Stability and Kinetics of Acid- and Anion-Assisted Dissociation Reactions of Hexaamine Macrobicyclic Mercury(II) Complexes

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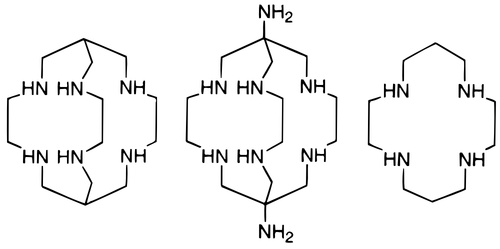
The H^+- and Cl^--assisted dissociation kinetics and the stabilities of the complexes $[Hg(sar)]^{2+}$ and $[Hg((NH_2)_2\text{-}sar)]^{2+}$ (sar = 3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane and $(NH_2)_2$-sar = 1,8-diamino-sar) were determined. The Hg^{2+} dissociation rates depend on both the proton and the chloride ion concentrations. H^+ competes with the metal ion for dissociated amine groups, and Cl^- competes with the amine for vacant coordination sites. The rate laws are complicated. For the $[Hg(sar)]^{2+}$ system ($0.1 \le [H^+] \le 1.0$ M, $0.01 \le [Cl^-] \le 1.0$ M, $I = 2.0$ M (NaO_3SCF_3), 25.0 °C) the observed rate law is $v_{-Hg^{2+}} = (a + b[Cl^-])[H^+][Hg(sar)^{2+}]/(1 + c[Cl^-])$, with $a = 35(3)$ M^{-1} s^{-1}, $b = 2.9(4) \times 10^3$ M^{-2} s^{-1}, and $c = 33(5)$ M^{-1}. For the $[Hg((NH_3)_2\text{-}sar)]^{4+}$ system ($0.001 \le [H^+] \le 1.0$ M, $0.01 \le [Cl^-] \le 1.0$ M, $I = 1.0$ M ($LiClO_4$), 25.0 °C) the observed rate law is $v_{-Hg^{2+}} = (a + b[H^+] + c[H^+]^2)[Cl^-][Hg((NH_3)_2\text{-}sar)^{4+}])/((1 + d[Cl^-])(1 + e[H^+]))$, with $a = 0.056(6)$ M^{-1} s^{-1}, $b = 8(3)$ M^{-2} s^{-1}, $c = 5(3)$ M^{-3} s^{-1}, $d = 1.3(4)$ M^{-1}, and $e = 1.1(5) \times 10^2$ M^{-1}. Intimate mechanisms for the dissociation reactions are proposed. Using iodide ion or sar ligand as competing ligands and the reported values for the stabilities of $HgI_3^-$and HgI_4^{2-} the stability constants at 25.0 °C were determined for $[Hg(sar)]^{2+}$ ($10^{28.1(1)}$ M^{-1}), $[Hg(sar)I]^+$ ($10^{29.1(1)}$ M^{-2}), $[Hg((NH_2)_2\text{-}sar)I]^+$ ($10^{28.5(1)}$ M^{-2}), and $[Hg(cyclam)I]^+$ ($10^{30.8(1)}$ M^{-2}) (cyclam = 1,4,8,11-tetraazacyclotetradecane) with $[OH^-] = 0.1$ M, $I = 0.5$ M ($NaClO_4$) and for $[Hg((NH_2)_2\text{-}sar)]^{2+}$ ($10^{26.4(3)}$ M^{-1}) with $[OD^-] = 0.1$ M, $I = 0.1$ M (NaOD).

Introduction

A range of transition and group 12 metal ions form cage complexes with the hexaamine macrobicyclic ligands sar[3] (**1**, Chart I) and $(NH_2)_2$-sar (**2**) in which the metal is totally enclosed by the ligand.[4,5] The syntheses, electrochemical properties, and structural aspects of those complexes have been studied extensively in recent years.[6−12] However, relatively little is known about their thermodynamic stability as well as details on the mechanisms of their complexation and decomplexation reactions. In most instances, the decomplexation rate is too slow for the stability constants to be measured.

Chart 1



1 sar **2** $(NH_2)_2$-sar **3** cyclam

Thermodynamic stabilities of a large number of macrocyclic amine ligands, such as cyclam (**3**), with various metal ions have been studied in detail.[13−16] In general, Hg^{2+} complexes with azamacrocyclic ligands are very stable and their stability constants cannot be determined by conventional potentiometric methods. In this respect, the bicyclic cages mirror the problems encountered with the macromonocycles. The Hg^{2+} ion generally forms very labile complexes, and even with the cages equilibration is relatively rapid. Therefore, the stability constants of the Hg^{2+} cage complexes could be determined by the competition method using ligands that form complexes for which the stabilities approach those to be measured. Iodide

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(3) Abbreviations: sar = 3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane; $(NH_2)_2$-sar = 1,8-diamino-sar; cyclam = 1,4,8,11-tetraazacyclotetradecane; [18]aneN_2O_4 = 4,7,13,16-tetraoxa-1,10-diazacyclooctadecane; [2.2.2]-cryptand = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-[8.8.8]hexacosane.

(4) Comba, P.; Sargeson, A. M.; Engelhardt, L. M.; Harrowfield, J. MacB.; White, A. H.; Horn, E.; Snow, M. R. *Inorg. Chem.* **1985**, *24*, 2325.

(5) Sargeson, A. M. *Pure Appl. Chem.* **1984**, *56*, 1603.

(6) Geue, R. J.; Hambley, T. W.; Harrowfield, J. M.; Sargeson, A. M.; Snow, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 5478.

(7) Bottomley, G. A.; Clark, I. J.; Creaser, I. I.; Engelhart, L. M.; Geue, R. J.; Lay, P. A.; Sargeson, A. M.; See, A. J.; Skelton, B. W.; White, A. H.; Wilner, F. R. *Aust. J. Chem.* **1994**, *47*, 143.

(8) Bond, A. M.; Lawrence, G. A.; Lay, P. A.; Sargeson, A. M. *Inorg. Chem.* **1983**, *22*, 2010.

(9) Comba, P.; Creaser, I. I.; Gahan, L. R.; Harrowfield, J. M.; Lawrence, G. A.; Martin, L. L.; Mau, A. W. H.; Sargeson, A. M.; Sasse, W. H. F.; Snow, M. R. *Inorg. Chem.* **1986**, *25*, 384.

(10) Comba, P.; Engelhardt, L. M.; Harrowfield, J. M.; Lawrance, G. A.; Martin, L. M.; Sargeson, A. M.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1985**, 174.

(11) Clark, I. J.; Creaser, I. I.; Engelhardt, L. M.; Harrowfield, J. M.; Krausz, E. R.; Moran, G. M.; Sargeson, A. M.; White, A. H. *Aust. J. Chem.* **1993**, *46*, 111.

(12) Bernhardt, P. V.; Bramley, R.; Engelhardt, L. M.; Harrowfield, J. M.; Hockless, D. C. R.; Korybut-Daszkiewicz, B. R.; Krausz, E. R.; Morgan, T.; Sargeson, A. M.; Skelton, B. W.; White, A. H. *Inorg. Chem.* **1995**, *34*, 3589.

(13) Izatt, R. M.; Bradshaw, J. S.; Nielsen, S. A.; Lamb, J. D.; Christensen, J. J.; Sen, D. *Chem. Rev.* **1985**, *85*, 271.

(14) Christensen, J. J.; Eatough, D. J.; Izatt, R. M. *Chem. Rev.* **1974**, *74*, 351.

(15) Bianchi, A.; Micheloni, M.; Paoletti, P. *Coord. Chem. Rev.* **1991**, *110*, 17.

(16) Bhula, R.; Osvath, P.; Weatherburn, D. C. *Coord. Chem. Rev.* **1988**, *91*, 89.

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ion proved to be an effective reagent to remove Hg^{2+} from the cage complexes, and their stability constants were determined in competition with HgI_n^{2-n} ($n = 3, 4$) ions in basic solution. This method is analogous to that applied by Hinz and Margerum for macrocyclic nickel(II) complexes with cyanide ion as the competing ligand.[17] Furthermore, competition between two cage ligands for Hg^{2+} may be used to deduce the relative stability of the corresponding complexes.

