated hexacyclen species shows both differences and similarities. The most notable difference is that chloride, nitrate, and iodate form readily detectable complexes with H_3L^{3+}, while the corresponding complexes with triprontonated hexacyclen species were not detected. Indeed, we were unable to find any reports of complexes of tripositive macrocyclic amine with monovalent anions. Since the H_3L^{3+} complexes with monoanions reported here are quite weak, it seemed possible that similar weak complexes are formed in hexacyclen mixtures but were simply not detected.

3.1. COMPARISONS OF ANION COMPLEXES OF 3+ HEXACYCLEN WITH THOSE OF H_3L^{3+}

In order to investigate this possibility, we generated hypothetical pH vs. composition data assuming that both the tetra- and triprotonated hexacyclen species form 1 : 1 chloride complexes. We set $K_{4\text{Cl}}$, the chloride complexation constant with tetraprotonated hexacyclen, equal to 30, a value approximately equal to its value at 25°C in a solution of ionic strength 0.44 M [7]. We performed three calculations in which $K_{3\text{Cl}}$ was set equal to 1.0, 0.5, and 0.2, respectively. The hypothetical pH vs. composition data were analyzed using the methods employed in the earlier work. We assumed that no chloride complexes of 3+ hexacyclen were present, defined Z as

$$Z = \frac{1}{[\text{H}^+]}\left(\frac{C_\text{L} + [\text{H}^+]}{C_\text{L} - [\text{H}^+]}\right) = \frac{1}{K_{\text{a}3}}\left(\frac{\gamma_3\gamma_\text{H}}{\gamma_4}\right)\left(1 + \frac{\gamma_4\gamma_\text{Cl}}{\gamma_3'}K_\text{Cl}[\text{Cl}^-]\right) \tag{10}$$

and plotted Z versus $[\text{Cl}^-]$. In this equation, C_L is the analytical concentration of hexacyclen; $K_{\text{a}3}$ is the acid dissociation constant of the 4+ species; and the various γs are ionic activity coefficients, all of which are constants at a fixed ionic strength.

If the graph of Z vs. $[\text{Cl}^-]$ were linear over the range of concentrations used in the earlier work, then it is possible that weak 3+ hexacyclen-chloride complexes exist but were simply not detected. However, if the regression analysis of the hypothetical data shows large uncertainties in the slope and intercept indicating significant curvature, then we would conclude that such complexes were not present.

The hypothetical pH vs. composition data consisted of seven points at chloride concentrations roughly equally spaced between 0.04 M and 0.3 M. These concentrations are similar to those used previously [7]. When $K_{3\text{Cl}} = 1.0$, the plot of Z vs. $[\text{Cl}^-]$ was visibly curved. The regression analysis gave standard error estimates of the slope and intercept equal to about 3% and 9% of their respective values. The error estimates from regression based on the actual experimental data were 0.6% and 2.5% of the values of the slope and intercept. Clearly, the original experimental results are inconsistent with the presence of a chloride complex with tripotonated hexacyclen with $K_{3\text{Cl}}$ of 1.0 or larger.

When $K_{3\text{Cl}}$ was set equal to 0.5 the standard error estimates for the slope and intercept were also unsatisfactorily large. However, the standard error estimates using $K_{3Cl} = 0.2$ were only 1% and 3% of the values of the slope and intercept. Because these uncertainties are comparable with those actually observed, we conclude that if chloride complexes of triprotonated hexacyclen exist at all, they are very weak with formation constants of 0.2 or less. It is clear that the interactions of chloride with H_3L^{3+} are significantly stronger than those with the corresponding hexacyclen species.

The situation is similar for iodate. An iodate complex of triprotonated hexacyclen of comparable strength to $H_3L(IO_3)^{2+}$ ($K_{3IO3} = 4.2$ at 25°C and $I = 0.25$ M) would have been readily detected in our earlier work [4]. For nitrate, however, we are unable to draw the same conclusion. The value obtained here for K_{3NO3} is only about 0.26 at 25°C and $I = 0.25$ M. A similar or slightly weaker hexacyclen complex might well have gone undetected. Nevertheless, it seems reasonable to conclude that interactions of monoanions with H_3L^{3+} are appreciably stronger than the corresponding reactions with hexacyclen.

