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Hexacyclen Complexes of Sulfate Anion

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Stoichiometries and temperature-dependent complexation constants for reactions of protonated hexacyclen species with sulfate anions are determined by pH potentiometric methods and by conductometric titration. Three complexes are detected, 1:1 complexes of sulfate with both tri- and tetraprotonated hexacyclen species and an electrically neutral complex containing two sulfate anions per tetraprotonated macrocycle. Enthalpy and entropy changes for each complexation are estimated from van't Hoff analysis of formation constant data. These thermodynamic results lead to the interpretations that water loss from both the hexacyclen and sulfate solvation spheres provides the driving forces for these complexation reactions.

1,4,7,10,13,16-Hexaazacyclooctadecane, to be called hexacyclen and symbolized by L, is one of a family of macrocyclic polyamines capable of complexing anions in aqueous solution.[1-3] Although these complexation reactions have been discovered only recently, several investigations involving a number of macrocyclic polyamine complexes with a variety of anion species have been reported already.[4-7] These studies report anion complexes with highly protonated amine species including tetra-, hexa- and octaprotonated polyamines. The complexation reactions are generally assumed to involve 1:1 anion-to-macrocycle stoichiometries, and some of us have confirmed exclusive 1:1 stoichiometries in complexes of tetraprotonated hexacyclen H_4L^{4+} with monovalent anions Cl^-, Br^-, NO_3^-, ClO_4^-, $C_6H_5SO_3^-$, and $CF_3CO_2^-$ but find no detectable complexation between these anions and other protonated hexacyclen species.[6,7] However, in one recent study we report complexation reactions of H_4L^{4+} with IO_3^- involving both 1:1 and 2:1 (IO_3^-:H_4L^{4+}) stoichiometries. The discovery of this 2:1 complex demonstrates that exclusively 1:1 stoichiometries cannot be assumed to exist. In this paper we report another variation, the complexation properties of a dianion species. A study of divalent anion complexes serves to elucidate the bonding properties of these complexes as follows.

Complexation reactions between protonated macrocyclic polyamines and anions have generally been rationalized on the basis of electrostatic and ionic hydrogen bonding interactions. These interactions provide the driving force while the relative size and shape of the macrocycle cavity with respect to that of the complexed anion account for bonding selectivity. However, we have recently described a bonding process that relies primarily on solvent release as a driving force.[7] This inference was based on an examination of the thermodynamic parameters ΔH and ΔS for the H_4L^{4+} complexation reactions with monoanionic species and also on an X-ray crystallographic analysis of several hexacyclen salts.[6,8] The purpose of the present study is to compare these thermodynamic data with analogous results on divalent anion complexation. We expect that this comparison will shed light on the role of electrostatic interactions in the bonding.

For this purpose we examined the hexacyclen complexation of sulfate ion. We determined the stoichiometries and the temperature-dependent formation constants of hexacyclen-sulfate complexes by using pH potentiometric acid–base titrations and conductometric titrations. A second pH potentiometric method employed a nonlinear regression analysis to determine formation constants from the experimental data.

Experimental Methods

Materials. All chemicals were reagent grade. We took the precaution of testing sodium sulfate samples for the presence of possible trace acidic or basic impurities by a procedure of adding very small amounts of HCl or NaOH to ~0.1 M Na_2SO_4 solutions and monitoring the pH. This procedure confirmed that these impurities could not have exceeded 0.01 mM concentration levels in these solutions. Hexacyclen hexahydrochloride ($C_{12}H_{30}N_6 \cdot 6HCl \cdot 3H_2O$) and hexacyclen hemihydrate ($C_{12}H_{30}N_6 \cdot {}^1/_2H_2O$) were obtained from the commercial tris(hydrogen sulfate) salt (Parish Chemical Co.). Weighted samples of the commercial preparation were dissolved in water and treated with stoichiometric amounts of $BaCO_3$. After being mixed for 2 h at 80 °C, the filtered hot solution was concentrated in a rotary evaporator. Treatment of the concentrate with excess 6 M HCl gave the crude hexahydrochloride salt, which was subsequently recrystallized twice from fresh portions of 6 M HCl. The polyamine hemihydrate was obtained by vacuum sublimation of the concentrated filtrate taken to dryness. Fresh solutions of either the polyamine or the hexahydrochloride were analyzed by pH potentiometric titration in the presence of 0.4 M $NaNO_3$. Under these conditions two end points were discernible, and these corresponded to the stoichiometric formation of H_4L^{4+} and H_3L^{3+} species. Each of these end points provided an independent assay for the polyamine, and these two assays always agreed to within the estimated precision limits of the experiments. For example, one H_6LCl_6 sample required 1.29 and 1.93 mL of 0.1000 M NaOH to reach the $a = 2$ mol of NaOH/mol of H_6LCl_6 and $a = 3$ mol of NaOH/mol of H_6LCl_6 end points, respectively. The experimental ratio of $1.93/1.29 = 1.49_6$ compares accurately with the theoretical ratio of $^3/_2$.

Measurements. pH potentiometric measurements employed an Orion 801 pH meter equipped with conventional glass and calomel electrodes. The meter was standardized with 0.05 *m* potassium hydrogen phthalate (KHP) solutions, whose temperature-dependent pH values were taken from Bates.[9] Because we later derive hydrogen ion concentrations from the pH meter readings, we made the following additional verification measurements. At each temperature, the KHP standardized meter measured the pH of 1.00 mM HCl in a supporting electrolyte of 0.20 M NaCl. The measured values were corroborated with the pH values calculated from the known hydrogen ion concentration and an estimate of the hydrogen ion activity coefficient obtained from the Debye–Hückel equation taking $a = 0.9$ nm and employing the temperature-dependent *A* and *B* coefficients of Robinson and Stokes.[10] For example, the pH value of a 1.00 mM HCl solution in 0.20 M NaCl was measured as 3.100 at 25 °C. This value is in agreement with the calculated estimate of 3.098. Measured pH values always agreed with the calculated estimates to within ±0.004 pH unit.

Measurements of the electrolytic conductance of hexacyclen solutions during titration with HCl or H_2SO_4 employed a Leeds and Northrup Model 4959 conductance bridge equipped with a glass dip-type cell. Solutions were thermostated at 25.0 ± 0.1 °C, and ample time was allowed for thermal equilibration after each addition of acid reagent.

Potentiometric and Conductometric Titration Experiments

In order to obtain a qualitative picture of the equilibria involved in complexation reactions of sulfate and hexacyclen, we made a series of pH potentiometric titrations with NaOH of H_6LCl_6 solutions having a fixed ionic strength of 0.44 M but containing differing proportions of NaCl and Na_2SO_4. The titration curves pictured in Figure 1 illustrate two main effects due to sulfate ions.

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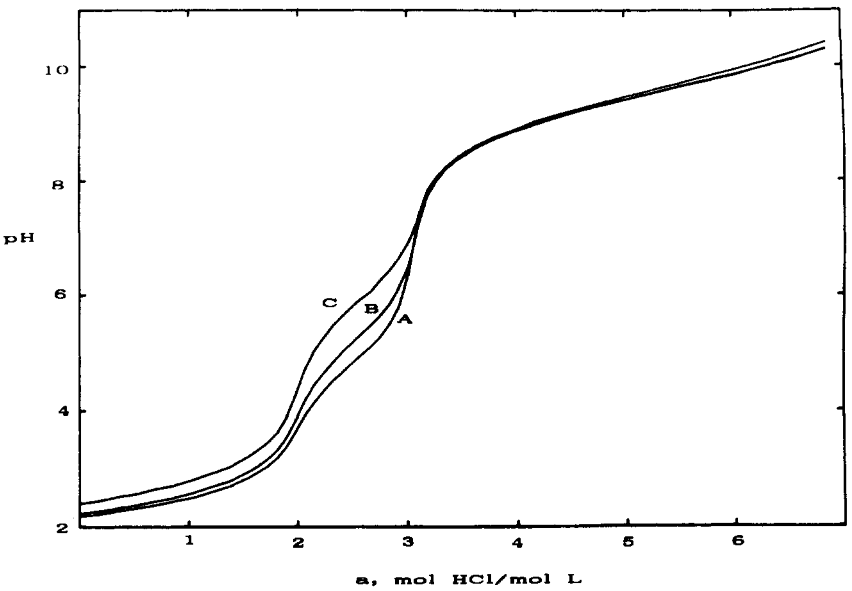

Figure 1. pH potentiometric titration of hexacyclen hexahydrochloride with NaOH. Each curve represents pH vs. *a* (mol of NaOH/mol of H_6LCl_6) data obtained from titrations of 18 mL of 3.2 mM H_6LCl_6 with 0.100 M NaOH. Solutions A–C contain 0, 0.007, and 0.037 M Na_2SO_4, respectively and are made up to an ionic strength of 0.44 M with NaCl.