Studies on acid-induced metal liberation from azamacrocyclic complexes have mainly been concerned with Ni^{2+} and Cu^{2+} complexes.[18-20] In one instance, the effect of the concentration and kind of anion on the metal ion liberation rate has been reported and no dependence was found.[21] With the metal ion cage complexes only preliminary studies relating to the inertness displayed by these compounds have been made.[22,23] For example, $[Co(sar)]^{2+}$ is very stable and the Co^{2+} ion is only removed at high temperatures in concentrated HBr or HCl, whereas simple Co^{2+} amine complexes usually form and dissociate on the microsecond time scale. This displays a large ($>10^{10}$ fold) change in kinetic stability, and the Co^{2+} cage complex can be viewed as an inert species.

Not all the cage complexes are as inert as the Co^{2+} systems, however, and the Mn^{2+}, Zn^{2+}, Cd^{2+}, and Hg^{2+} complexes are more amenable to study under reasonable conditions. Therefore, the reactivity of the more labile mercury(II) systems, $[Hg(sar)]^{2+}$ and $[Hg((NH_3)_2\text{-sar})]^{4+}$, was explored in order to provide some understanding of the chemical inertness observed for the cage complexes.

Experimental Section

Safety Note. Although we have experienced no problems with the compounds reported in this work, perchlorate salts are potentially explosive and should only be handled in small quantities and never heated in the solid state nor scraped from sintered-glass frits.

Syntheses. All reagents were of analytical grade and were used without further purification. For all thermodynamic and kinetic measurements microfiltered doubly deionized water was used. The cage ligands were obtained by cyanide-assisted liberation from the Co^{2+} complexes[7] and analyzed as sar and $(NH_2)_2\text{-sar}\cdot5H_2O$, respectively.

$[Hg(sar)](ClO_4)_2$. A solution of equimolar amounts of $Hg(CH_3COO)_2$ (66 mg) and sar (56 mg) in water (4 mL) was heated over a steam bath for a few minutes. The complex was precipitated as the perchlorate salt by addition of $LiClO_4$ (43 mg in 1 mL of water). The crystals were collected and dried in air. Anal. Calc for $[Hg(sar)](ClO_4)_2$, $HgC_{14}N_6H_{32}Cl_2O_8$: C, 24.59; N, 12.29; H, 4.72. Found: C, 24.6; N, 12.3; H, 4.8. ^{1}H-NMR (300 MHz, D_2O/NaCl, internal standard TPS): 2.0 (multiplet, 2H, CH caps); 2.32, 3.29 (AB coupling pattern, 12 H, $J = 8.7$ Hz, CH_2CH_2); 2.84 (AB doublet, 6 H, $J = 13.8$ Hz, CH_2 caps); 3.61 (AB doublet of doublets, 6 H, $J = 13.8$ Hz, CH_2 caps).

$[Hg((NH_3)_2\text{-sar})](NO_3)_4\cdot H_2O$. A solution of equimolar amounts of $Hg(CH_3COO)_2$ (44 mg) and $(NH_2)_2\text{-sar}\cdot5H_2O$ (42 mg) in water (3 mL) was heated over a steam bath for 10 min. The complex was precipitated as the nitrate salt by slow addition of concentrated HNO_3 (0.4 mL) to the stirred solution. The crystals were collected, washed with ethanol and ether, and dried in air. Anal. Calc for $[Hg((NH_3)_2\text{-sar})](NO_3)_4\cdot H_2O$, $HgC_{14}N_{12}H_{38}O_{13}$: C, 21.47; N, 21.46; H, 4.89. Found: C, 21.3; N, 21.2; H, 5.0. ^{1}H-NMR (300 MHz, $D_2O/DClO_4$; internal standard TPS): 2.46 (AB doublet, 6H, $J = 9.3$ Hz, CH_2 caps), 3.5 (AA′BB′ coupling pattern, 12 H, CH_2CH_2), 3.44 (AB doublet, 6 H, $J = 9.3$ Hz, CH_2 caps).

Equilibrium Studies. Stability Relative to Iodide. Equilibrium measurements were performed with a Hewlett-Packard UV−visible spectrophotometer thermostated to 25.0 ± 0.1 °C. The solutions contained 0.10 M NaOH to minimize protonation of the ligand, $I = 0.50$ M ($NaClO_4$). The total mercury(II) concentration was 4.0×10^{-5} M, and the total ligand concentration was 1.0×10^{-3} or 4.0×10^{-4} M. "Titrations" were performed in a batchwise manner in order to minimize the possibility of slow precipitation of the complex or reduction of any free mercury(II). Equilibrium was approached from both directions.

When one starts from $[Hg(L)]^{2+} + I^-$, solutions of $[Hg(sar)](ClO_4)_2$ and sar or $[Hg((NH_3)_2\text{-sar})](NO_3)_4\cdot H_2O$ and $(NH_2)_2\text{-sar}\cdot5H_2O$ were mixed with solutions of NaOH, NaI and $NaClO_4$. Sodium iodide concentrations ranged from 0.02 to 0.40 M ensuring that the amount of HgI_4^{2-} varied from 10% to 90% of total mercury(II). Concentrations of HgI_4^{2-} were determined from the absorbance maximum at 322 nm using the value $\epsilon = 1.97 \times 10^4\ M^{-1}\ cm^{-1}$ ($I = 5$ M NaI).[24] The stability constants were calculated using the programs SUPERQUAD[25] and KaleidaGraph,[26] and the formation constants for HgI_3^- and HgI_4^{2-} were taken to be $\beta_3 = 10^{27.6}\ M^{-3}$ and $\beta_4 = 10^{29.8}\ M^{-4}$ ($I = 0.5$ M, 25 °C), respectively.[27,28]

The approach to equilibrium from the direction $HgI_4^{2-} + L$ was hampered by the formation of an amorphous precipitate in the concentration range $0.06\ M < [I^-] < 0.2$ M. However, when solutions of HgI_2, NaI, NaOH, and $NaClO_4$ were mixed with solutions of sar, no precipitation was observed for $[I^-] \geq 0.2$ M and $[I^-] \leq 0.06$ M. At these concentrations good agreement between the sets of experiments was observed.

Relative Stability of Macrocyclic Ligand Complexes. Equilibrium measurements were performed at 25 °C using a UNITY 400 MHz NMR spectrometer with a relaxation delay of 10 s and a pulse width of 18.5 ms. Equimolar amounts of complex and ligand (weighed on a microbalance) were dissolved in D_2O, and NaOD was added to the level of $[OD^-] = 0.1$ M before transferring the solution to an NMR tube. Typically, 1−3 mmol of each species was mixed and dissolved in 500−700 mL of D_2O. The equilibrium was approached from both directions: $[Hg(sar)]^{2+} + (NH_2)_2\text{-sar}$ and $[Hg((NH_2)_2\text{-sar})]^{2+}$ + sar. The ^{1}H-NMR spectra were recorded within 10 min, after a few days, and again after 2−4 weeks to ensure that equilibrium was attained. The relative stabilities of $[Hg(D_6\text{-sar})]^{2+}$ and $[Hg((ND_2)_2\text{-}D_6\text{-sar})]^{2+}$ were determined from integrating the ^{1}H-NMR spectra.

Kinetics. UV-Spectrophotometric Studies. The dissociation kinetics were monitored spectrophotometrically by recording the rise in absorbance at 230 nm due to the formation of $HgCl_4^{2-}$. The kinetic data were fitted to appropriate rate laws using the programs KaleidaGraph[26] and AMOEBA.[29] The latter program uses the downhill simplex method and is a more powerful strategy since the analysis can be carried out in more than two dimensions.

The kinetics of $[Hg(sar)]^{2+}$ dissociation were followed using a Durrum D110 stopped-flow reactor maintained at 25.0 ± 0.1 °C. Reactions were initiated by mixing solutions of 5.0×10^{-5} M $[Hg(sar)](ClO_4)_2$ in 2.0 M LiO_3SCF_3 with solutions containing 0.02−2.0 M chloride and 0.2−2.0 M acid ($I = 2.0$ M, NaO_3SCF_3). Rate constants were calculated from at least 5 replicates.

The kinetics of the $[Hg((NH_3)_2\text{-sar})]^{4+}$ system were followed with a Cary 118 spectrophotometer equipped with a hand-driven stopped-flow

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(17) Hinz, F. P.; Margerum, D. W. *Inorg. Chem.* **1974**, *13*, 2941.

(18) Curtis, N. F.; Osvath, S. R. *Inorg. Chem.* **1988**, *27*, 305 and references therein.