3.2. COMPARISONS OF ANION COMPLEXES OF 4+ HEXACYCLEN WITH THOSE OF H_4L^{4+}

The behavior for the tetrapronated complexes is opposite: the hexacyclen complexes with the monanions are much stronger than the corresponding H_4L^{4+} complexes. For example, 1 : 1 complexation constants for chloride, nitrate, and iodate ions with H_4L^{4+} are 2.5, 0.49, and 39 at 25°C and $I = 0.25$ M. At the same temperature and at $I = 0.22$ M, the corresponding complexes with tetraprotonated hexacyclen have formation constants of 63, 2.3×10^2, and 6.0×10^2 respectively. Not only is the H_4L^{4+} affinity for these monovalent anions much weaker than that of tetraprotonated hexacyclen, the order of complexation strengths is different as well. For the H_4L^{4+} complexation strengths, $IO_3^- > Cl^- > NO_3^-$; for hexacyclen, Cl^- and NO_3^- are interchanged.

Comparing complexation constants for sulfate with L and hexacyclen species is more difficult because hexacyclen data are available only at relatively low ionic strengths while the sulfate complexation data with L species pertain to an ionic strength of 0.50 M. The empirical ionic activity coefficient correlations of Equations 9 and 10 are based on data up to an ionic strength of 0.44 M and may be taken as accurate only to that value. Nevertheless, we will use these correlations to obtain approximate ionic activity coefficients for $I = 0.5$ M.

In order to adjust the hexacyclen constants to $I = 0.5$ M we require ionic activity coefficient estimates for H_2J^{2+}, $H_3J(SO_4)^+$, $H_4J(SO_4)^{2+}$, and SO_4^{2-} where J denotes hexacyclen. These are obtained from the Debye–Huckel equation using ion sizes of 1.2 and 0.3 nm for the hexacyclen species and SO_4^{2-}, respectively. The ionic activity coefficient for uncharged $H_4J(SO_4)_2$ is set equal to 1.0. Estimates of ionic activity coefficients at $I = 0.22$ M and $I = 0.5$ M, along with hexacyclen complexation constants with sulfate given in Reference 5, provide the complexation constants required for comparison with present values. At 25°C and $I = 0.5$ M, the H_3J^{3+} complexation constant with SO_4^{2-} is 21, compared with the $H_3L(SO_4)^+$ formation constant of about 8. At the same temperature and ionic strength, the formation constant for $H_4J(SO_4)^{2+}$ is 2.8×10^3, significantly larger than the $H_4L(SO_4)^{2+}$ formation constant of about 90 (83.5 and 93.7 in Table I). Finally, our estimate for the stepwise addition $H_4J(SO_4)^{2+} + SO_4^{2-} = H_4J(SO_4)_2$ is 46 compared to a value of about 10 ($= K_{4SO42}/K_{4SO4}$ in Table I) for the corresponding reaction with L. In all cases, the hexacyclen complex is stronger than the corresponding L complex.

3.3. COMPARISON OF ANION COMPLEXES OF 4+ HEXACYCLEN AND H_4 L^{4+} – KINETIC BEHAVIOR

The protonated hexacyclen and L species complexes also differ in their kinetic behavior. Hexacyclen complexations are sluggish even on the slow time scale of pH and conductometric titrimetry, and the complexes appear inert on the NMR time scale. For example, in certain pH ranges, chloride solutions of hexacyclen (containing H_4JCl^{3+}, H_4J^{4+}, and H_3J^{3+}) show two well-defined ^{13}C NMR resonances despite the fact that all twelve hexacyclen carbon atoms are NMR equivalent. One of the peaks shifts with the pH value, and corresponds to the concentration weighted average of intrinsic resonances of uncomplexed triprotonated and tetraprotonated hexacyclen species. The second ^{13}C NMR peak position is pH independent and represents the NMR resonance of the chloride complex of tetraprotonated hexacyclen. The half-widths of these peaks appear to be pH independent suggesting that the rate of chloride ion exchange is slow. In contrast to this behavior, the complexation reactions involving L are fast; none of the ^{13}C NMR spectra of L solutions measured here showed line splitting or detectable broadening. The ^{13}C NMR studies of L are described in the following paper.

3.4. SIMILARITIES BETWEEN ANION COMPLEXES OF HEXACYCLEN AND L

We now discuss the similarities between complexation reactions involving L and hexacyclen. Both tetraprotonated amines form 1 : 1 and 1 : 2 complexes with sulfate and iodate ions, but only 1 : 1 complexes with chloride and nitrate. An analysis of this behavior provides insight into the mechanism of these reactions.