These are (1) a slight increase in the pH values observed in the initial portion of the titration curve between $a = 0$ and $a = 2$ mol of NaOH/mol of H_6LCl_6 and (2) a marked shift to higher pH values in the region between $a = 2$ and $a = 3$ mol of NaOH/mol of H_6LCl_6. We ascribe the first of these effects to partial protonation of sulfate ions and will discuss this further in a later section. The second, more pronounced effect is due to complexation of the H_4L^{4+}/H_3L^{3+} conjugate species, which dominate the acid–base equilibrium in the region between $a = 2$ and $a = 3$ mol of NaOH/mol of H_6LCl_6. We note that the presence of sulfate ions increases the pH. This means that the $[H_4L^{4+}]/[H_3L^{3+}]$ ratio has decreased in order to decrease the hydrogen ion concentration, and so we conclude that H_4L^{4+} is complexed with sulfate in these solutions or, if both H_4L^{4+} and H_3L^{3+} are complexed, that the extent of H_4L^{4+} complexation is greater. But because of the similarity of the three titration curves beyond $a = 3$ mol of NaOH/mol of H_6LCl_6, there seems to be little if any H_3L^{3+} complexation under the conditions of these experiments. Thus, the pH potentiometric titration data by themselves seem to suggest a rather simple reaction scheme consisting of a complexation of tetraprotonated hexacyclen by sulfate ions. In order to shed additional light on this system we titrated solutions of unprotonated hexacyclen with H_2SO_4 and, for the sake of comparison, also with HCl. Conductance measurements would provide a far different and more detailed picture of hexacyclen–sulfate interactions than do potentiometric measurements. Figure 2 shows the conductometric results as a plot of conductance $(1/R)$ corrected for dilution by $(V + v)/V$ vs. a. Here V is the initial solution volume, v is the volume of titrant added, and a is the ratio of equivalents of acid to moles of hexacyclen.

We note that the HCl curve in the region from $a = 0$ to $a = 3$ equiv of HCl/mol of L is as expected for the titration of a weak trifunctional base with strong acid. After an initial curvature due to conductance of OH^- from hydrolysis of L, the linear segment above $a \sim 0.5$ equiv of HCl/mol of L reflects the increasing concentrations of HL^+ and Cl^-, which are proportional to the volume of added titrant. The slope between $a = 1.0$ and 2.5 equiv of HCl/mol of L is 1.9_3 mmho/mL of HCl. We compare this value with the corresponding slope of a conductometric titration of pure water with HCl (this curve is not shown in Figure 2), and estimate that the chloride ions alone account for 1.4_0 of the 1.9_3 mmho/mL of HCl. Thus, the contribution from HL^+ and other protonated hexacyclen species is only about 0.5_3 mmho/mL of HCl, and knowing that the equivalent conductance of Cl^- is about 76 mho cm^{-2} equiv^{-1}, we estimate that the average of equivalent conductance of protonated hexacyclen species to be $(0.5_3/1.4_0)76 = 29$ mho cm^{-2} equiv^{-1}. This value is only a rough estimate but it is useful to have an approximate measure of the contribution of protonated hexacyclen species to the electrolytic conductance.

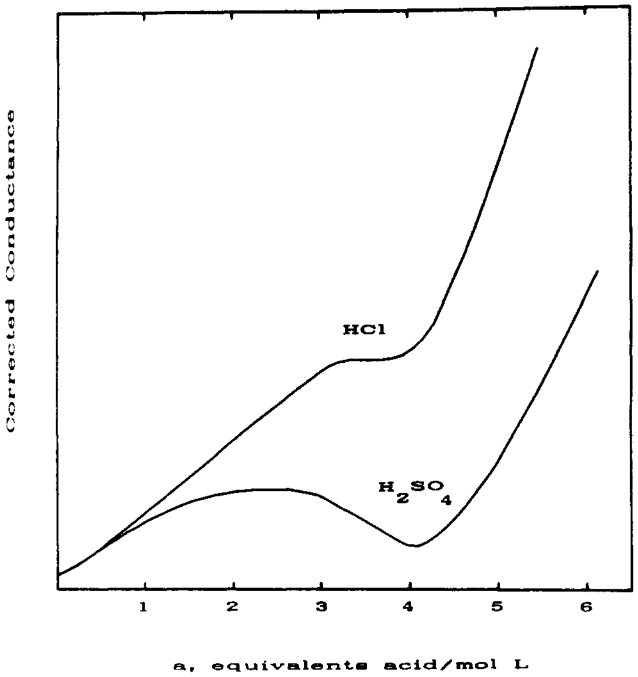

Figure 2. Conductometric titration curves for hexacyclen titration with hydrochloric and sulfuric acids. Curves represent volume corrected conductance, $(1/R)(V + v)/V$ vs. a (equiv acid/mol of L) obtained from titration of 19 mL of 9.0 mM hexacyclen with 0.400 M HCl (curve A) and 0.200 M H_2SO_4 (curve B).

In the titration range between $a = 3$ and $a = 4$ equiv of HCl/mol of L, the conductometric titration curve is essentially horizontal. This phenomenon is due to the formation of H_4L^{4+} complexes with chloride ions in these solutions containing excess chloride. The titration reaction here is best written as $H_3L^{3+} + HCl = H_4Cl^{3+}$. Because H_3L^{3+} and H_4LCl^{3+} species are similar in size and charge they should have similar equivalent conductances. Also because chloride ions are present in a 3:1 mole ratio relative to H_3L^{3+} at $a = 3$ equiv of HCl/mol of L, these chloride ions are the primary current carriers. However, at $a > 4$ equiv of HCl/mol of L the titration curve slope increases steeply and becomes linear between $a \sim 4.5$ and $a = 7$ equiv of HCl/mol of

L when the titration was discontinued. The large slope of the titration curve in this region is consistent with the presence of H^+ ions as the primary current-carrying species. We interpret this behavior as indicating no further protonation, complexation, or release of chloride occurs involving the H_4LCl^{3+} species at lower pH values.

We now turn our attention to the conductometric titration of hexacyclen with H_2SO_4 as also shown in Figure 2. We note that after the addition of the first small portions of sulfuric acid, the conductance lies increasingly below that observed in the HCl titration. The equivalent conductances of Cl^- and SO_4^{2-} are so similar that we cannot attribute this effect to different conductances of the anions. Even allowing for the greater ionic strength dependence of the sulfate-equivalent conductance, we must conclude that some chemical reaction results in decreased ion concentrations with consequently lower conductances. Furthermore, the complexation between H_4L^{4+} ions and sulfate proposed earlier cannot account for the observed behavior in this $a < 3$ equiv of H_2SO_4/mol of L region of the titration curve. Also if there were appreciable complexation of H_4L^{4+} by sulfate at values of a less than 3 of equiv H_2SO_4/mol of L, the pH potentiometric titration curve would not feature the discernible end point at $a = 3$ mol of NaOH/mol of H_6LCl_6, which is observed, in fact. We conclude that sulfate ions form complexes with at least one of the hexacyclen species present in $a < 3$ equiv of H_2SO_4/mol of L solutions, which are L, HL^+, H_2L^{2+}, and H_3L^{3+}. In order to determine the nature of the complexing species we must first establish that each of the L, HL^+, H_2L^{2+}, and H_3L^{3+} species are capable of existing in solution at an appropriate pH. We make this verification by measuring acidity constants of H_6L^{6+} and so make pH potentiometric titrations of approximately 2 mM H_6LCl_6 solutions with 0.020 M NaOH in the range of 3–5.5 mol of NaOH/mol of H_6LCl_6. We analyze these data using a calculational procedure described previously,[11] which calculates thermodynamic acidity constants and relies on Debye–Hückel estimates of the activity coefficients of charged species. We have taken the ion-size parameter to be equal to 1.2 nm for HL^+, H_2L^{2+}, and H_3L^{3+} in solutions with ionic strengths that varied between 0.016 M and 0.012 M during the course of titration. The results are $pK_4 = 7.70 \pm 0.01$, $pK_5 = 8.89 \pm 0.02$ and $pK_6 = 9.42 \pm 0.02$ at 25 °C. The fact that these pK values are in successive order implies that protonation of L occurs in stepwise fashion so that each of the species HL^+, H_2L^{2+}, and H_3L^{3+} exists as a major solution component at the proper pH level. We couple this fact with the observation that solutions formed near the start of the conductometric titration ($a < 0.5$ equiv of H_2SO/mol of L), where L and HL^+ are the dominant hexacyclen species, have conductance values virtually identical with those observed in the conductometric titration of L with HCl reagent. Thus we conclude that L and HL^+ are not detectably complexed by sulfate. The remaining possibilities are H_2L^{2+} and H_3L^{3+}, and we shall examine the ramifications of sulfate complexation of either or both of these species in terms of idealized conductometric titration behavior.

We will simplify the complicated protonation and complexation equilibria between these species and imagine a stepwise reaction between L and H_2SO_4 consisting of the protonation reactions

$$L + {}^1/_2H_2SO_4 = HL^+ + {}^1/_2SO_4^{2-} \quad (1)$$

$$HL^+ + {}^1/_2H_2SO_4 = H_2L^{2+} + {}^1/_2SO_4^{2-} \quad (2)$$

$$H_2L^{2+} + {}^1/_2H_2SO_4 = H_3L^{3+} + {}^1/_2SO_4^{2-} \quad (3)$$

and complexation reactions

$$H_2L^{2+} + SO_4^{2-} = H_2L(SO_4) \quad (4)$$

$$H_3L^{3+} + SO_4^{2-} = H_3L(SO_4)^+ \quad (5)$$

We further simplify by assuming that the sulfate complexations are essentially complete reactions; i.e., $H_2L(SO_4)$ and $H_3L(SO_4)^+$ complexes are the dominant solution forms of di- and triprotonated hexacyclen species, respectively.