(19) Rideo, T. J.; Kaden, T. A. *Helv. Chim. Acta* **1979**, *62*, 1089.

(20) Chen, J.-W.; Wu, D.-S.; Chung, C.-S. *Inorg. Chem.* **1986**, *25*, 1940.

(21) Murphy, L. J.; Zompa, L. J. *Inorg. Chem.* **1979**, *18*, 3278.

(22) Sargeson, A. M. *Pure Appl. Chem.* **1986**, *58*, 1511.

(23) Anderson, P. A.; Creaser, I. I.; Dean, C.; Harrowfield, J. M.; Horn, E.; Martin, L. L.; Sargeson, A. M.; Snow, M. R.; Tiekink, E. R. T. *Aust. J. Chem.* **1993**, *46*, 449.

(24) Coleman, J. S.; Penneman, R. A.; Jones, L. H.; Kressin, I. K. *Inorg. Chem.* **1968**, *7*, 1174.

(25) Gans, P.; Sabatini, A.; Vacca, A. *J. Chem. Soc., Dalton Trans.* **1985**, 1195.

(26) KaleidaGraph (version 3.0.4) graph and fitting program software for Macintosh.

(27) Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum Press: New York, 1975; Vols. 1−4.

(28) Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum Press: New York, 1982; Vol. 5.

(29) Press, W. H.; Flannery, B. P.; Teukolsky, S. A.; Vetterling, W. T. *Numerical Recipies*; Cambridge University Press: Cambridge, U.K., 1988.

Table 1. Equilibrium Constants at 25 °C

equilibrium	log *K*
$Hg^{2+} + sar \rightleftarrows [Hg(sar)]^{2+}$	28.1(1)[a]
$Hg^{2+} + sar + I^- \rightleftarrows [Hg(sar)I]^+$	29.1(1)[a]
$[Hg(sar)]^{2+} + I^- \rightleftarrows [Hg(sar)I]^+$	1.0(2)[b]
$[Hg(D_6\text{-}sar)]^{2+} + (ND_2)_2\text{-}(D_6\text{-}sar) \rightleftarrows [Hg((ND_2)_2\text{-}(D_6\text{-}sar))]^{2+} + D_6\text{-}sar$	−1.7(2)[c]
$Hg^{2+} + (NH_2)_2\text{-}sar \rightleftarrows [Hg((NH_2)_2\text{-}sar)]^{2+}$	26.4(3)[b]
$Hg^{2+} + (NH_2)_2\text{-}sar + I^- \rightleftarrows [Hg((NH_2)_2\text{-}sar)I]^+$	28.5(1)[a]
$[Hg((NH_2)_2\text{-}sar)]^{2+} + I^- \rightleftarrows [Hg((NH_2)_2\text{-}sar)I]^+$	2.1(4)[b]
$Hg^{2+} + cyclam \rightleftarrows [Hg(cyclam)]^{2+}$	23.0[d]
$Hg^{2+} + cyclam + I^- \rightleftarrows [Hg(cyclam)I]^+$	30.8(1)[a]
$[Hg(cyclam)]^{2+} + I^- \rightleftarrows [Hg(cyclam)I]^+$	7.8[b]

[a] $[OH^-] = 0.1$ M, $I = 0.5$ M ($NaClO_4$). [b] Deduced. [c] $[OD^-] = 0.1$ M, $I = 0.1$ M (NaOD). [d] Reference 40.

apparatus (mixing time ∼0.5 s) and a thermostated cell holder maintained at 25.0 ± 0.1 °C. Reactions were initiated by mixing a solution of 5.0×10^{-5} M $[Hg((NH_3)_2\text{-}sar)](NO_3)_4\cdot H_2O$ in water with a solution containing 0.02−2.0 M chloride ion and 0.002−2.0 M acid ($I = 1.0$ M, $LiClO_4$). The rate constants were calculated from duplicate experiments.

^{1}H-NMR Studies. Spectra were recorded with a Varian XL300 spectrometer. Typically, 2 mg of complex was dissolved in 1 mL of D_2O and the reagent (NaCl, $DClO_4$, etc.) was added. For the determination of the stoichiometry of the reactions, a few milligrams of the complex were dissolved in $DClO_4$/NaCl solutions corresponding to the lower limit used in the kinetic experiment. These solutions were left for $\sim 10t_{1/2}$ before the ^{1}H-NMR spectra were recorded. For $[Hg(sar)]^{2+}$: $[D^+] = 0.1$ M, $[Cl^-] = 0.01$ M. For $[Hg((NH_3)_2\text{-}sar)]^{4+}$: $[D^+] = 0.001$ M, $[Cl^-] = 1.0$ M; $[D^+] = 1.0$ M, $[Cl^-] = 0.01$ M.

A rapid-mixing experiment was performed with equal volumes of $[Hg(sar)](ClO_4)_2$ (4×10^{-3} M) and $DClO_4$ (6×10^{-2} M). Three holes were drilled into a 5 mm NMR tube cap, and two pieces of plastic tubing (2 m each, capillary tubing PTFE, code no. 19-0041-01, Pharmacia) were threaded through two of these holes but not into the area where rf pulses were transmitted and the receiver coil was located. The third hole of the NMR tube cap allowed air to escape when solutions were injected. Both pieces of plastic tubing were attached to syringes located outside the instrument, and simultaneous injection from both syringes was performed manually. Acquisition of spectra was commenced at 3 s after injection was accomplished. Prior to the experiment the instrument had been locked and shimmed using a solution of $[Hg(sar)](ClO_4)_2$ in D_2O with the spinner turned off. Rapid-mix experiments were performed using 0 s pulse delay between each of altogether 4 scans, with 1088 data points and 0.237 s acquisition time. The total acquisition time was 1 s.

Results

Equilibrium Studies. The stability constants of $[Hg(sar)]^{2+}$ and $[Hg((NH_2)_2\text{-}sar)]^{2+}$ were determined by the use of competing ligands whose complex stabilities approach those to be measured. The models for the equilibria and the results are given in Table 1. The use of iodide ion also led to stability constants for the $[Hg(sar)I]^+$ and $[Hg((NH_2)_2\text{-}sar)I]^+$ complexes. The ligand cyclam can be viewed as a fragment of the cage, and therefore, the stability constant for $[Hg(cyclam)I]^+$ was also determined.

Competition with I^-. UV-absorption spectra were recorded for $[Hg(sar)]^{2+}$ with varying concentrations of added iodide ion resulting in formation of between 10 and 90% HgI_4^{2-}. Under the experimental conditions used, the inclusion of species HgI_3^-, HgI_4^{2-}, $[Hg(cage)]^{2+}$, and $[Hg(cage)I]^+$ in the models representing the equilibria is sufficient to reproduce the data. The concentrations of other species such as $HgOH^+$, $Hg(OH)_2$, HgI^+, HgI_2, and Hg(OH)I should not exceed 0.2% of the total mercury(II) concentration[27,28] and, therefore, were not included in the model for calculations and did not appear to be necessary. The $[Hg(cage)I]^+$ complexes were required in order to fit the calculated titration curve to the observed data. Further comments on the $[Hg(cage)I]^+$ complexes are given in the Discussion section.

Equation 1 is derived from the model, and stability constants (K_L and K_{LI})[30] were calculated independently from the data using

$$[HgI_4^{\ 2-}] = \frac{[Hg]_{tot}[I^-]^4}{(K_L[L]/\beta_4) + (K_{LI}[L][I^-]/\beta_4) + (\beta_3/\beta_4[I^-]^3) + [I^-]^4} \quad (1)$$

both the programs SUPERQUAD[25] and KaleidaGraph,[26] Table 1. The combination of these two constants yields the binding constant for $[Hg(sar)]^{2+} + I^-$ (K_I). For the $(NH_2)_2$-sar system it was not possible to incorporate $[Hg((NH_2)_2\text{-}sar)]^{2+}$ as a significant part of the model since only the stability constant for $[Hg((NH_2)_2\text{-}sar)I]^+$ (K_{LI}) came out of the analysis (Table 1). The reason for this outcome is probably that the binding constant for $[Hg((NH_2)_2\text{-}sar)]^{2+} + I^-$ is too large (i.e. the concentration of $[Hg((NH_2)_2\text{-}sar)]^{2+}$ is always low in the presence of I^-) and hence the term $K_L[L]/\beta_4$ is too small compared to the other terms in the denominator of eq 1. Likewise, for the cyclam data, $[Hg(cyclam)]^{2+}$ was assumed not to be relevant for the analysis since iodide ion was expected to bind even more strongly to this complex than to the cage complexes. The results support this assumption, Table 1.