We begin with a brief review of our earlier interpretation of hexacyclen complexations of anions. The interactions fall into three classes: (a) enthalpy-driven reactions having only small negative entropy changes and appearing to involve simple ion association phenomena (for example, ternary complex formation with iodate: $H_4J(IO_3)^{3+} + IO_3^- = H_4J(IO_3)_2^{2+}$); (b) entropy-driven reactions with significantly positive enthalpy changes, which we ascribe to extensive inner sphere solvent loss from the tetraprotonated amine (complexation with chloride and benzenesulfonate); and (c) entropy-driven reactions with ΔH^* near zero, corresponding to solvent mediated complexations (complexation with nitrate and iodate).

This classification scheme is based on three observations. First, tetraprotonated hexacyclen has unusual dissociation properties. While the H_4J^{4+} acidity constant at 25°C is similar to that of other tetraprotonated polyamines, the values of ΔH^* and ΔS^* are substantially different, with $\Delta H^* = +14\ \text{kcal mol}^{-1}$ and $\Delta S^* = 32\ \text{cal mol}^{-1}\ \text{K}^{-1}$ compared with values near to $+8\ \text{kcal mol}^{-1}$ and 0 to $+15\ \text{cal mol}^{-1}\ \text{K}^{-1}$ respectively for a variety of 4+ ammonium acids. We ascribe these differences to an unusual enhancement of solvent ordering around tetraprotonated hexacyclen.

Second, the ^{13}C NMR properties of hexacyclen mentioned earlier, support the existence of an extensive and relatively inert solvent sphere around 4+ hexacyclen. Over a range of pH values, the ^{13}C NMR signals for the chloride complex of tetraprotonated hexacyclen and also the uncomplexed tri- and tetraprotonated hexacyclen equilibrium mixture each consist of only one resonance line. Thus, all 12 carbon atoms in the chloride complex rapidly interchange on the NMR time scale. This result suggests a rapid exchange of anion binding sites and of protonation sites within the solvent cage of the complex. Similarly, the acid-base conjugate pair which constitutes the uncomplexed hexacyclen mixture gives rise to a single resonance line because the solvent cage surrounding these species is readily penetrated by hydrogen ions.

Third, there is a connection between X-ray crystallographic analysis and the thermodynamic properties of hexacyclen complexations with nitrate and chloride ions. In the solid phase, a water molecule intercedes between nitrate and 4+ hexacyclen while chloride ions interact directly with ammonium sites of hexacyclen. The chloride complexation is more endothermic and entropy producing than the nitrate complexation by about 5 kcal mol^{-1} and 12 cal mol^{-1} K^{-1}, respectively. The large positive entropy change upon chloride complexation probably results from the loss of more solvating water molecules from the chloride complex than from the nitrate complex.

Thus, the three types of reactions of hexacyclen complexes with anions may be characterized in terms of the degree to which the hexacyclen solution sphere is penetrated and/or expelled by the complexing anions. The same analysis applies to anion complexes of L.

3.5. THERMODYNAMIC PROPERTIES AND BONDING MECHANISMS OF ANION COMPLEXES OF L SPECIES

ΔH^* and ΔS^* for the acid dissociation reaction in noncomplexing media of H_4L^{4+} are equal to +8.6 kcal mol^{-1} and +12.0 cal mol^{-1} K^{-1}, respectively (Table IV), compared with previous values of $\Delta H^* = 7.7$ kcal mol^{-1} and $\Delta S^* = 9.4$ cal mol^{-1} K^{-1} obtained using a KNO_3 solution with $I = 0.5$ M [12]. Because nitrate ions form complexes with both H_3L^{3+} and H_4L^{4+} species, the two sets of values are not directly comparable. Nevertheless, we can adjust the earlier values to account for nitrate complexations by using the values of ΔH^* and ΔS^* for these reactions which appear in Table IV. We estimate a dissociation enthalpy and entropy by well-known computational methods of thermodynamics. The results of these calculations are $\Delta H^* = 8.1$ kcal mol^{-1} and $\Delta S^* = 10.8$ cal mol^{-1} K^{-1} for the acid dissociation reaction of H_4L^{4+} in non-complexing media with $I = 0.5$ M. These values appear in reasonable agreement with the results obtained here.