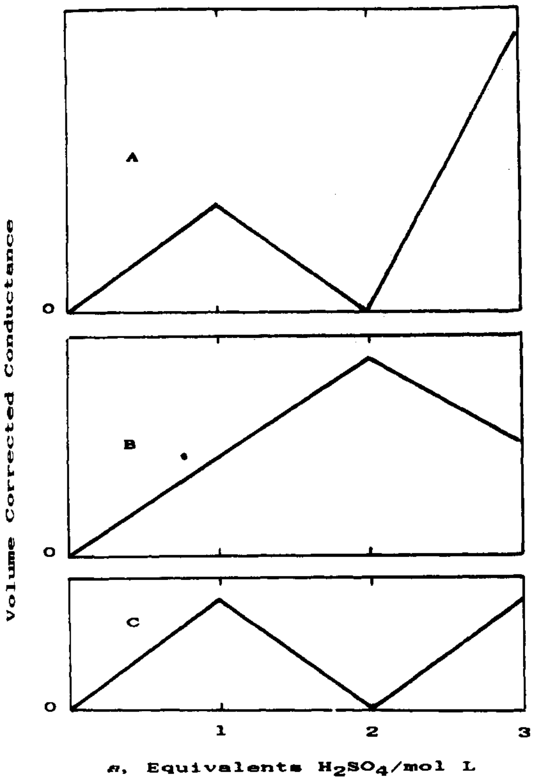

Figure 3. Idealized conductometric titration curves for various hexacyclen–sulfuric acid reaction schemes. Curve A represents idealized conductance vs. a (equiv of H_2SO_4/mol of L) for $H_2L^{2+} + SO_4^{2-} = H_2L(SO_4)$ taken as the only complexation reaction between $a = 0$ and $a = 3$. Curve B results from $H_3L^{3+} + SO_4^{2-} = H_3L(SO_4)^+$ taken as the only complexation in this titration region, and curve C depicts idealized conductance vs. a (equiv of H_2SO_4/mol of L) when both H_2L^{2+} and H_3L^{3+} form strong 1:1 complexes with sulfate ions.

Three possible reaction schemes exist: In scheme A sulfate complexes with H_2L^{2+} only, in scheme B sulfate complexes with H_3L^{3+} only, and in scheme C both H_2L^{2+} and H_3L^{3+} are complexed. We sketch idealized conductometric titration curves for these schemes in Figure 3. By comparing these idealized titration curves with the experimental curve in the region $a = 0$ to 3 equiv of H_2SO_4/mol of L shown in Figure 2, we see that the scheme B curve has features most similar to those of the experimental curve. In particular, schemes A and C feature declining conductances after $a = 1$ equiv of H_2SO_4/mol of L due to formation of uncharged $H_2L(SO_4)$, but the experimental curve continues to rise between $a = 1$ and $a = 2$ equiv of H_2SO_4/mol of L. The downward curvature exhibited by the experimental curve between $a = 1$ and $a = 2$ equiv of H_2SO_4/mol of L reflects production of some H_3L^{3+} and subsequent complexation with sulfate in this region. This behavior is expected in hexacyclen titrations because of the closely spaced values of pK_4, pK_5, and pK_6 for H_6L^{6+} and the absence of distinct inflections in the pH potentiometric titration curves (Figure 1) beyond $a = 3$ mol of NaOH/mol of H_6LCl_6. We attribute both the displacement of the peak at $a = 2.2$ equiv of H_2SO_4/mol of L in figure 2 and also the rounded appearance of the experimental peak to incomplete sulfate complexation. Thus, we conclude that the conductometric titration results imply that $H_3L(SO_4)^+$ is the dominant sulfate complex in titration solutions between $a = 0$ and $a = 3$ equiv of H_2SO_4/mol of L. However, we cannot exclude the possibility that a minor amount of $H_2L(SO_4)$ complex forms in these solutions. The presence of such a complex, if it exists at all, appears to have an insignificant affect on the conductometric curve, and so we exclude it from further consideration.

Continuing with our interpretation of the conductometric data pictured in Figure 2, we now examine the curve in the region beyond $a = 3$ equiv of H_2SO_4/mol of L where the volume-corrected conductance drops sharply and approximately linearly until

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[11] Schwartz, L. M.; Gelb, R. I. *Anal. Chem.* **1978**, *50*, 1571.

$a = 4$. This behavior corresponds to the protonation and complexation reactions

$$H_3L(SO_4)^+ + H^+ = H_4L(SO_4)^{2+} \qquad (6)$$

$$H_4L(SO_4)^{2+} + SO_4^{2-} = H_4L(SO_4)_2 \qquad (7)$$

The first of these reactions describes the additional protonation of a triprotonated hexacyclen–sulfate complex, which is the dominant solution species as indicated by our earlier arguments. The second reaction corresponds to further complexation of the tetraprotonated hexacyclen species to form an electrically neutral dissolved species. We observed no precipitation during these titration experiments and conclude that this complex is the dominant solution species near $a = 4$ equiv of H_2SO_4/mol of L. We note that complete formation of this complex would have resulted in zero conductance at $a = 4$. In fact the measured conductance reached a minimum value of 0.44 mmho near $a = 4$. From this value we can make a rough estimate of the equilibrium constant for reaction 7. On the basis of approximate values of equivalent conductances of $H_4L(SO_4)^{2+}$ and SO_4^{2-} along with relevant solution composition data, we estimate that the equilibrium constant for complexation reaction 7 is about 10^3 at an ionic strength of about 0.01 M and at the measurement temperature of 25 °C. Although the value 10^3 is only an order-of-magnitude estimate, it is clear that $H_4L(SO_4)_2$ formation must be accounted for in an analysis of hexacyclen complexation by sulfate.

Having established the existence of $H_3L(SO_4)^+$, $H_4L(SO_4)^{2+}$, and $H_4L(SO_4)_2$ species, we considered possible formation of sulfate complexes with H_5L^{5+} and H_6L^{6+}. We note the steeply rising portion of the hexacyclen–sulfuric acid conductometric titration curve in Figure 2 beyond $a = 4$ equiv of H_2SO_4/mol of L, which suggests that no further complexes are formed beyond $H_4L(SO_4)_2$. We confirmed this observation through an analysis of pH potentiometric titration data pictured in Figure 1 and now focus on curve C, which was measured with a titration solution constituted by 3.2 mM H_6LCl_6, 0.037 M Na_2SO_4, and NaCl to make up the ionic strength. We assumed that the $H_4L(SO_4)_2$ complex is completely formed at this high sulfate concentration and recast the solution composition as 6.4 mL HCl, 0.031 M Na_2SO_4 and NaCl, and 3.2 mM $H_4L(SO_4)_2$, which we assume to be an inert solution component at the early stages of NaOH titration, i.e., when $a < 2$ mol of NaOH/mol of H_6LCl_6. We verified this formulation by a comparison of the curve C titration data with data obtained from NaOH titration of a solution made 6.4 mM in HCl and 0.031 M Na_2SO_4 and adjusted to $I = 0.44$ M with NaCl. The two data sets were superimposable to within ±0.02 pH unit, and we conclude that no further protonation of $H_4L(SO_4)_2$ species occurs in these solutions.

In summary, we used pH potentiometric and conductometric titrations in order to provide qualitative information about hexacyclen complexation by sulfate. These experiments indicate three principal sulfate complexes: $H_3L(SO_4)^+$, $H_4L(SO_4)^{2+}$, and $H_4L(SO_4)_2$. We now seek to verify this scheme by measuring precise values of the complexation constants and their temperature dependences. Our methodology is pH potentiometry of H_4L^{4+}, H_3L^{3+} buffer solutions.

pH Potentiometric Methodology

We prepare H_4L^{4+}, H_3L^{3+} mixtures with total concentrations of 1–2 mM and determine analytical concentrations of the buffer species by NaOH or HCl titration in a separate experiment. We add appropriate amounts of NaCl to bring ionic strengths to 0.205 M. Aliquots of the hexacyclen buffers are equilibrated at the measurement temperature for about 1 h and "titrated" with 0.0668 M Na_2SO_4 solution having an ionic strength of 0.20_4 M. After each addition we allow ample equilibration time before recording pH values. Because titration continues until the original solution volume is approximately tripled, the hexacyclen concentration ranges from about 2 to 0.6 mM in some experiments and from about 1.0 to 0.3 mM in others.