Competition with sar. Using iodide ion as a competitor, it was not possible to deduce a stability constant for the $[Hg((NH_2)_2\text{-}sar)]^{2+}$ complex. Consequently, the sar ligand was employed as a competing ligand to determine the relative stability (K_{rel}, eq 5) between the two cage complexes. The combination of this equilibrium constant with the known stability constant for $[Hg(sar)]^{2+}$ yields the equilibrium constant for the $[Hg((ND_2)_2\text{-}(D_6\text{-}sar))]^{2+}$ complex (Table 1), and these values are not expected to differ for the proton- and deuteron-exchanged systems except by a few percent.

The equilibration of $[Hg((ND_2)_2\text{-}(D_6\text{-}sar))]^{2+}$ with D_6-sar and of $[Hg(D_6\text{-}sar)]^{2+}$ with $(ND_2)_2\text{-}(D_6\text{-}sar)$ (eq 2) was complete

$$[Hg(D_6\text{-}sar)]^{2+} + (ND_2)_2\text{-}(D_6\text{-}sar) \rightleftarrows [Hg((ND_2)_2\text{-}(D_6\text{-}sar))]^{2+} + D_6\text{-}sar \quad (2)$$

within 10 min at 25 °C as seen from ^{1}H-NMR spectroscopy. To ensure that equilibrium was reached the reaction was followed over weeks. Due to mutual coupling of ligand protons within the complexes and overlap of signals, the integrals of most absorption signals do not reflect the relative concentrations. Instead, isolated single resonances ($\delta = 2.8$ ppm (s) for $(ND_2)_2\text{-}(D_6\text{-}sar)$; $\delta = 2.9$ ppm (d) for D_6-sar) representing the free ligands D_6-sar and $(ND_2)_2\text{-}(D_6\text{-}sar)$ were used to gauge relative concentrations.

The total concentrations of the essential components of the mixture of Hg^{2+}, D_6-sar, and $(ND_2)_2\text{-}(D_6\text{-}sar)$ were identical within three significant figures. At equilibrium, therefore, eqs 3 and 4 apply and they reduce the equation for the relative stability of the $[Hg(D_6\text{-}sar)]^{2+}$ and $[Hg((ND_2)_2\text{-}(D_6\text{-}sar))]^{2+}$

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(30) Notation: $K_L = [HgL^{2+}]/[Hg^{2+}][L]$; $K_{LI} = [HgLI^+]/[Hg^{2+}][L][I^-]$; $K_I = [HgLI^+]/[HgL^{2+}][I^-]$; $K_{rel} = [HgL'^{2+}][L]/[HgL^{2+}][L']$; $K_{IP} = [HgL^{n+}\cdot Cl^-]/[HgL^{n+}][Cl^-]$; $K_H = [Hg(sarH)^{3+}]/[Hg(sar)^{2+}][H^+]$; $K_{Cl} = [Hg(sarH)Cl^{2+}]/[Hg(sarH)^{3+}][Cl^-]$; $K_T = [Hg((NH_3)_2\text{-}sar)Cl^{3+}]/[Hg((NH_3)_2\text{-}sar)^{4+}\cdot Cl^-]$; $K_{H1} = [Hg((NH_3)_2\text{-}sarH)Cl^{4+}]/[Hg((NH_3)_2\text{-}sar)Cl^{3+}][H^+]$; $K_{H2} = [Hg((NH_3)_2\text{-}sarH_2)Cl^{5+}]/[Hg((NH_3)_2\text{-}sarH)Cl^{4+}][H^+]$.

complexes (eq 5) to eq 6 from which the constant was determined.

$$[\mathrm{Hg}(\mathrm{D}_6\text{-sar})^{2+}] = [(\mathrm{ND}_2)_2\text{-}(\mathrm{D}_6\text{-sar})] \qquad (3)$$

$$[\mathrm{Hg}((\mathrm{ND}_2)_2\text{-}(\mathrm{D}_6\text{-sar}))^{2+}] = [\mathrm{D}_6\text{-sar}] \qquad (4)$$

$$K_{\mathrm{rel}} = \frac{[\mathrm{D}_6\text{-sar}][\mathrm{Hg}((\mathrm{ND}_2)_2\text{-}(\mathrm{D}_6\text{-sar}))^{2+}]}{[(\mathrm{ND}_2)_2\text{-}(\mathrm{D}_6\text{-sar})][\mathrm{Hg}(\mathrm{D}_6\text{-sar})^{2+}]} \qquad (5)$$

$$K_{\mathrm{rel}} = [\mathrm{D}_6\text{-sar}]^2/[(\mathrm{ND}_2)_2\text{-}(\mathrm{D}_6\text{-sar}))]^2 \qquad (6)$$

In a control experiment, the resonances of the ^{1}H-NMR spectrum of equimolar amounts of sar and $(NH_2)_2$-sar in 0.1 M NaOD gave integrals in excellent agreement. Furthermore, OH^- (0.1 M) did not lead (to any measurable extent) to the liberation of Hg^{2+} ion from the $[Hg(sar)]^{2+}$ and $[Hg((ND_2)_2\text{-sar})]^{2+}$ complexes, thus confirming the validity of the procedure.

Kinetic Studies of the $[Hg(sar)]^{2+}$ Complex. The rate of H^+/D^+ exchange at the secondary amine groups of the $[Hg(sar)]^{2+}$ ion in D_2O was followed by ^{1}H-NMR spectroscopy to give $k_{ex} \sim 5 \times 10^{-5}$ s^{-1}. On addition of chloride ion (1 M NaCl, pD ~ 7) the proton exchange rate increased by a factor of 10.

From the ^{1}H-NMR experiments, it was evident that at pD ~ 7 chloride ion did not effect metal liberation. However, $DClO_4$ (0.2 M) immediately led to complete dissociation of the complex, even in the absence of chloride ion. In a rapid-mix ^{1}H-NMR experiment ($DClO_4$, 3×10^{-2} M; $[Hg(sar)](ClO_4)_2$, 2×10^{-3} M) intermediates were sought in the metal liberation reaction. A typical spectrum obtained after approximately 3 s ($\sim 0.2t_{1/2}$ of the dissociation reaction under the conditions studied) is given in the Supporting Information (Figure E) together with the spectrum of amine-deuterated $[Hg(sar)](ClO_4)_2$ in D_2O. Only $[Hg(sar)]^{2+}$ and $\mathrm{sarD}_n{}^{n+}$ were present in detectable amounts after approximately 3 s and throughout the remainder of the reaction. No loss in symmetry was observed, and therefore, no build up of intermediates with partially dissociated ligand was evident.

The reaction of $[Hg(sar)]^{2+}$ with excess hydrochloric acid led to the formation of $HgCl_4{}^{2-}$ and the protonated ligand according to the overall reaction of eq 7. Within the acid range

$$[\mathrm{Hg(sar)}]^{2+} + 4\mathrm{H}^+ + 4\mathrm{Cl}^- \rightleftarrows \mathrm{HgCl_4}^{2-} + \mathrm{sarH_4}^{4+} \qquad (7)$$

studied, this reaction (eq 7) went to completion by a single first-order process (evident from ^{1}H-NMR and UV spectroscopy). Always, both H^+ and Cl^- were in at least 100-fold excess.

The rate of dissociation of Hg^{2+} from $[Hg(sar)]^{2+}$ was strongly dependent on acid and, to a lesser degree, on the chloride ion concentration. This is evident from Figures 1 and 2, respectively. The proton dependence, determined for $[Cl^-] = 1.0$ M, was first order in $[H^+]$ with an intercept indistinguishable from zero. The chloride ion dependence, determined for $[H^+] = 0.1$ and 1.0 M, reached a limiting condition for $[Cl^-]$ ~0.5 M.

The simplest rate law consistent with the observed data is given in Table 2, which also contains the rate laws for the decay of the related Zn^{2+} and Mn^{2+} complexes for comparison. The rate constant data and the fitting to the proposed rate law are presented in Figures 1 and 2.