We interpret these values as indicating a significantly smaller change in the solvation sphere of H_4L^{4+} upon acid dissociation than in the acid dissociation of tetraprotonated hexacyclen. ΔH^* and ΔS^* for H_4L^{4+} dissociation are about 5 kcal mol^{-1} and about 20 cal mol^{-1} K^{-1}, less positive than corresponding values for hexacyclen dissociation. (ΔH^* and ΔS^* for L and for hexacyclen dissociations refer to different ionic strength conditions. However, ΔH^* and ΔS^* are weak functions of the ionic strength, and we will ignore this difference.) The less positive

ΔH^* value for H_4L^{4+} compared with hexacyclen dissociation indicates a lesser decrease in hydrogen bonding, while the less positive value of ΔS^* indicates less solvent loss upon H_4L^{4+} dissociation.

It does not seem possible to directly determine which 4+ species (L or hexacyclen) has a larger solvation sphere. We will assume that both H_4L^{4+} and H_3L^{3+} have less extensive outer solvation spheres than do the corresponding hexacyclen species and that the inner solvation spheres of H_4L^{4+} and H_3L^{3+} species are more firmly bound than those of hexacyclen. We justify these assumptions by first considering differences in the charge distributions in the protonated L and hexacyclen species and second by examining the experimental evidence.

Average charge densities on the nitrogen atoms for the 4+ and 3+ hexcacyclen species are 2/3 and 1/2 respectively, while corresponding values for L species are 1 and approximately 3/4. (Even though the nitrogen atoms are not equivalent in H_3L^{3+}, we assume that their sites are sufficiently similar so that the 3 protons are distributed equally among them.) The higher charge densities for H_4L^{4+} and H_3L^{3+} imply that the inner sphere of water molecules bound closely to each of these sites will be more strongly attracted than is the case in hexacyclen species. At the same time, the presence of six nitrogen sites in 4+ and 3+ hexacyclen is more effective in assembling a large outer or secondary solvation sphere than in the corresponding L species which have only four nitrogen sites.

Turning to the experimental evidence, we note that the H_4L^{4+} complexes with all the anions studied here are sufficiently labile to give ^{13}C NMR spectra characteristic of rapid-exchange equilibria in contrast to nitrate and chloride complexes of hexacyclen, which appear inert on the NMR time scale. We envision the rate-determining process in the anion exchange reaction as involving anion penetration through a large solvent cage which is significantly altered in the process. As mentioned earlier, all 12 hexacyclen carbons are equivalent in both the anion complex and in the uncomplexed 4+ species. Furthermore, the uncomplexed 3+ and 4+ hexacyclen species are also in rapid exchange equilibrium. Consequently, molecular conformational changes involved in the protonation process as well as formation of the solvent cage around the uncomplexed 4+ species are rapid processes. Moreover, anion distribution between binding sites in the complex along with any consequent conformational changes must also be rapid. Thus, it seems reasonable that the slow anion exchange in hexacyclen complexes relates to the slow rate of anion penetration of the solvent cage. H_4L^{4+} forms a much less structured outer solvent network so that anion penetration is a much more rapid process with consequent rapid anion exchange.

These structural effects can be understood from a somewhat different but equivalent point of view. In tetraprotonated hexacyclen, four protons are distributed among six nitrogen sites on the ring. Pairwise internal hydrogen bonding interactions are capable of stabilizing only two $R_2NH_2^+$ groups at any given time. We represent such internal interactions as formation of $R_2NH\text{-}H^+\text{—}NHR_2$ bonding networks. These interactions may involve direct ionic hydrogen bonding between neighboring protonated and unprotonated nitrogen sites, or may be mediated by inner sphere water. The formation of internal hydrogen bonding networks results in a negative contribution to the enthalpy because $R_2NH_2^+\text{—}OH_2$ bonds are replaced with presumably stronger $R_2NH\text{—}H^+\text{—}NHR_2$ bonds. It also results in a positive contribution to the enthalpy because the primary solvation sphere is loosened. Similarly, there are both negative and positive contributions to the entropy. The negative contribution, resulting from the stiffening of the macrocyclic ring structure, is likely to be a minor effect since the ring is already constrained by numerous solvent interactions. The positive contribution results from the loosening or partial loss of the solvent network.

With these factors in mind, we examine the acidic dissociations of tetra- and triprotonated hexacyclen. The loss of a proton from the 4+ species results in an ion in which 3 protons are distributed on six basic nitrogen sites. This ion achieves complete internal stabilization by 3 sets of pairwise interactions. The unusually large positive enthalpy and entropy changes for this dissociation shows that the solvent interactions are more important than the internal stabilization of the 3+ ion.