We calculate hexacyclen complexation constant values using a nonlinear regression procedure detailed elsewhere for a pH potentiometric study of cyclodextrin complexation.[12,13] In the present case, the model equations corresponding to the hypothesized physicochemical behavior are

$$K_{a_3} = \frac{[H^+][H_3L^{3+}]}{[H_4L^{4+}]} \qquad (8)$$

$$K_{Cl} = \frac{[H_4LCl^{3+}]}{[H_4L^{4+}][Cl^-]} \qquad (9)$$

$$K_w = [H^+][OH^-] \qquad (10)$$

$$K_{3SO_4} = \frac{[H_3L(SO_4)^+]}{[H_3L^{3+}][SO_4^{2-}]} \qquad (11)$$

$$K_{(4SO_4)_1} = \frac{[H_4L(SO_4)^{2+}]}{[H_4L^{4+}][SO_4^{2-}]} \qquad (12)$$

$$K_{(4SO_4)_2} = \frac{[H_4L(SO_4)_2]}{[H_4L(SO_4)^{2+}][SO_4^{2-}]} \qquad (13)$$

$$F_{Cl} = F_{NaCl} + 6F_L = [H_4LCl^{3+}] + [Cl^-] \qquad (14)$$

$$F_{SO_4} = F_{Na_2SO_4} = [H_3L(SO_4)^+] + [H_4L(SO_4)^{2+}] + 2[H_4L(SO_4)_2] + [SO_4^{2-}] \qquad (15)$$

$$F_L = [H_3L^{3+}] + [H_4L^{4+}] + [H_3L(SO_4)^+] + [H_4LCl^{3+}] + [H_4L(SO_4)^{2+}] + [H_4L(SO_4)_2] \qquad (16)$$

$$F_{Na^+} = [Na^+] = 3F_{H_3L^{3+}} + 2F_{H_4L^{4+}} + F_{NaCl} + 2F_{SO_4} \qquad (17)$$

$$[Na^+] + 3[H_3L^{3+}] + [H_3L(SO_4)^+] + 4[H_4L^{4+}] + 2[H_4L(SO_4)^{2+}] + [H^+] = [Cl^-] + 2[SO_4^{2-}] + [OH^-] \qquad (18)$$

In these equations subscripted F symbols represent species or compound analytical (formal) concentrations. For example, F_{NaCl} represents the analytical concentration of NaCl added as NaCl solution at the start of the experiment while F_{Cl} represents the total analytical concentration of chloride ion. Equation 14 thus reflects the fact that chloride ions are derived from two sources, the partially titrated hexahydrochloride salt as well as NaCl. Similarly, eq 17 accounts for sodium ions derived from addition of Na_2SO_4 and NaCl and also from titration of H_6LCl_6 to $a = 2.7$ mol of NaOH/mol of H_6LCl_6 with NaOH.

Of the six equilibrium constants defined by eq 8–13, four are regarded as unknown parameters, but K_{Cl} and K_w are regarded as knowns based on previously obtained information. K_w estimates are obtained from the tabulated[10] temperature-dependent values for the water autoprotolysis constant. K_{Cl} estimates at various temperatures are available from previous published results.[6,7] However, in this source K_{Cl} values were obtained at an ionic strength of 0.22 M, which is somewhat higher than the 0.20_5 M ionic strength used in the present work. We will correct conditional formation constants for H_4LCl^{3+} to an ionic strength of 0.20_5 M by methods detailed in ref 7. Briefly, $K_{Cl}^{(0.22)}$ values at a given temperature and at I = 0.22 M are obtained from the weighted least-squares regression of $\log K_{Cl}^{(0.22)}$ vs. $1/T$. Activity coefficient ratios, γ_3/γ_4, for the 3+ and 4+ hexacyclen species are obtained from an empirical correlation based on measurements with a chemical model system. The correlation yields the γ_3/γ_4 ratio at any ionic strength between 0.11 and 0.44 M relative to the same ratio at 0.22 M ionic strength. This information together with activity coefficient values for chloride ion derived from the Debye–Hückel equation is sufficient to correct K_{Cl} at 0.22 M ionic strength to K_{Cl} at 0.20_5 M ionic strength. Both the values of $K_{Cl}^{(0.22)}$ and their adjusted values $K_{Cl}^{(0.205)}$ are listed in Table I along with derived hexacyclen–sulfate formation constants. The

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Table I. Conditional Formation Constants of Hexacyclen Complexes with Sulfate and Chloride Ions and Their Uncertainties at Various Temperatures

t, °C	$K_{Cl}^{(0.22)}$	$K_{Cl}^{(0.205)}$[b]	$pK_{a_3}^{(0.205)}$[c]	$K_{3SO_4}^{(0.205)}$[d]	$K_{4SO_4}^{(0.205)}$[e]	$K_{(4SO_4)_2}^{(0.205)}$[f]	rms fit[g]
15	55 ± 2[h]	58 ± 2	3.588 ± 0.006 (±0.023)[j]	34 ± 8	1.03 (±0.03) × 10^4 (±0.06 × 10^4)[j]	62 ± 24	0.0032
25	70 ± 4	74 ± 4	3.236 ± 0.003 (±0.022)	47 ± 6	1.44 (±0.02) × 10^4 (±0.007 × 10^4)	83 ± 8	0.0015
		78[i]	3.214 ± 0.003	47 ± 6	1.51 (±0.002) × 10^4		
35	88 ± 5	93 ± 5	2.889 ± 0.006 (±0.023)	45 ± 6	1.91 (±0.05) × 10^4 (±0.12 × 10^4)	116 ± 12	0.0030
45	108 ± 6	114 ± 6	2.593 ± 0.003 (±0.022)	50 ± 4	2.52 (±0.03) × 10^4 (±0.12 × 10^4)	96 ± 7	0.0016
55	132 ± 7	140 ± 7	2.295 ± 0.005 (±0.023)	70 ± 7	3.49 (±0.06) × 10^4 (±0.18 × 10^4)	123 ± 11	0.0026
		147[i]	2.274 ± 0.005	70 ± 7	3.63 (±0.06) × 10^4	123 ± 11	0.0026

[a] Conditional constant for $H_4L^{4+} + Cl^- = H_4L(Cl)^{3+}$ at $I = 0.22$ M. [b] Conditional constant for $H_4L^{4+} + Cl^- = H_4L(Cl)^{3+}$ adjusted to $I = 0.205$ M. [c] Acidity constant for $H_4L^{4+} = H^+ + H_3L^{3+}$ at $I = 0.205$ M derived from data analysis procedures. [d] Conditional constant for $H_3L^{3+} + SO_4^{2-} = H_3L(SO_4)^+$ at $I = 0.205$ M. [e] Conditional constant for $H_4L^{4+} + SO_4^{2-} = H_4L(SO_4)^{2+}$ at $I = 0.205$ M. [f] Conditional constant for $H_4L(SO_4)^{2+} + SO_4^{2-} = H_4L(SO_4)_2$ at $I = 0.205$ M. [g] The rms fit of experimental data to model equations. [h] Uncertainties represent standard error estimates derived by propogation-of-variance calculations based on ±0.002 pH unit uncertainties. [i] Adjusted values of $K_{Cl} = K_{Cl} + s$ are used to analyze the same data set obtained at the indicated temperatures. [j] Values in parentheses are standard error estimates derived from statistical uncertainties in both $K_{Cl}^{(0.205)}$ and fluctuations in the pH vs. composition data.

acidity constant K_{a_3} is a fitted parameter in the nonlinear regression calculations, and these values are also listed in Table I.

The rms fit values given in the last column of Table I represent the root-mean-square of deviations between pH data calculated from the model equations and the 8–12 experimental pH values recorded in each experiment. These rms fit values are comparable to our a priori estimate of ±0.002 pH precision. Moreover, the pattern of residuals, deviations between experimental and calculated pH data, appears randomly scattered and never exceeds 0.005 pH. Consequently, we are confident that the model equations and derived equilibrium constant values accurately describe the behavior of these hexacyclen solutions at least at the level of precision of our experiments. For further verification we made some additional calculations. First we attempted to fit the experimental data with model equations assuming that $H_4L(SO_4)^{2+}$ is the only hexacyclen complex of sulfate. The fit of experimental vs. model data was unacceptably poor (rms fit ~0.1 pH unit) and showed a clear nonrandom pattern in the residuals. A second calculation including both $H_4L(SO_4)^{2+}$ and $H_4L(SO_4)_2$ formation likewise yielded unacceptable results with rms fits greater than 0.02 pH unit, a clear trend in residuals, and some residuals exceeding 0.05 pH unit. A third calculation based on only $H_4L(SO_4)^{2+}$ and $H_3L(SO_4)^+$ likewise gave unacceptable fits.

The nonlinear regression procedure provides standard error estimates of those equilibrium constants that are taken as adjustable parameters. These standard error estimates, whose values appear as entries beside equilibrium constants in Table I, reflect the scatter of experimental pH values from theoretical values predicted by the model equations. However, these uncertainty estimates do not take into account the uncertainty in the K_{Cl} value, which is input as a fixed parameter in the nonlinear regression.

The uncertainty in K_{Cl} is represented by its standard error estimate, s, but this K_{Cl} is derived from a previous set of data and so is statistically uncorrelated with the equilibrium constants derived from the present data. To propogate the uncertainty in K_{Cl} into these equilibrium constants, we replace the fixed value K_{Cl} by $K_{Cl} + s$, repeat the nonlinear regression calculations, and obtain a new set of equilibrium constants. The squared value of the difference between each new equilibrium constant value and the original value represents an estimate of the variance due to uncertainty in the K_{Cl} input values. We take the variance of derived equilibrium constant values as the sum of the two uncorrelated variances, one due to K_{Cl} uncertainty and the second due to fluctuations in the experimental data. The square root of this composite variance constitutes a standard error estimate accounting for statistical uncertainty in both input K_{Cl} data and uncertainties in the present experimental data. The results of these calculations appear in parentheses below the equilibrium constant entries in Table I. We note that the uncertainty in K_{Cl} appears to propogate a significant uncertainty into pK_{a_3} and K_{4SO_4} but not into K_{3SO_4} and $K_{(4SO_4)_2}$. Thus, pK_{a_3} and K_{4SO_4} uncertainties stem both from the present data and the data from which K_{Cl} was derived, but K_{3SO_4} and $K_{(4SO_4)_2}$ uncertainties derive only from the former.