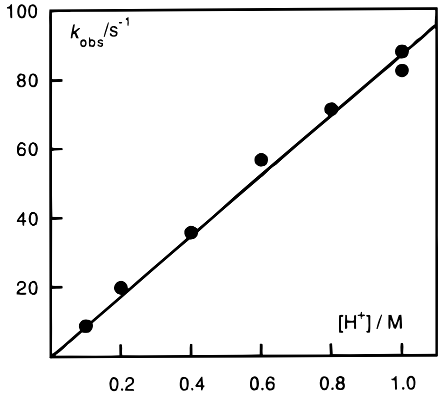

Figure 1. Plot of k_{obs} for Hg^{2+} liberation from $[Hg(sar)]^{2+}$ as a function of $[H^+]$ ($[Cl^-] = 1.0$ M, $I = 2.0$ M (LiO_3SCF_3), 25.0 °C).

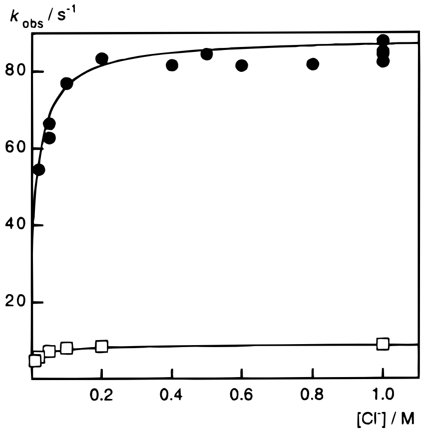

Figure 2. Plot of k_{obs} for Hg^{2+} liberation from $[Hg(sar)]^{2+}$ as a function of $[Cl^-]$ ($[H^+] = 1.0$ M (●) and $[H^+] = 0.1$ M (□); $I = 2.0$ M (LiO_3SCF_3), 25.0 °C).

Table 2. Kinetic Data for Acid- and Cl^--Induced Dissociation Reactions at 25.0 °C

complex	obsd rate expression
$[Hg(sar)]^{2+}$	$k_{obs} = \frac{(a + b[Cl^-])[H^+]}{1 + c[Cl^-]}$ [a] $a = 35(3)$ M^{-1} s^{-1}, $b = 2.9(4) \times 10^3$ M^{-2} s^{-1}, $c = 33(5)$ M^{-1} s^{-1}
$[Hg((NH_3)_2\text{-sar})]^{4+}$	$k_{obs} = \frac{[Cl^-](a + b[H^+] + c[H^+]^2)}{(1 + d[Cl^-])(1 + e[H^+])}$ [b] $a = 0.056(6)$ M^{-1} s^{-1}, $b = 8(3)$ M^{-2} s^{-1}, $c = 5(3)$ M^{-3} s^{-1}, $d = 1.3(4)$ M^{-1}, $e = 1.1(5) \times 10^2$ M^{-1}
$[Zn(sar)]^{2+}$	$k_{obs} = a[D^+] + b[D^+][Cl^-]$ [c] $a = 3.8 \times 10^{-4}$ M^{-1} s^{-1}, $b = 1.3 \times 10^{-3}$ M^{-2} s^{-1}
$[Mn(sar)]^{2+}$	$k_{obs} = a[H^+] + b[H^+][Cl^-]$ [d,e] $a = 2.0 \times 10^{-4}$ M^{-1} s^{-1}, $b = 3.9 \times 10^{-4}$ M^{-2} s^{-1}

[a] $I = 2$ M (NaO_3SCF_3). [b] $I = 1$ M ($LiClO_4$). [c] $I = 2$ M ($NaNO_3$), followed by ^{1}H-NMR spectroscopy in DCl/DNO_3; see Supporting Information. [d] $I = 1$ M (NaO_3SCF_3). [e] Reference 23.

Kinetic Studies of the $[Hg((NH_3)_2\text{-sar})]^{4+}$ Complex. In the presence of D^+ (1 M), the $[Hg((ND_3)_2\text{-}(D_6\text{-sar}))]^{4+}$ ion showed a nearly 50-fold increase in the proton exchange rate at the secondary amines relative to the situation in D_2O ($k_{ex} \sim 10^{-5}$ s^{-1}, pD ~ 7). Furthermore, addition of chloride ion (1 M) as well as hydroxide ion (1 M) led to complete proton exchange within 5 min along with some ligand loss. Thus, proton exchange at the secondary amines was faster than ligand loss.

The reaction of $[Hg((NH_3)_2\text{-sar})]^{4+}$ with hydrochloric acid led to the quantitative liberation of Hg^{2+} according to the overall reaction of eq 8. Always, acid and chloride ion were in, at

$$[\mathrm{Hg}((\mathrm{NH_3})_2\text{-sar})]^{4+} + n\mathrm{H}^+ + 4\mathrm{Cl}^- \rightleftarrows \mathrm{HgCl_4}^{2-} + (\mathrm{NH_3})_2\text{-sarH}_n{}^{(n+2)+} \quad (n = 2 \text{ or } 3) \qquad (8)$$

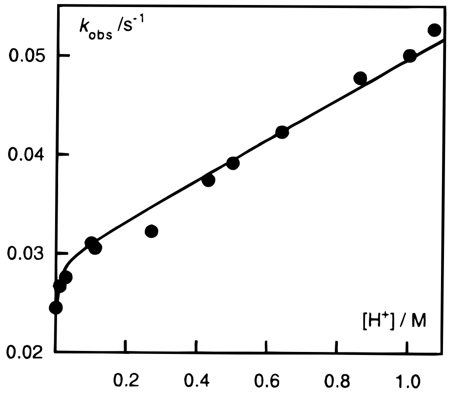

Figure 3. Plot of k_{obs} for Hg^{2+} liberation from $[Hg((NH_3)_2\text{-sar})]^{4+}$ as a function of $[H^+]$ ($[Cl^-] = 1.0$ M, $I = 1.0$ M (LiCl), 25.0 °C).

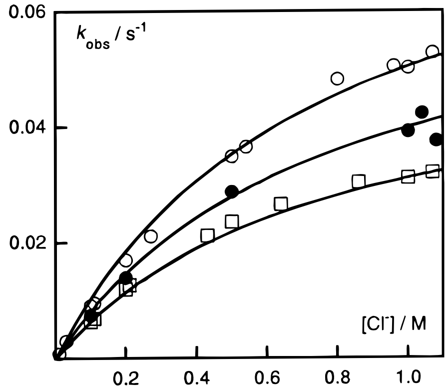

Figure 4. Plot of k_{obs} for Hg^{2+} liberation from $[Hg((NH_3)_2\text{-sar})]^{4+}$ as a function of $[Cl^-]$ ($[H^+] = 1.0$ (○), 0.5 (●), and 0.1 M (□); $I = 1.0$ M ($LiClO_4$), 25.0 °C).

least, 20-fold excess. Under the acidic conditions employed in the dissociation study, the $[Hg((NH_3)_2\text{-sar})]^{4+}$ complex always carried a charge of 4+ ($pK_{a1} = 6.32(1)$ and $pK_{a2} = 5.44(1)$, $I = 0.1$ M).[31] The rate of dissociation of Hg^{2+} from $[Hg((NH_3)_2\text{-sar})]^{4+}$ was strongly dependent on the chloride ion concentration and, to a lesser extent, on the proton concentration, Figures 3 and 4. The proton dependence was determined largely for $[Cl^-] = 1$ M in HCl/LiCl mixtures, but HCl/NaCl mixtures gave essentially the same results. A plot of k_{obs} versus $[H^+]$ was linear in the acid range $0.1 \leq [H^+] \leq 1.0$ M whereas for lower acid concentrations ($[H^+] \geq 0.001$ M) a more complicated $[H^+]$ dependence was observed (Figure 3). The $[Cl^-]$ dependence, determined for $[H^+] = 0.1$ M, 0.5 M and 1.0 M, approached limiting conditions at $[Cl^-] = 1$ M (Figure 4).

The ^{1}H-NMR spectra of $[Hg((ND_3)_2\text{-sar})]^{4+}$ in 1 M $DClO_4$ and 1 M CF_3COOD, respectively, indicated no ligand liberation after 1 week. The implication is that the purely proton-dependent pathway is negligible and a capable coordinating anion is required to assist metal ion elimination. The presence of NaCl alone (1 M, pD ~ 7) led to slow liberation of the metal (evident from ^{1}H-NMR spectroscopy). The simplest rate law consistent with all the data (obtained from 36 data points using the routine AMOEBA[29]) appears in Table 2. The data and the four two-dimensional fits to the data are included in Figures 3 and 4.