These phenomena can also be described in terms of the strengths of the acids. The pK value for 4+ hexacyclen is 2.55 at $I = 0.05$ M at 25°C, while the thermodynamic value for the pK of triprotonated hexacyclen at the same ionic strength and temperature is 7.70. The tetraprotonated acid is so much stronger because the 3+ acid acquires no additional stabilization from pairwise internal bonding as a result of proton loss.

The acidic L species follow the same pattern. At an ionic strength of 0.5 M at 25°C, the 4 pK s are 3.65, 5.23, 10.38 and 11.08 [13]. pK_1 and pK_2 are relatively small because of the increased internal hydrogen bonding as H_3L^{3+} and H_2L^{2+} are formed. However, no such increased stabilization results with proton loss from H_2L^{2+} or HL^+, and these are much weaker acids.

Enthalpies and entropies of dissociation for H_4L^{4+} and 4+ hexacyclen are readily compared in these terms as well. We examine the proton redistribution reaction $H_3L^{3+} + H_4J^{4+} = H_4L^{4+} + H_3J^{3+}$ for which ΔH^* is about +5 kcal mol^{-1} and ΔS^* is near +20 cal mol^{-1} K^{-1}. In this reaction H_3L^{3+} loses one internal stabilization interaction while 4+ hexacyclen gains one. The significantly positive values are consistent with our hypothesis that an extensive solvent cage present in 4+ hexacyclen is replaced by a much less organized outer solvation sphere in H_4L^{4+}. We are unable to make a similar comparison with the triprotonated species because the appropriate data is not available. Nevertheless, describing the thermodynamic properties of hexacyclen and L in terms of internal hydrogen bonding interactions and solvation changes seems to explain many features of the acid-base reactions of these compounds.

This analysis also provides a simple rationale for many of the observed anion complexing properties. We view the monoanion complexation reactions as interactions between $R_2NH_2^+$ groups of H_4L^{4+} or tetraprotonated hexacyclen and anions capable of hydrogen bonding with these groups, either directly or through a solvent bridge. Thus, iodate anions, which are capable of strong hydrogen bonding interactions, form stronger complexes with both 4+ polyamines than the more weakly bonding chloride and nitrate ions, and neither polyamine forms detectable complexes with iodide ions. The hexacyclen complexes are stronger than corresponding H_4L^{4+} complexes because complexation of the anion with 4+ hexacyclen decreases the net charge and leads to collapse of the solvent cage present around this ion. Because H_4L^{4+} does not carry a large solvent cage, the complexation reactions result in release of lesser amounts of solvent with resultant smaller entropy gains and weaker complexes.

Primary sulfate complexation with 4+ hexacyclen may involve solvent cage collapse as well as the expulsion of inner sphere water from either 4+ hexacyclen or sulfate, consistent with the large positive values of ΔS^* of about +38 cal mol^{-1} K^{-1}. Addition of the second sulfate ion resembles numerous other outer sphere complexes like those of sulfate with Ni^{2+}, Co^{2+}, and Mn^{2+}, with ΔH^* values of +3.2, +1.6, and +3.7 kcal mol^{-1}, respectively and ΔS^* values of +22, +17, and +23 cal mol^{-1} K^{-1}, respectively [14]. These appear similar to the corresponding hexacyclen complexation values of $\Delta H^* = 2.1$ kcal mol^{-1} and $\Delta S^* = 15.6$ cal mol^{-1} K^{-1}, and likely result from similar processes, namely expulsion of loosely bound outer sphere water from the 2+ and 2− ions to form the much more poorly solvated neutral complex.

The primary sulfate addition reaction with H_4L^{4+} is similar. ΔH^* and ΔS^* are 3.4 kcal mol^{-1} and 20.3 cal mol^{-1} K^{-1}. The reaction appears to involve only expulsion of outer sphere water while leaving the ‘hard’ inner sphere solvation shell associated with four $R_2NH_2^+$ groups intact.