Equilibrium constant values obtained by our data analysis refer to an ionic strength of 0.205 M. We will soon wish to compare these constants to other values at 0.22 M. While the difference between these conditions is not large we will nevertheless adjust the present equilibrium constant values to account for the ionic strength variation of activity coefficients between $I = 0.205$ M and $I = 0.22$ M. For the sake of brevity we will describe only the calculation of $K_{4SO_4}^{(0.22)}$, the conditional constant for $H_4L(SO_4)^{2+}$ formation at an ionic strength of 0.22 M. This value as well as the conditional constant at ionic strength 0.205 M is related to the thermodynamic constant $K_{4SO_4}^{(0)}$ by

$$K_{4SO_4}^{(0)} = K_{4SO_4}^{(0.22)}\left(\frac{\gamma_2}{\gamma_4\gamma_{SO_4}}\right)^{(0.22)} = K_{4SO_4}^{(0.205)}\left(\frac{\gamma_2}{\gamma_4\gamma_{SO_4}}\right)^{(0.205)} \tag{19}$$

where subscripted γ notations indicate the charge on hexacyclen species. As a consequence of this equation $K_{4SO_4}^{(0.22)}$ may be obtained from the experimental $K_{4SO_4}^{(0.205)}$ value and the relative values of activity coefficient ratios at the two ionic strengths. We estimate the required activity coefficient ratios from empirical activity coefficient correlations that have been successfully employed in describing the behavior of 4+, 3+, and 2+ hexacyclen species.

The correlation equations are

$$\log(\gamma_4/\gamma_3)^{(I)} - \log(\gamma_4/\gamma_3)^{(0.22)} = \Delta(\log(\gamma_4/\gamma_3)) = 0.962 - 3.46I^{1/2} + 3.75I - 1.59I^{3/2} \tag{20}$$

$$\log(\gamma_3/\gamma_2)^{(I)} - \log(\gamma_3/\gamma_2)^{(0.22)} = \Delta(\log(\gamma_3/\gamma_2)) = 0.924 - 4.11I^{1/2} + 6.11I - 3.31I^{3/2} \tag{21}$$

A comparison of these equations with eq 19 yields

$$\log K_{4SO_4}^{(0.22)} = \log K_{4SO_4}^{(0.205)} - \Delta(\log(\gamma_4/\gamma_3)) - \Delta(\log(\gamma_3/\gamma_2)) - \Delta(\log(\gamma_{SO_4})) \tag{22}$$

which enables us to calculate $K_{4SO_4}^{(0.22)}$ from correlations 20 and 21 and an estimate of $\Delta(\log(\gamma_{SO_4}))$, which we derive from the Debye–Hückel correlation, taking $a = 0.3$ nm for SO_4^{2-}. The ionic strength adjustment in this case amounts to a 9.1% decrease in $K_{4SO_4}^{(0.205)}$ to obtain $K_{4SO_4}^{(0.22)}$. The results of our ionic strength adjustments appear in Table II. The calculational methods are outlined in the footnotes of Table II. Also listed are values of $\Delta(\log(\gamma_2))$, and $\Delta(\log(\gamma_1))$, which refer to activity coefficients

Table II. Hexacyclen Complexation Constants, Acidity Constants, and Their Uncertainties at Ionic Strength 0.22 M at Various Temperatures

t, °C	$pK_{a_3}{}^{(0.22)\,a}$	$K_{3SO_4}{}^{(0.22)\,b}$	$K_{4SO_4}{}^{(0.22)\,c}$	$K_{(4SO_4)_2}{}^{(0.22)\,d}$
15	3.602 ± 0.006[g] (±0.023)	32 ± 8	0.94 (±0.03)[g] × 10^4 (±0.05 × 10^4)	60 ± 24
25	3.248 ± 0.003 (±0.022)	44 ± 6	1.32 (±0.02) × 10^4 (±0.06 × 10^4)	80 ± 8
35	2.903 ± 0.006 (±0.023)	42 ± 6	1.75 (±0.05) × 10^4 (±0.07 × 10^4)	111 ± 12
45	2.607 ± 0.003 (±0.022)	47 ± 4	2.31 (±0.03) × 10^4 (±0.11 × 10^4)	92 ± 7
55	2.309 ± 0.005 (±0.023)	66 ± 7	3.20 (±0.06) × 10^4 (±0.16 × 10^4)	118 ± 11

$\Delta(\log \gamma)$

$\Delta(\log(\gamma_4/\gamma_3)) = 0.016$[e]
$\Delta(\log(\gamma_3/\gamma_2)) = 0.009$[e]
$\Delta(\log(\gamma_2)) = 0.004$[f]
$\Delta(\log(\gamma_1)) = 0.001$[f]
$\Delta(\log(\gamma_{SO_4})) = 0.013$[f]
$\Delta(\log(\gamma_H)) = 0.002$[f]

[a] $pK_{a_3}{}^{(0.22)} = pK_{a_3}{}^{(0.205)} + \Delta(\log(\gamma_4/\gamma_3)) - \Delta(\log(\gamma_H))$. [b] $\log K_{3SO_4}{}^{(0.22)} = \log K_{3SO_4}{}^{(0.205)} - \Delta(\log(\gamma_3/\gamma_3)) + \Delta(\log(\gamma_2)) - \Delta(\log(\gamma_{SO_4})) + \Delta(\log(\gamma_1))$. [c] $\log K_{4SO_4}{}^{(0.22)} = \log K_{4SO_4}{}^{(0.205)} - \Delta(\log(\gamma_4/\gamma_3)) - \Delta(\log(\gamma_3/\gamma_2)) - \Delta(\log(\gamma_{SO_4}))$. [d] $\log K_{(4SO_4)_2}{}^{(0.22)} = \log K_{(4SO_4)_2}{}^{(0.205)} - \Delta(\log(\gamma_2)) - \Delta(\log(\gamma_{SO_4}))$. [e] Calculated from eq 20 and 21. $\Delta(\log \gamma)$ values are taken in the sense: log (activity coefficients at $I = 0.205$) − log (activity coefficients at $I = 0.22$). [f] Calculated from the extended Debye–Hückel equation, taking $a° = 0.3, 0.9, 1.2$ nm for SO_4^{2-}, H^+, and L species, respectively. [g] Standard error estimates derived from fluctuations in pH vs. composition data.

Table III. Hexacyclen Acidity and Complexation Constants with Chloride and Sulfate Ions and Derived Equilibrium Constants at Various Ionic Strengths at 25 °C

	conditional equilibrium constants[a]			thermodynamic equilibrium constants		
	$I = 0.05$	$I = 0.11$	$I = 0.21$	$I = 0.05$	$I = 0.11$	$I = 0.21$
reaction						
$H_4L^{4+} = H_3L^{3+} + H^+$	2.82 (±0.03) × 10^{-3}	0.828 (±0.006) × 10^{-3}	0.607 (±0.004) × 10^{-3}			
$H_4L^{4+} + Cl^- = H_4L(Cl)^{3+}$	377 ± 26	112 ± 6	73 ± 4			
$H_3L^{3+} + SO_4^{2-} = H_3L(SO_4)^+$	240 ± 18	120 ± 11	32 ± 4			
$H_4L^{4+} + SO_4^{2-} = H_4L(SO_4)^{2+}$	79 (±2) × 10^3	21.9 (±0.3) × 10^3	14.0 (±0.1) × 10^3			
$H_4L(SO_4)^{2+} + SO_4^{2-} = H_4L(SO_4)_2$	10.4 (±0.5) × 10^2	3.2 (±0.3) × 10^2	0.71 (±0.07) × 10^2			
$H_3L^{3+} + H^+ + Cl^- = H_4L(Cl)^{3+}$	1.34 (±0.02) × 10^5[b]	1.35 (±0.01) × 10^5	1.20 (±0.01) × 10^5	2.0 (±0.1) × 10^5[d]	2.2 (±0.1) × 10^5	2.2 (±0.1) × 10^5
$H_3L(SO_4)^+ + H^+ + SO_4^{2-} = H_4L(SO_4)_2$	12.1 (±0.3) × 10^7[c]	7.15 (±0.15) × 10^7	5.1 (±0.1) × 10^7	38 (±2) × 10^7[e]	33 (±2) × 10^7	34 (±2) × 10^7
ionic activity coeff terms						
$\gamma_H\gamma_{Cl}$	0.688 ± 0.020[f]	0.613 ± 0.018	0.551 ± 0.016			
$\gamma_1\gamma_H\gamma_{SO_4}$	0.314 ± 0.011	0.216 ± 0.008	0.150 ± 0.005			

[a] Values of hexacyclen conditional complexation constants with sulfate and pK_{a_3} values derived from pH vs. composition data. The rms fits were ±0.002 pH unit or better. Uncertainties are standard error estimates derived by propagation-of-variance methods and based on ±0.002 pH unit uncertainty. [b] $K^{(I)} = K_{Cl}{}^{(I)}/K_{a_3}{}^{(I)}$. Uncertainties are standard error estimates. [c] $K^{(I)} = K_{4SO_4}{}^{(I)}K_{(4SO_4)_2}{}^{(I)}/K_{3SO_4}{}^{(I)}K_{a_3}{}^{(I)}$. Uncertainties are standard error estimates described in the text. [d] $K^{(0)} = K^{(I)}/\gamma_H\gamma_{Cl}$. Uncertainties are standard error estimates. [e] $K^{(0)} = K^{(I)}/\gamma_H\gamma_{SO_4}\gamma_1$. Uncertainties are standard error estimates. [f] Calculated from the Debye–Hückel equation. Uncertainties are based on random fluctuation of ±2% in each γ value.

of 2+ and 1+ hexacyclen species. These values were estimated from the Debye–Hückel equation, taking $a = 1.2$ nm. In these calculations we employed the temperature-dependent values of A and B coefficients referred to earlier. In spite of this, $\Delta(\log(\gamma))$ values were essentially temperature-independent in the narrow range of ionic strengths between 0.205 and 0.22 M.