Discussion

Proton Exchange Studies. For the fully coordinated cage ligands, the secondary amines are effectively quaternary and hence are not susceptible to protonation while coordinated. However, the proton exchange rate of the secondary amine protons in the $[Hg((ND_3)_2\text{-sar})]^{4+}$ complex was enhanced on addition of D^+ ($[D^+] = 0.2$ M). It follows that in the region pH 0−7 the dominant proton exchange path cannot be OD^- catalyzed. Therefore, in acid, exchange must occur by spontaneous metal−nitrogen bond rupture, addition of a deuteron to the dissociated amine, loss of a proton from the alkylammonium ion, and recombination at the metal center.

This Hg−N dissociation mechanism also accounts for the observed Cl^--induced enhancement of the proton exchange rate for the $[Hg(sar)]^{2+}$ and $[Hg((ND_2)_2\text{-sar})]^{2+}$ complexes. Here, chloride ion competes with the amine for the vacant coordination site at the metal center once metal−nitrogen bond rupture has occurred. By the replacement of the nitrogen atom on the metal, the chloride ion forces the uncoordinated nitrogen atom to spend more time dissociated from the metal center and thereby increases the probability of proton exchange taking place before recoordination occurs. The first two mechanistic steps in Scheme 2 can therefore be regarded as equilibria since proton exchange is faster than ligand loss.

Similar effects from added D^+ on the H^+/D^+-exchange rate of the amines in the $[Hg(sar)]^{2+}$ complex would be expected. However, such an effect was difficult to observe due to the fast decomplexation in this situation.

The above interpretation of the observed effects on the proton exchange rates is consistent with the proposed mechanisms for acid-assisted dissociation reactions of related systems for which initial metal−nitrogen bond rupture is invoked.[32,33] Initially, the cage ligand is compactly coordinated by six secondary amine donor atoms to the metal center and the ligand strands completely bury the metal ion. Thus no site for protonation (other than the metal) and no room for coordination of an anion is available. Once Hg−N bond rupture occurs, the ligand and Hg^{2+} rearrange creating space and a site to bind the anion or H_2O. The rate of recoordination of the amine group would also be very fast. Since the primary process is dissociative in character the rate-limiting feature in the re-formation would be breaking of a $Hg-OH_2$ or Hg−Cl bond,[34] and for mercury(II) such a process would be very fast.[35] Unless the uncoordinated amine group is trapped by protonation, or the metal center trapped by another ligand, no net dissociation reaction should occur because of the rapidity of these recombination reactions.

$[Hg(cage)X]^{n+}$ Complexes. In the studies of Hg^{2+} liberation from the Hg^{2+} cage complexes, species with the metal ion partly coordinated to the cage but also coordinated to a halide ion play a central role. In the iodide ion competition studies, $[Hg(cage)I]^+$ complexes had to be included in the models in order to obtain satisfactory fitting to the data. This is in analogy to the $[Ni(cyclam)CN]^+$ complex implied in the CN^--assisted Ni^{2+}-ion removal from the $[Ni(cyclam)]^{2+}$ complex.[17] The extent of iodide ion interaction with $[Hg(sar)]^{2+}$ ($K_I = 10$ M^{-1}, Table 1) indicates that the resulting species is best described as an inner-sphere complex with the iodide ion directly bound to the metal and not as a simple ion pair between $[Hg(sar)]^{2+}$ and I^-. For comparison, ion pairing constants (K_{IP}) are much less for ion pairs involving ions of even higher charge: $[Co(NH_3)_6]^{3+}\cdot Cl^-$ ($K_{IP} < 0.2$ M^{-1}, $I = 0.9$ M, 35 °C), $[Co(CH_3,NH_3\text{-sar})]^{4+}\cdot Cl^-$ ($K_{IP} = 2.9$ M^{-1}, $I = 1.0$ M, $HClO_4$, 25

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(31) Creaser, I. I. Unpublished results.

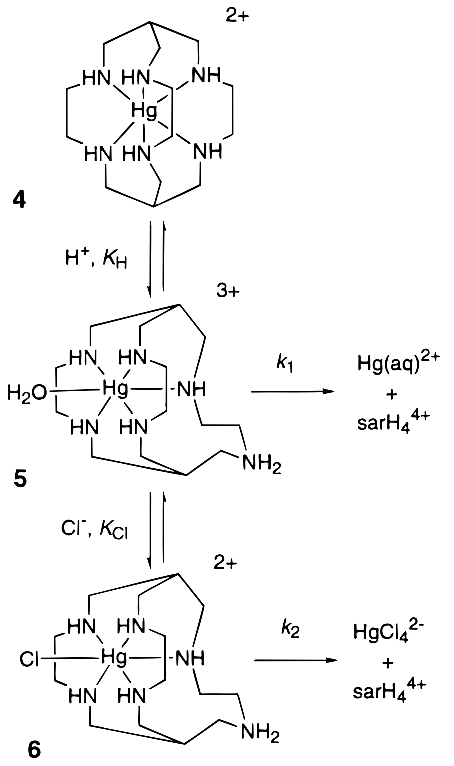
(32) Schwarzenbach, G.; Bürgi, H.-B.; Jensen, W. P.; Lawrance, G. A.; Mønsted, L.; Sargeson, A. M. *Inorg. Chem.* **1983**, *22*, 4029.

(33) Read, R. A.; Margerum, D. W. *Inorg. Chem.* **1981**, *20*, 3143.

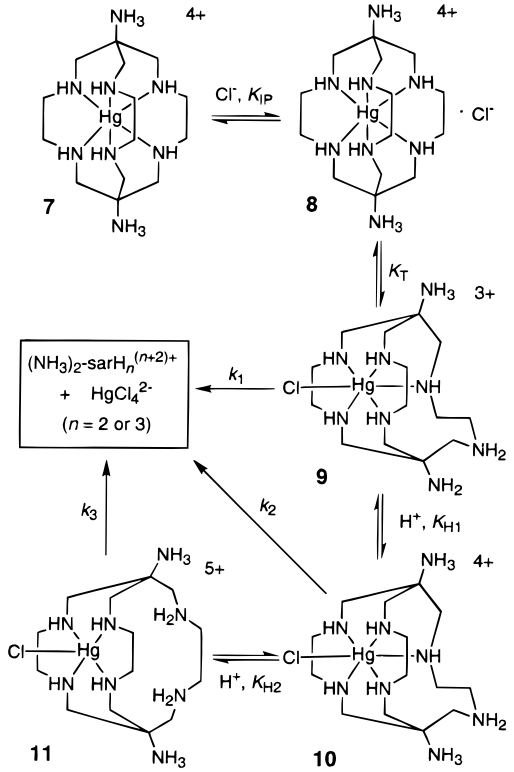
(34) Jordan, R. B. *Reaction Mechanisms of Inorganic and Organometallic Systems*; Oxford University Press: New York, 1991; p 81.

(35) Ducommun, Y.; Merbach, A. E. In *Inorganic High Pressure Chemistry*; van Eldik, R., Ed.; Elsevier: Amsterdam, 1986.

Scheme 1



Scheme 2



°C), and $[Co((NH_3)_2\text{-sar})]^{5+}\cdot Cl^-$ ($K_{IP} = 5.2$ M^{-1}, $I = 1.0$ M, $HClO_4$, 25 °C).[36,37]

Similar species in which chloride ion and cage ligand are both coordinated to the metal are invoked as intermediates in the proposed mechanism accounting for the Cl^- enhancement of the proton exchange rate in the $[Hg(sar)]^{2+}$ complex (above) and in the study of the acid-induced dissociation of the mercury(II) ion (below). These intermediates must be present only in low concentrations since they are not observed and, obviously, must be less stable than their iodide ion analogues. Generally, the chloride ion is a poorer ligand toward Hg^{2+} than the iodide ion.[27] However, simply for electrostatic reasons increased stability of such complexes is expected when, in addition, the uncoordinated amine groups are protonated.