Comparisons of ΔH^* and ΔS^* for outer sphere ion associations of tetravalant cations with sulfate would be useful but the appropriate data are not now available. We make the less satisfactory comparison for the ion association between La^{3+} and $Fe(CN)_6^{3-}$ for which $\Delta H^* = 2.1$ kcal mol^{-1} and $\Delta S^* = 24$ cal mol^{-1} K^{-1} [15]. The similarity of these values with those for divalent ions seems to indicate that outer solvation spheres of di- and trivalent species are perturbed to similar extents by the ion association reaction. Thus, it seems reasonable that association of H_4L^{4+} with sulfate involves a similar degree of outer sphere perturbation.

The present analysis also provides some explanation for the complexation of monoanions with H_3L^{3+} but not with 3+ hexacyclen. We have already noted that H_3L^{3+} is capable of only one pairwise internal hydrogen bonding interaction while the corresponding hexacyclen species may stabilize all three $R_2NH_2^+$ groups in this way. Apparently, monoanions do not interact effectively with the internally stabilized positive sites on 3+ hexacyclen and no complexes are detected. Such interactions are possible with the $R_2NH_2^+$ group of H_3L^{3+} and complexes are formed. However, these are weak complexes whose formation does not appear to result in significant solvent expulsion. In accord with previous discussion, this ion is presumed not to have an extensive outer solvation sphere, and anion complexation provides only minor solvent loss as indicated by chloride, nitrate, and iodate complexation entropies of +6.0, +1, and +1 cal mol^{-1} K^{-1} respectively.

The complexation of sulfate with H_3L^{3+} seems to reflect the same property, i.e., a relatively small outer solvation sphere. ΔH^* and ΔS^* for $H_3L(SO_4)^+$ formation are 1.5 kcal mol^{-1} and 9.0 cal mol^{-1} K^{-1}, respectively, compared with 2.8 kcal mol^{-1} and 17. cal mol^{-1} K^{-1} for the corresponding hexacyclen complexation. If we assume that both complexations can be characterized as outer sphere types similar to those of divalent metal ions with sulfate, the magnitudes of the positive ΔH^* and ΔS^* reflect the extent of outer sphere solvent loss from the ions. The lesser extent of the expulsion of water from H_3L^{3+} compared with triprotonated hexacyclen suggests a smaller degree of outer sphere solvent association with the L species.

In summary, we find explanations for protonated macrocyclic polyamine complexation reactions with anions based principally on the solvation state of the polyamine and hydrogen bonding capabilities of the anions. The polyamine solvation structure depends, in turn, on the extent of protonation, the number of protonated and unprotonated sites, and the extent of internal stabilization of protonated nitrogen sites.

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References

1. B. Dietrich, J. Guilkem, J. M. Lehn, C. Pascard, and E. Sonveaux: *Helv. Chim. Acta* **67**, 91 (1984).
2. E. Kimura, M. Kodama, and T. Yatsunami: *J. Am. Chem. Soc.* **104**, 3182 (1982).
3. B. Dietrich, M. Husseini, J. M. Lehn, and R. B. Sessions: *J. Am. Chem. Soc.* **103**, 1282 (1981).
4. R. I. Gelb, B. T. Lee, and L. J. Zompa: *J. Am. Chem. Soc.* **107**, 909 (1985).
5. R. I. Gelb, L. M. Schwartz, and L. J. Zompa: *Inorg. Chem.* **25**, 1527 (1986).
6. M. W. Hosseini and J. M. Lehn: *J. Am. Chem. Soc.* **104**, 3525 (1982).
7. J. Cullinane, R. I. Gelb, T. N. Margulis, and L. J. Zompa: *J. Am. Chem. Soc.* **104**, 3048 (1982).
8. J. S. Alper, R. I. Gelb, and M. H. Schwartz: *J. Incl. Phenom.* **11**, 349 (1991).
9. D. W. Marquardt: *J. Soc. Ind. Appl. Math* **11**, 431 (1963).
10. W. H. Press, B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling: *Numerical Recipes: The Art of Scientific Computing*, Cambridge University Press, Cambridge (1986).
11. W. H. Jeffreys: *Astron. J.* **85**, 177 (1980).
12. M. Micheloni, P. Paoletti, and A. Vacca: *J. Chem. Soc. Perkin Trans. 2* 945 (1978).
13. M. Micheloni, A. Sabatini, and P. Paoletti: *J. Chem. Soc. Perkin Trans. 2* 828 (1978).
14. C. W. Davies: *Ion Association*, Butterworths, London (1962).
15. W. J. Hamer: *The Structure of Electrolytic Solutions*, Wiley, New York (1959).