Before proceeding to analyze the equilibrium constant data of Table II, we describe another series of experiments that estimate hexacyclen complexation constants at different ionic strengths. These serve to verify the calculational and experimental procedures used here. A fresh stock of H_6LCl_6 solution was made up to $a = 2.7$ mol of NaOH/mol of H_6LCl_6 and used to prepare hexacyclen buffers in NaCl with ionic strengths of 0.05, 0.11, and 0.21. pH vs. composition data were obtained with each solution during addition of Na_2SO_4 solution whose concentration was adjusted to maintain an essentially constant ionic strength during each experiment. The data thus obtained would provide estimates of hexacyclen complexation constants. In order to analyze the data, however, we required estimates of K_{Cl}, the $H_4L(Cl)^{3+}$ formation constant, at these ionic strengths. Values of K_{Cl} at $I = 0.21$ and 0.11 M were available from the tabulated value of $K_{Cl}{}^{(0.22)}$ and from the activity coefficient correlations employed earlier. However, the correlation equations that are derived in the range between I = 0.11 and 0.44 M could not be applied to the I = 0.05 M data. In order to obtain the necessary $K_{Cl}{}^{(0.05)}$ value, we carried out an experiment in which an $a = 2.7$ mol of NaOH/mol of H_6LCl_6 hexacyclen buffer (about 1 mM) was made up to 0.05 ionic strength with NaI, which does not complex with hexacyclen species. pH vs. composition data obtained during addition of 0.05 M NaCl to the mixture were analyzed to yield $K_{Cl}{}^{(0.05)}$. Values of 377 ± 26 and 2.55 ± 0.03 were obtained for $K_{Cl}{}^{(0.05)}$ and $pK_{a_3}{}^{(0.05)}$, respectively. The nine experimental pH data fit model-predicted values with an rms scatter of ±0.003 pH unit. The value of $K_{Cl}{}^{(0.05)}$ thus obtained allowed analysis of the data obtained with sulfate solutions and provided estimates of hexacyclen complexation constants with sulfate, and these are listed in Table III along with other pertinent data.

We recall at this point an earlier order-of-magnitude estimate for the $H_4L(SO_4)^{2+} + SO_4^{2-} = H_4L(SO_4)_2$ equilibrium constant. The approximate value of 10^3, derived from conductometric titration data at an ionic strength near 0.01 M, seems consistent with the value of 10.4 (±0.5) × 10^2 pertinent to $I = 0.05$ M in Table III. However, a more detailed analysis follows.

Our purpose in making these experiments was to verify the consistency of formation constant values determined over a range of ionic strengths. Comparison of complexation constants at differing ionic strengths necessarily involves correlation of ionic activity coefficients as a function of ionic strength. As we have noted, however, the empirical correlations relating activity coefficients of highly charged hexacyclen species to the ionic strength are valid within a limited range. In order to avoid this difficulty we will recast the equilibrium constant data in such a way as to avoid the necessity for correlating activity coefficients of 4+ and 3+ species. The chemical reaction

$$H_3L(SO_4)^+ + H^+ + SO_4^{2-} = H_4L(SO_4)_2 \qquad (23)$$

involves only singly charged species and the sulfate dianion. We assume that the activity coefficients of these species are accurately described by the Debye–Hückel correlation. The thermodynamic equilibrium constant for reaction 23 is related to conditional constants obtained here by

$$K^{(0)}(\text{eq } 23) = \frac{K_{4SO_4}{}^{(0)}K_{(4SO_4)^2}{}^{(0)}}{K_{3SO_4}{}^{(0)}K_{a_3}{}^{(0)}} = \frac{K_{4SO_4}{}^{(I)}K_{(4SO_4)^2}{}^{(I)}}{K_{3SO_4}{}^{(I)}K_{a_3}{}^{(I)}}\left(\frac{1}{\gamma_1\gamma_H\gamma_{SO_4}}\right) \qquad (24)$$

For the sake of comparison we examine the ionic strength dependence of the equilibrium

$$H_3L^{3+} + H^+ + Cl^- = H_4L(Cl)^{3+} \qquad (25)$$

The thermodynamic equilibrium constant is given by

$$K^{(0)}(\text{eq } 25) = \frac{K_{Cl}{}^{(0)}}{K_{a_3}{}^{(0)}} = \frac{K_{Cl}{}^{(I)}}{K_{a_3}{}^{(I)}}\left(\frac{1}{\gamma_H\gamma_{Cl}}\right) \qquad (26)$$

and where we take ionic activity coefficients of the 3+ hexacyclen species H_3L^{3+} and $H_4L(Cl)^{3+}$ to have a common value. Consequently, estimation of $K^{(0)}$(eq 25) requires conditional constants $K_{Cl}{}^{(I)}$ and $K_{a_3}{}^{(I)}$ and relies only on H^+ and Cl^- activity coefficients up to an ionic strength of 0.21, which can be calculated with reasonable accuracies. Results are described in Table III and its footnotes. Interpretation of these data relies in part on an ability to estimate uncertainties in the derived constant values, $K^{(0)}$.

The nonlinear regression procedure yields variance estimates for three parameters: $K_{a_3}{}^{(I)}$, $K_{3SO_4}{}^{(I)}$, and the product $(K_{4SO_4}{}^{(I)}K_{(4SO_4)^2})$. It also provides covariances for each pair of these three parameters. As seen from eq 24, we are interested in the variance of the derived quantity $F = P_1/(P_2P_3)$, where we are abbreviating $(K_{4SO_4}{}^{(I)}K_{(4SO_4)^2}{}^{(I)})$ by P_1, $K_{3SO_4}{}^{(I)}$ by P_2, and $K_{a_3}{}^{(I)}$ by P_3. Propagation of variance procedures leads to the relationship

$$\frac{\text{var } F}{F^2} = \frac{\text{var } P_1}{P_1{}^2} + \frac{\text{var } P_2}{P_2{}^2} + \frac{\text{var } P_3}{P_3{}^2} - \frac{2\text{ cov}(P_1,P_2)}{P_1P_2} - \frac{2\text{ cov}(P_1,P_3)}{P_1P_3} - \frac{2\text{ cov}(P_2,P_3)}{P_2P_3} \qquad (27)$$

The nonlinear regression provides F and all the quantities on the right-hand side of eq 27. Thus the standard error estimate in F is calculated as the square root of its variance. We applied the same methods to estimate the standard errors in $K_{Cl}{}^{(I)}/K_{a_3}{}^{(I)}$ of eq 26. The results of these calculations appear in the three right-hand columns of Table III and we interpret the essential constancy of $K^{(0)}$(eq 23) and $K^{(0)}$(eq 25) values derived from experiments at ionic strengths of 0.05, 0.11, and 0.21 M as verifying that the model equations and equilibrium constant values derived here adequately describe hexacyclen complexation with sulfate ions in these experimental systems. In other words, we are able to account for minor variations in $K^{(0)}$(eq 23) and $K^{(0)}$(eq 25) as resulting entirely from statistical fluctuation unrelated to additional chemical processes. As a further consequence of these results at varying ionic strengths we are able to exclude possible formation of mixed complexes of chloride and sulfate with hexacyclen species in these solutions. A detailed account of the considerations that lead to this conclusion has been given in ref 7. The following discussion assumes the existence of only those solution species that are written into the model equations 9–18.

van't Hoff analysis of the temperature-dependent equilibrium constant data in Table II provides estimates of ΔH^* and ΔS^*, the complexation enthalpies and entropies at $I = 0.22$ M. In order to derive the desired values we made weighted least-squares regressions of $T \ln K$ against T with weighting factors derived from uncertainties in equilibrium constants. ΔH^* and ΔS^* and their standard error estimates are calculated from the least-squares analysis. The results of these calculations are compared with similar results from hexacyclen complexations with monovalent anions in Table IV. In addition we have obtained ΔH^* and ΔS^* values for the acidic dissociation of tetraprotonated hexacyclen from the temperature dependence of pK_{a_3}. These values are in good agreement with past results.