In the $[Hg(cage)X]^{n+}$ complexes the metal ion is probably coordinated to five or four nitrogen atoms of the cage ligand. The pentadentate form requires dissociation of one nitrogen−metal bond and coordination of one iodide or chloride ion at a vacant metal coordination site generated *trans* to the partly dissociated strand (**6**, Scheme 1; **9** and **10**, Scheme 2). The tetradentate form would probably have one strand dissociated and one iodide or chloride ion *trans* to the dissociated ligand segment occupying the apex in an approximately square pyramidal coordination arrangement (**11**, Scheme 2). This would resemble the structure found in the crystal structure for $[Hg(cyclam)Cl]^+$.[38] On the basis of the present data, it is not possible to decide which of the two structures applies in the different situations. In the acid-induced dissociation studies we propose intermediates in which a minimum number of metal−nitrogen bonds are cleaved.

Thermodynamic Stability. The stability constants for the $[Hg(sar)]^{2+}$ and $[Hg((NH_2)_2\text{-sar})]^{2+}$ complexes of log $K_L = 28.1(1)$ and 26.4(3), respectively, evince very stable complexes and are comparable to values found for other mercury(II) amine complexes. The ligands sar (**1**) and cyclam (**3**) contain the same basic 14-membered ring structure but differ with respect to the extra strand of the sar ligand. The enhancement in stability of the $[Hg(sar)]^{2+}$ complex compared to that of the $[Hg(cyclam)]^{2+}$ complex (log $K_L = 23.0$) of over 5 orders of magnitude could be attributed to the extra strand in the former ligand. However, the bicyclic nature of the sar ligand seems to be of less importance for the overall stability. This can be seen by comparing its stability with that of the Hg^{2+} complex with the monocyclic hexaamine ligand 1,4,7,10,13,16-hexaazacyclooctadecane (log $K_L = 29.1$).[39] Furthermore, the noncyclic hexaamine *N*,*N*,*N*′,*N*′-tetrakis(2-aminoethyl)ethane-1,2-diamine also displays high stability with Hg^{2+} (log $K_L = 29.6$)[27,28] and so does the cyclic pentaamine 1,4,7,10,13-pentaazacyclopentadecane (log $K_L = 28.5$).[27,28] Thus, the enhancement in stability between the sar and cyclam complexes must be attributed to the two extra amine donors in the former rather than its bicyclic character. A similar conclusion was reached by Kodama and Kimura[40] for mercury(II) tetraamine complexes where neither changing from acyclic to macrocyclic ligands nor the size of the macrocyclic ring (12−15 members) affected the stability constants to any significant degree.

In this light, the similar stabilities of the mercury(II) complexes of the [18]aneN_2O_4 ligand (log $K_L = 17.85$) and the [2.2.2]-cryptand (log $K_L = 18.2$) are not surprising. The extra strand of the bicyclic system contains two ether groups which are weaker ligators toward mercury(II) than amines.[41]

In the determination of stability constants using I^- as a competing ligand, $[Hg(cage)I]^+$ species were required to fit the data adequately. The uptake of an iodide ion by the $[Hg(sar)]^{2+}$ and $[Hg((NH_2)_2\text{-sar})]^{2+}$ complexes necessitates prior dissociation

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(36) King, E. L.; Espenson, J. T.; Visco, R. E. *J. Phys. Chem.* **1959**, *63*, 755.

(37) Walker, G. Private communication.

(38) Alcock, N. W.; Curson, E. H.; Herron, N.; Moore, P. *J. Chem. Soc., Dalton Trans.* **1979**, 1987.

(39) Kodama, M.; Kimura, E. *J. Chem. Soc., Dalton Trans.* **1980**, 2536.

(40) Kodama, M.; Kimura, E. *J. Chem. Soc., Dalton Trans.* **1976**, 2335.

(41) Martell, A. E.; Hancock, R. D.; Motekaitis, R. J. *Coord. Chem. Rev.* **1994**, *133*, 39.

of one or two nitrogen atoms in these complexes. The low iodide binding constants for the sar and $(NH_2)_2$-sar systems (Table 1, log $K_I = 1.0(2)$ and 2.1(4), respectively) compared to that found for the $[Hg(cyclam)I]^+$ system (Table 1, log $K_I = 7.8$) are consistent with this notion. Clearly, the relative affinity of amine-N and I^- for the binding site appears rather closely balanced. Comparing the overall stability for binding a ligand and I^- in the same complex the most stable complex is formed when the ligand is cyclam (log K_{LI}: cyclam, 30.8; sar, 29.1; $(NH_2)_2$-sar, 28.5). This implies some degree of steric repulsion in the $[Hg(cage)I]^+$ complexes associated with the partly dissociated amine ligand.

Acid- and Chloride Ion-Induced Dissociation of the $[Hg(sar)]^{2+}$ Complex. The rate law (Table 2) for the dissociation reaction of the $[Hg(sar)]^{2+}$ complex implies two parallel pathways. Both paths are first-order in $[H^+]$, but one path also invokes a first-order term in $[Cl^-]$. Thus, a proton is required to remove the metal from the cage, but chloride ion assists the process. When compared with the iodide ion binding constant of $K_I = 10$ M^{-1} from the equilibrium study (Table 1) the constant $c = 33(5)$ M^{-1} (Table 2) cannot be interpreted as the binding constant of chloride ion to $[Hg(sar)]^{2+}$. It must apply for a species with a higher positive charge. Thus uptake of a proton, and not a chloride ion, must occur in a previous step of the overall dissociation process.

One likely explanation assumes a synergistic relation between protonation at a dissociated amine site and chloride ion binding at the resulting coordinatively unsaturated metal center. A rate law for this situation, including a second-order term in $[H^+]$, failed to fit all the data. Such a mechanism was proposed earlier on the basis of more limited experimental data.[23] However, the additional experiments included here, together with the approach of fitting both proton and anion dependencies to one equation synchronously, obviate such a mechanism.

The mechanism now proposed is the simplest consistent with all observations and is illustrated in Scheme 1. Fast spontaneous metal nitrogen bond rupture in the starting complex (**4**) is followed by trapping of the uncoordinated amine by protonation and coordination of water yielding **5**. In **5** the somewhat rearranged ligand is presumably coordinated through five amine donors. Rate-determining metal liberation from **5** presumably begins *via* loss of another amine donor and addition of water to the metal ion. Clearly, there must be several steps involved here which are not rate determining.

In a parallel path, following the complex rearrangement of **5**, chloride ion replaces H_2O at the metal center yielding **6** from which metal liberation slowly occurs, also by a complex path. The assistant role of the chloride ion is probably 2-fold. By coordinating to the metal center, the ion assists dissociation of other amine groups and facilitates further protonation of the ligand by lowering the overall positive charge of the intermediate complexes.

The assumption that the starting complex (**4**) is favored relative to the pentacoordinated species (**5**) is consistent with the fact that no intermediates were observed in the course of the dissociation reactions in Cl^--free media and with the apparent D_3 symmetry. It implies that $K_H[H^+] << 1$ in the rate law (eq 9) deduced for the mechanism of Scheme 2 and effectively reduces this to eq 10 which is mathematically equivalent to the observed rate law (Table 2), with $a = k_1K_H = 35(3)$ M^{-1}s^{-1}, $b = (k_1 + k_2)K_HK_{Cl} = 2.9(4) \times 10^3$ M^{-2}s^{-1}, and $c = K_{Cl} = 33(5)$ M^{-1}. Within this model, the dissociation rate constant for the Cl^--containing species (**6**) is slightly larger than that for **5** for which no chloride ion assistance obtains ($k_1K_H = 35$ M^{-1} s^{-1} and $k_2K_H = 53$ M^{-1} s^{-1}). The $[Zn(sar)]^{2+}$ and $[Mn(sar)]^{2+}$ complexes display similar rate laws[23] (Table 2) with two first-order $[H^+]$-dependent terms, one of which is also first-order in $[Cl^-]$. However, unlike the $[Hg(sar)]^{2+}$ complex they do not show limiting conditions for $[Cl^-]$ up to 1 M. The apparently different rate laws arise simply because the magnitude of K_{Cl} is too small, for the $[Zn(sar)]^{2+}$ and $[Mn(sar)]^{2+}$ complexes, to be influential. The stability constant for binding the first chloride ion to a Hg_{aq}^{2+} ion is $\sim 10^7$-fold larger than the equivalent constants for the Zn_{aq}^{2+} and Mn_{aq}^{2+} ions.[27,28] On the basis of a comparison of the rate constants in Cl^--free media, $k_{obs} = a[H^+]$, the order of reactivity for the three complexes parallels the reactivity with respect to water exchange for the three metal ions.[35] Thus, it seems likely that the $[Hg(sar)]^{2+}$, $[Zn(sar)]^{2+}$, and $[Mn(sar)]^{2+}$ complexes follow similar reaction paths for their acid-induced dissociation reactions.