Discussion

We begin our discussion of the present results with a brief review of an earlier interpretation of H_4L^{4+} complexation with monovalent anions. These complexations appear to fall into three classes: (a) enthalpy-driven reactions having only small negative entropy changes that appear to involve simple ion association phenomena (examples being H_4L^{4+} complexation with ClO_4^- and ternary complex formation with IO_3^- ($H_4L(IO_3)^{3+} + IO_3^- = H_4L(IO_3)_2{}^{2+}$)); (b) entropy-driven reactions with positive enthalpy changes, which we ascribe to extensive solvent loss from the H_4L^{4+} species (examples being Cl^- and benzenesulfonate); (c) entropy-driven reactions with ΔH^* near zero corresponding to solvent-intermediated complexation reactions. H_4L^{4+} complexations of NO_3^- and IO_3^- seem to be examples of this reaction scheme. Three observations are central to these interpretations. First, H_4L^{4+} has unusual dissociation properties. The acidity constant at 25 °C for H_4L^{4+} is similar to that of other tetraprotonated polyamines, but the values of ΔH^* and ΔS^* for proton dissociation are substantially different. The enthalpy change accompanying H_4L^{4+} dissociation of about +14 kcal mol^{-1} reflects a substantially greater loss in bonding interactions from the solvated H_4L^{4+} species upon dissociation compared with typical dissociation enthalpies of about +8 kcal mol^{-1} for other tetraprotonated polyamine acids not known to possess anion binding capabilities.[6] At the same time the entropic contribution to H_4L^{4+} dissociation is very much larger than that for similar ammonium acids (+32 cal mol^{-1} K^{-1} for H_4L^{4+} compared with values between 0 and +15 cal mol^{-1} K^{-1} for a variety of 4+ ammonium acids). We connect these differences to an unusual enhancement of solvent ordering around H_4L^{4+} compared with that around other noncomplexing 4+ ammonium species. We ascribe the phenomenon of anion complexation by hexacyclen (and perhaps by other protonated polyamine macrocycles) to this enhanced solvent network.

Second, we note the results of our earlier ^{13}C NMR investigation of 3+ and 4+ hexacyclen species in nitrate and chloride media.[7] These experiments first confirmed the general description of the equilibria in these solution—that of a rapidly equilibrating H_4L^{4+}/H_3L^{3+} acid–base reaction coupled to a kinetically slow complexation between H_4L^{4+} and chloride or nitrate ions, which is evident even at the slow time scale of pH potentiometric measurements. More relevant to the present discussion, however, is the fact that in the slowly exchanging anion complexes all 12 carbon atoms of hexacyclen remain equivalent and give rise to single sharp pH-independent resonances for both $H_4L(Cl)^{3+}$ and $H_4L(NO_3)^{3+}$ (at 47.15 and 46.67 ppm downfield from Me_4Si, respectively). The appearance of a single carbon resonance in these complexes indicates a rapid exchange of both H^+- and anion-binding sites in the H_4L^{4+}–anion complexes. However, if the exchange process were to involve an anion dissociation process the single pH-independent resonance would not be observed. Instead we interpret the ^{13}C NMR spectral observations as resulting from an exchange, rapid on the ^{13}C NMR time scale, of both H^+ and anion binding sites within the complex solvent cage and essentially independent of the bulk solvent. Thus, the ^{13}C NMR behavior of hexacyclen species seems to support a model consisting of a relatively inert and extensive solvation sphere around even the H_4LCl^{3+} and $H_4L(NO_3)^{3+}$ complexes.

Third, we note the apparent connection between the structures as determined by X-ray crystallographic analysis and the thermodynamic properties of H_4L^{4+} complexations with nitrate and chloride ions.[7,8] In the solid phase at least a water molecule intercedes between H_4L^{4+} and nitrate while the chloride ion seems

Table IV. ΔH^* and ΔS^* and Their Uncertainties for Acidic Dissociation of H_4L^{4+} and Complexation Reactions of Hexacyclen Species with Sulfate Ions and Various Monovalent Anions

reaction	ΔH^*, kcal mol^{-1}	ΔS^*, cal mol^{-1} K^{-1}
$H_4L^{4+} = H_3L^{3+} + H^+$	14.0 ± 0.1[a] 14.1 ± 0.1[b]	32.0 ± 0.3[a] 32 ± 1[b]
$H_4L^{4+} + ClO_4^- = H_4L(ClO_4)^{3+}$	-2.5 ± 0.7	-3.8 ± 2.1
$H_4L(IO_3)^{3+} = IO_3^- = H_4L(IO_3)^{2+}$	-2.3 ± 0.3	-2.8 ± 1.1
$H_4L^{4+} + Cl^- = H_4L(Cl)^{3+}$	4.9 ± 0.6	24 ± 2
$H_4L^{4+} + CF_3CO_2^- = H_4L(CF_3CO_2)^{3+}$	6.5 ± 0.2	25.9 ± 0.6
$H_4L^{4+} + C_6H_5SO_3^- = H_4L(C_6H_5SO_3)^{3+}$	6.6 ± 0.2	24.6 ± 0.7
$H_4L^{4+} + NO_3^- = H_4L(NO_3)^{3+}$	-0.4 ± 0.6	12 ± 2
$H_4L^{4+} + IO_3^- = H_4L(IO_3)^{3+}$	1.3 ± 0.1	17.1 ± 0.5
$H_4L^{4+} + SO_4^{2-} = H_4L(SO_4)^{2+}$	5.6 ± 0.2	37.8 ± 0.6
$H_4L(SO_4)^{2+} + SO_4^{2-} = H_4L(SO_4)_2$	2.1 ± 0.8	15.6 ± 2.4
$H_3L^{3+} + SO_4^{2-} = H_3L(SO_4)^+$	2.8 ± 0.9	16.7 ± 2.8

[a] This work. [b] Reference 6.

to interact directly with ammonium sites of hexacyclen. At the same time, the values of ΔH^* and ΔS^* for the nitrate and chloride complexation reactions differ by about 5 kcal mol^{-1} and 12 cal mol^{-1} K^{-1}, respectively, with the chloride complexation being more endothermic and more entropy producing. Thus, we interpret the larger positive entropy change accompanying chloride complexation to loss of additional solvation water from $H_4L(Cl)^{3+}$ compared with $H_4L(NO_3)$.$^{3+}$

On the basis of the foregoing analysis we begin to interpret the present results relating to hexacyclen complexation by sulfate. We first consider the acidic dissociation reaction

$$H_4L(SO_4)^{2+} = H_3L(SO_4)^+ + H^+$$

for which we calculate $\Delta H^* = +11$ kcal mol^{-1} and $\Delta S^* = +11$ cal mol^{-1} K^{-1} and observe that these values do not differ substantially from other acidic dissociation reactions of polyammonium species that do not have anion-complexing properties. Viewed in this way, acidic dissociation of the tetraprotonated $H_4L(SO_4)^{2+}$ acid does not involve loss of an extensive solvation sphere, which we associate with uncomplexed H_4L^{4+}. As a result we conclude that the $H_4L(SO_4)^{2+}$ acid does not form an appreciably larger solvation sphere than typical noncomplexing ammonium acids. We associate H_4L^{4+} binding of sulfate with an "inner sphere" model similar to H_4L^{4+} interaction with chloride, trifluoroacetate, and benzenesulfonate. A direct comparison of H_4L^{4+} complexation with sulfate and with benzenesulfonate is provided by the metathesis reaction

$$H_4L(O_3SC_6H_5)^{3+} + SO_4^{2-} = H_4L(SO_4)^{2+} + C_6H_5SO_3^-$$

for which $\Delta H^* = -0.9$ kcal mol^{-1} and $\Delta S^* = 13$ cal mol^{-1} K^{-1}. This reaction involves two fundamental changes with respect to solvent interaction. First, the 3+ hexacyclen species becomes a 2+ species. This change involves some loss in ion–dipole interaction with the solvent and leads to a positive enthalpy contribution and a positive entropy change since the 2+ ion should cause less solvent bonding and less solvent ordering. At the same time, a benzenesulfonate anion is transferred to the solution in place of a more highly charged and more highly solvated sulfate ion. This process results in a net positive contribution to both the enthalpy and entropy changes since the transfer should provide a net loss in solvent–anion bonding along with a net loss in solvent ordering. Thus, the observed positive entropy change for the metathesis seems at least qualitatively accountable on the basis of solvent-ordering effects. We ascribe the observed negative value of ΔH^* to somewhat stronger H_4L^{4+} bonding with sulfate than with benzenesulfonate. The bonding interactions to be compared are the bonding difference between sulfate–hexacyclen and sulfate–water compared with the difference in bonding between benzenesulfonate–hexacyclen and benzenesulfonate–water. Apparently, the increased charge density on sulfate oxygens provides a relatively stronger interaction with ionic hexacyclen sites as might be expected. In this connection it is useful to compare the relative contributions of ΔH^* and ΔS^* to the free energy of the transfer process. These values are -0.9 kcal mol^{-1} for ΔH^* and -3.9 kcal mol^{-1} for $-T\Delta S^*$ at 298 °K. We conclude that the primary driving force in this reaction is entropy production due to loss of solvation water from both $H_4L(O_3SC_6H_5)^{3+}$ and sulfate ions. The magnitude of the entropy change seems accountable on the basis of combined outer-sphere solvation loss from hexacyclen and sulfate species but may also reflect additional processes including loss of some inner sphere water from hexacyclen.