$$k_{obs} = \frac{k_1K_H[H^+]}{1 + K_H[H^+]} + \frac{k_2K_HK_{Cl}[H^+][Cl^-]}{1 + K_{Cl}[Cl^-]} \qquad (9)$$

$$k_{obs} = \frac{k_1K_H[H^+] + (k_1 + k_2)K_HK_{Cl}[H^+][Cl^-]}{1 + K_{Cl}[Cl^-]} \qquad (10)$$

Acid- and Chloride Ion-Induced Dissociation Reaction of the $[Hg((NH_3)_2\text{-sar})]^{4+}$ Complex. The observed rate law for the $[Hg(NH_3)_2\text{-sar})]^{4+}$ complex (Table 2) implies three different pathways leading to metal liberation. All three paths require uptake of a chloride ion but differ with respect to the number of protons involved. A proposed mechanism is given in Scheme 2 and the corresponding rate law by eq 11. Assuming formation of a quadruply-protonated cage complex (**11**) to be very unfavorable, i.e. $K_{H2}[H^+] << 1$, eq 11 reduces to eq 12 which is equivalent to the observed rate law (Table 2) with $a = k_1K_{IP}K_T/(1 + K_T) = 0.056(6)$ M^{-1} s^{-1}, $b = (k_1 + k_2)K_{H1}K_{IP}K_T/(1 + K_T) = 8(3)$ M^{-2} s^{-1}, $c = k_3K_{H1}K_{H2}K_{IP}K_T/(1 + K_T) = 5(3)$ M^{-3} s^{-1}, $d = K_{IP} = 1.3(4)$ M^{-1}, and $e = K_{H1} = 1.1(5) \times 10^2$ M^{-1}.

$$k_{obs} = \frac{k_1K_{IP}K_T[Cl^-]}{(1 + K_{IP}[Cl^-])(1 + K_T)} + \frac{k_2K_{IP}K_TK_{H1}[Cl^-][H^+]}{(1 + K_{IP}[Cl^-])(1 + K_T)(1 + K_{H1}[H+])} + \frac{k_3K_{IP}K_TK_{H1}K_{H2}[Cl^-][H^+]^2}{(1 + K_{IP}[Cl^-])(1 + K_T)(1 + K_{H1}[H^+])(1 + K_{H2}[H^+])} \qquad (11)$$

$$k_{obs} = \frac{K_{IP}K_T[Cl^-](k_1 + (k_1 + k_2)K_{H1}[H^+] + k_3K_{H1}K_{H2}[H^+]^2)}{(1 + K_{IP}[Cl^-])(1 + K_T)(1 + K_{H1}[H^+])} \qquad (12)$$

Within this model the starting complex (**7**), a 4+ cation, forms an ion-pair (**8**) with a chloride ion but without loss of symmetry as judged from the ^{1}H-NMR spectra. The deduced ion-pairing constant (K_{IP}) for this ion pair is comparable to the ion pairing constant of 2.9 M^{-1} ($I = 1.0$ M, $HClO_4$) found for an analogous ion pair $[Co(Me,NH_3\text{-sar})]^{4+}\cdot Cl^-$.[37] The ion-pair formation is then followed by dissociation of a coordinated amine and internal proton transfer from a primary amine group to a more basic secondary amine group of the dissociated strand, possibly *via* the solvent. Collapse of the ion pair allows the metal ion to capture Cl^-, yielding **9**. This complex may now go on to liberate the metal ion or add one or two more extraneous protons forming **10** and **11**, respectively. These complexes can then go on to liberate the metal by two other pathways. The values of the constants $K_{H1} = 1.1(5) \times 10^2$ M^{-1} and $K_{H2}[H^+] << 1$ indicate that the species **10** is the most dominant down to $[H^+] = 0.01$ M and at least up to $[H^+] = 1.0$ M. The magnitudes of the rate constants in eq 12 yield the unexpected result that dissociation of the metal ion from **9** is faster than from **10** (k_1:$k_2 \sim 4$).

The ion pair formation implied in the overall metal liberation reaction of $[Hg((NH_3)_2\text{-sar})]^{4+}$ could not be observed directly. However, for the similar $[Cd((NH_3)_2\text{-sar})]^{4+}$ complex addition of NaCl produced a chemical shift change in the ^{1}H-NMR spectrum but no reduction of the apparent symmetry. This probably reflects a labile ion-pairing with the D_3 symmetry of the metal ion intact. With the $[Zn((NH_3)_2\text{-sar})]^{4+}$ complex, however, no such phenomenon was observed. In a similar manner to that seen for the mercury(II) complex, these complexes all show no sign of metal ion liberation in acid with poorly-coordinating anions. The rate of metal ion liberation in 1 M DCl follows the reactivity order for water exchange of the hexaaqua ions as it did for the sar complexes: $k(\text{Hg(II)}) = 5 \times 10^{-2}$ s^{-1} > $k(\text{Cd(II)}) = 1 \times 10^{-3}$ s^{-1} > $k(\text{Zn(II)}) = 7 \times 10^{-4}$ s^{-1} at 25 °C. Clearly, the same remarks apply for the rate-determining steps of the intermediates in Scheme 2 as for those in Scheme 1.

Conclusion

The mercury(II) cage complexes display high thermodynamic stability and strong resistance to net dissociation in aqueous solution. In order to achieve decomplexation, competition with protons for the amine donor sites and/or competition with another ligand for the metal coordination sites are necessary.

The Hg^{2+} and Zn^{2+} cage complexes liberate the metal in acid and show only a single rate step for this reaction. However, the rate laws reveal several parallel reaction paths. Attempts were made to observe intermediates in the metal liberation reaction but without success. The metals have d^{10} electronic configurations, and therefore, no particular coordination geometry is favored due to the lack of ligand field stabilization. Thus, the structure is decided, essentially, by the ligand and the size of the metal ion and this may be the reason for the lack of observable intermediates. Similarly, for the $[Mn(sar)]^{2+}$ complex (high-spin d^5) no intermediates could be observed.[22] By contrast, in the dissociation kinetics of the $[Cu(sar)]^{2+}$ complex (d^9) several consecutive reactions involving at least two relatively stable intermediates are evident.[5,22,42]

Generally, for the two mercury(II) cage complexes equilibration is fast in basic solution, and, for the $[Hg(sar)]^{2+}$ complex, also in acid. However, the acid-induced metal liberation reaction for the $[Hg((NH_3)_2\text{-sar})]^{4+}$ system is much slower (by a factor of 10^3) compared with the $[Hg(sar)]^{2+}$ system. This undoubtedly reflects the difficulty of protonating an amine site which is dissociated from the metal center when the two exo-amine groups are already protonated. It also pinpoints an important reactivity difference between the $[M(sar)]^{2+}$ and the $[M((NH_3)_2\text{-sar})]^{4+}$ systems and a way of stabilizing, in a kinetic sense, such macrocyclic systems generally. Moreover, the $[Hg(sar)]^{2+}$ complex is kinetically stable in the presence of Cl^- but the presence of H^+ leads immediately to metal liberation. By contrast, the $[Hg((NH_3)_2\text{-sar})]^{4+}$ complex liberates the metal ion only in the presence of Cl^-. However, both complexes are labile in the presence of the strongly coordinating I^- ligand even in basic solution. Thus, the two cage ligands of this study, **1** and **2**, provide good examples of how ligand modification alters the reactivity of metal complexes and the factors which govern metal ion elimination. Obviously, in such systems rapid dissociation of the M−N bond occurs continuously but the ligand constraints ensures that the N is never far from the metal and that the return rate is therefore fast. This factor accounts for both the kinetic inertness and the high thermodynamic stability to a large extent, and it is clearly difficult to pinpoint a particular rate-determining step. The overall rate is governed by low concentrations of intermediates and near balance between rapid dissociation of the ligand N atoms and their rapid recoordination.

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Supporting Information Available: Tables of compound and solvent amounts and spectral data and figures of spectra and fitted curves relating to the determination of stabilities of Hg(II) complexes and kinetic data relating to the metal extrusion reaction of the Zn-$(sar)^{2+}$ complex (4 pages). Ordering information is given on any current masthead page.

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(42) Grøndahl, L. Ph.D. Dissertation, University of Copenhagen, 1994.