Some clarification of the processes involved in hexacyclen complexation by sulfate is provided by a comparison of the thermodynamic parameters ΔH^* and ΔS^* to corresponding values for ion-pairing processes. ΔH values for ion-pair formation of Ni^{2+}, Co^{2+}, and Mn^{2+} with sulfate are +3.2, +1.6, and +3.6 kcal mol^{-1}, respectively. Corresponding values of ΔS are +22, +17, and +23 cal mol^{-1} K^{-1}, respectively.[14] We will presume that these ion pairs of sulfate with divalent metal ions are of an outer-sphere type. We base this assumption on the observation that the visible spectra obtained with approximately 0.02 M concentrations of sulfate salts of these metals show no detectable change upon addition of excess sulfate up to about 0.1 M. In this concentration range the proportion of ion-paired metal ion present in solution varies from about 0.5 to about 0.9 so that any difference between the spectral properties of the aquated metal ion and the ion pair would be evident from our experiments. Presumably, any intrusion of sulfate ions into the inner $M(H_2O)_6^{2+}$ solvation sphere would have a profound effect on d-orbital symmetry in these ions, which would be reflected in the spectra. Because we observe no such spectral perturbation, we conclude that these metal–sulfate ion pairs may be represented as "ion-associates"[15] whose formation relies on "loosening" of outer water from the electrically neutral ion-paired species compared with isolated divalent ions.

The apparently similar values of both ΔH and ΔS for the metal–sulfate ion-pairing processes and ΔH^* and ΔS^* for both H_3L^{3+} complexation with sulfate and ternary H_4L^{4+} sulfate complexation ($H_4L(SO_4)^{2+} + SO_4^{2-} = H_4L(SO_4)_2$) suggest that these reactions also represent ion-pairing processes driven by weakening outer-sphere interactions. However, the primary H_4L^{4+}, sulfate complexation does not seem to fit this description, even allowing for the differences in ionic charge. This observation would be supported by comparisons of ΔH and ΔS for ion associations involving sulfate and various tetravalent cations, but the appropriate data are not currently available. Instead we make the somewhat less satisfactory comparison with the ion association reaction 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}.[14] The striking similarity of the enthalpy change in this reaction with those for divalent metal–sulfate ion associates reflects the relatively small electrostatic contribution to these processes. The similar entropy changes seem to indicate that the diffuse hydration spheres of di- and trivalent ions are perturbed approximately to the same extent by the ion association process. Thus, if the La^{3+},$Fe(CN)_6^{3-}$ association may be taken as representative of such processes among highly charged ions, we conclude that H_4L^{4+},sulfate complexation must be regarded as exceptional both in its substantially unfavorable ΔH value and its unusually large positive entropy change. These characteristics result from expulsion of inner-sphere water from the H_4L^{4+},sulfate complex compared with the separated ions.

We conclude this discussion with an observation that hexacyclen, and perhaps other macrocyclic polyamine complexes of anions, seem to be best characterized in terms of properties of the solvation spheres of the complexing species rather than in terms of any specific interactions between the macrocycle and anion species. The present results seem to indicate that electrostatic interactions or direct bonding interactions between complexing species seem not to play a significant role in complexation. Additionally the apparent lack of any relationship between complexation properties and steric factors leads to similar conclusion, namely that the complexation reactions represent for the most

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part properties of the macrocycle and anion solvation spheres rather than specific properties of the complexing ions. This formulation also provides a rationale for the anion complexation reactions of highly protonated macrocycle species while such reactions have not been observed with apparently similar linear polyamines. That is, the linear structures do not assemble a sufficiently large solvation sphere, which by its subsequent partial dispersal provides the driving force for anion complexation.

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Multinuclear NMR Characterization of Anionic Clusters of the Main-Group Elements Ge, Sn, Sb, Tl, Pb, and Bi in Nonaqueous Solution

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Anionic clusters of the elements Ge, Sn, Sb, Tl, Pb, and Bi have been generated by dissolving their alloys with alkali metals in liquid ethylenediamine. The clusters have been identified by ^{119}Sn, ^{205}Tl, and ^{207}Pb NMR techniques. Spin–spin coupling constants (^{119}Sn–^{117}Sn, ^{119}Sn–^{203,205}Tl, and ^{119}Sn–^{207}Pb) and chemical shifts (^{119}Sn and ^{207}Pb) are presented for a large number of clusters with a range of alkali-metal cations. Clusters not previously reported include $Sn_{8-x}Pb_xTl^{n-}$ (x = 1–4, n probably 5); $Sn_2Bi_2^{2-}$ is characterized in solution for the first time. A number of systematic trends in the data are presented and discussed. The origins of the spin–spin couplings are discussed in terms of the relativistic theory of the coupling with the aid of relativistically parametrized (REX) semiempirical molecular orbital calculations.

I. Introduction

A large number of anionic clusters of group 3B–5B (13–15)[49] elements have been generated by the extraction of Zintl alloylike phases with nonaqueous solvents such as ethylenediamine (en) or ammonia and characterized[3-8] by ^{119}Sn, ^{205}Tl, or ^{207}Pb NMR spectroscopy. Clusters that have been identified include $Sn_{9-x}Pb_x^{4-}$ (x = 0–9),[4,5] $Sn_{9-x}Ge_x^{4-}$ (x = 0–9),[6] Sn_8Tl^{5-},[6] Sn_4^{2-},[6] $SnTe_4^{4-}$,[6] $Sn_9ML_2^{4-}$, and $Sn_8TlML_2^{5-}$ (M = Pd, Pt; L_2 = en).[7,8] The list of clusters is similar to that of anionic clusters which have been isolated from solution as salts of alkali metals complexed with the bicyclic 2,2,2-crypt ligand. These include Sb_4^{2-} and Sb_7^{3-},[9,10] Te_3^{2-},[11] Bi_4^{2-},[12] Sn_5^{2-} and Pb_5^{2-},[13] Sn_9^{4-},[14] Ge_9^{4-} and Ge_9^{2-},[15] As_{11}^{2-},[16] $Tl_2Te_2^{2-}$,[17] $Sn_2Bi_2^{2-}$,[18] Sn_xTl^{3-} (x = 8, 9),[19] $HgTe_2^{2-}$,[20] and Sn_9^{3-}.[21] Closely related are the large number of known cationic clusters,[22] including Bi_5^{3+},[23] Bi_8^{2+},[24] Bi_9^{5+},[23-25] Se_8^{2+},[27] $Te_{4-x}Se_x^{2+}$ (x = 0–4),[28-31] $Te_{6-x}Se_x^{2+}$ (x = 0, 3, 4),[32] and Se_{10}^{2+}.[33] A key observation[3-8] from ^{119}Sn NMR of solutions of anionic clusters containing Sn is a single ^{119}Sn chemical shift δ and a single ^{119}Sn–^{117}Sn coupling constant for a given cluster, from which it is concluded[3-6] that clusters such as $Sn_{9-x}M_x^{4-}$ (M = Ge, Pb) are fluxional.

We report here for the first time the identification by NMR in solution of the clusters $Sn_{8-x}Pb_xTl^{5-}$ (x = 1–4) and $Sn_2Bi_2^{2-}$. We also present a compilation of ^{119}Sn and ^{207}Pb chemical shifts together with ^{119}Sn–^{117}Sn, ^{119}Sn–^{207}Pb, and ^{119}Sn–^{203,205}Tl coupling constants for a large number of nine-atom anionic clusters of the form $Sn_{9-x-y}A_xB_y^{q-}$ (A, B = Ge, Tl, Pb), with the data being presented as a function of the accompanying alkali cation, ranging from Li^+ to Cs^+ in some cases but more typically from Na^+ to Cs^+. Finally, we present a discussion and an interpretation of the nuclear spin–spin coupling constants in terms of the relativistic theory[34] of these couplings.

Table I. Clusters and Alloys from Which They Were Obtained

cluster	alloys[a]
Sn_9^{4-}	LiSn, $LiSn_2$, $NaSn_4$, Na_4Sn_9, $NaSn_2$, NaSn (NH_3, CH_3NH_2), KSn_2, KSn_3
Pb_9^{4-}	KPb_2, $NaPb_2$, $NaPb_3$, Li_4Pb_9, $LiPb_2$
$Sn_{9-x}Pb_x^{4-}$ (x = 0–9)	LiSnPb, NaSnPb, $Na_4Sn_3Pb_6$, $Na_4Sn_6Pb_3$, KSnPb, RbSnPb, CsSnPb
$Sn_{9-x}Ge_x^{4-}$ (x = 0–9)	NaSnGe, KSnGe, K_2SnGe_3, RbSnGe
Sn_8Tl^{5-}	$Na_2Sn_2Tl_3$, $K_2Sn_2Tl_3$
$Sn_{8-x}Pb_xTl^{5-}$ (x = 0–8)	$Na_2SnPbTl_3$, $K_2SnPbTl_3$
$Sn_2Bi_2^{2-}$	LiSnBi, NaSnBi
Sn_4^{2-}[b]	NaSn (en), Na_3Sn_2 (en), Na_2Sn (en), NaSnCu (en)
$SnTe_4^{4-}$[b]	NaSnTe

[a] Where important, the solvent is listed in parentheses after the alloy. The compositions of the alloys are nominal and are not intended to represent pure phases. [b] Reference 6.

II. Experimental Section

As described in our earlier papers,[4-6] alloys of group 3B–5B elements with alkali metals were prepared by fusion. Typically, the elements were heated in Vycor tubes under N_2 at 0.9 atm (at room temperature) and, after cooling, were extracted with en to form deeply colored solutions (orange-red for Sn_9^{4-}). To minimize contaminations, the extractions were carried out in NMR tubes, each sealed to a stopcock fitted with a ground-glass joint. Extraction times were typically 2–24 h but were 48 h–2 weeks for alloys containing Na. The times were selected to obtain

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