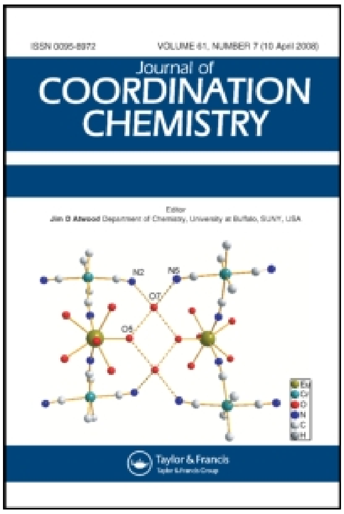

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NUCLEAR MAGNETIC RESONANCE STUDIES OF THE SOLUTION CHEMISTRY OF METAL COMPLEXES. X. DETERMINATION OF THE FORMATION CONSTANTS OF THE METHYLMERCURY COMPLEXES OF SELECTED AMINES AND AMINOCARBOXYLIC ACIDS

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The aqueous solution chemistry of the methylmercury complexes of a series of amines and amino acids has been investigated by proton magnetic resonance spectroscopy. Methylmercury-amine complexes form at intermediate pH values; in acidic solution the complex is dissociated due to protonation of the amine while in basic solution the complex dissociates through formation of methylmercuric hydroxide. Formation constants of the complexes were determined from the pH-dependence of the chemical shift of the methyl group of methylmercury, from the pH-dependence of the mercury-proton spin-spin coupling constant of methylmercury, and from the pH-dependence of the chemical shift of the carbon-bonded ligand protons in solutions containing amine and methylmercury at a molar ratio of either one or two. The nature of the complex formed by the amino acids is pH dependent, with methylmercury binding to the carboxylate group at low pH and to the amino group at higher pH. Formation constants were determined for binding of methylmercury by the carboxylate and amino groups. The methylmercury-phenylalanine complex (amino coordination) is appreciably more stable than the other complexes. The greater stability is discussed in terms of a specific interaction between the methyl group of methylmercury and the phenyl ring; the methyl protons are shifted upfield by 0.5 ppm consistent with the proposal that the methyl group lies close to and above the plane of the phenyl ring.

INTRODUCTION

Although the importance of methylmercury in environmental pollution by mercury is well-established,[3] its coordination chemistry has, in general, not been quantitatively characterized.[4–8] Recent work in this laboratory on the solution chemistry of methylmercury has led to the evaluation of the formation constants of the methylmercury complexes of a series of carboxylic acids from proton magnetic resonance (pmr) data.[8] This work demonstrated that pmr is a direct method for studying the coordination chemistry of methylmercury; the chemical shift of the methyl protons of methylmercury, the coupling constant for spin-spin coupling between mercury-199 (I = 1/2, natural abundance 16.9%) and the protons of the methyl group, and the chemical shifts of the ligand protons are all sensitive to complexation and thus provide information about the complexes at the molecular level.

In the present paper, the results of a study of the binding of methylmercury by selected amines and amino acids are reported. Using methods described previously,[8] the formation constants were obtained for methylmercury-amine complexes and for coordination of methylmercury to the amino dentate and to the carboxylic acid dentate of the aminoacids.

EXPERIMENTAL

Chemicals

Methylmercuric hydroxide (Alfa Inorganics) was purified and a standard solution (0.260 *M*) was prepared as described previously.[8] The amines and amino acids were of the highest grade commercially available and were used without further purification. Stock solutions of each of the amines were standardized by titration with nitric acid.

pH Measurements

All pH measurements were made at 25° with an Orion Model 801 pH meter equipped with a standard glass electrode and a fiber-junction, saturated-calomel reference electrode. Saturated potassium acid tartrate, 0.05 *M* phosphate, and 0.01 *M* sodium tetraborate solutions, pH values 3.56, 7.00 and 9.18, were used to standardize the pH meter.

Pmr Measurements

Pmr spectra were obtained on a Varian A–60–D high resolution spectrometer at a probe temperature of 25 ± 1°. Spectra were recorded at sweep rates of 0.2 Hz/sec for the chemical shift measurements and 0.5 Hz/sec for the spin-spin coupling measurements. Reported data are the average of from two to four scans.

Chemical shifts were measured relative to the central resonance of the tetramethylammonium (TMA) ion triplet or from the t-butyl resonance of t-butyl alcohol, as described previously.[8] All chemical shifts are reported in ppm relative to the central resonance of the TMA triplet; positive shifts indicate protons more shielded than those of TMA.

Solutions used in the nmr measurements were prepared from the stock solutions and had a ligand to methylmercury ratio of either one or two. Nitric acid or potassium hydroxide was added to bring the solution to the desired pH values. Typically 20-25 samples were prepared to cover the pH range from 0.5 to 13.0.

RESULTS

The pmr spectrum for the methyl protons of methylmercury consists of a singlet flanked symmetrically by two less intense satellite lines.[8] The satellite resonances are due to methyl groups bonded to mercury-199 (I = 1/2, natural abundance 16.9%) while the central resonance is due to methyl groups bonded to all other isotopes of mercury. The chemical shift of the methyl group for a solution containing 0.190 *M* CH_3Hg^+ is given by the points through which the solid curve is drawn in Figure 1, while the chemical shift for a solution containing 0.200 *M* CH_3Hg^+ and 0.400 *M* CH_3NH_2 is given by the points through which the dashed curve is drawn.

The pH dependence of the chemical shift for the 0.190 *M* CH_3Hg^+ solution is due to the pH-dependent equilibria:

$$CH_3Hg^+ + OH^- \rightleftarrows CH_3HgOH;$$

$$K_1 = \frac{[CH_3HgOH]}{[CH_3Hg^+]\,[OH^-]} \qquad (1)$$

$$CH_3Hg^+ + CH_3HgOH \rightleftarrows (CH_3Hg)_2OH^+;$$

$$K_2 = \frac{[(CH_3Hg)_2OH^+]}{[CH_3Hg^+]\,[CH_3HgOH]} \qquad (2)$$

Equilibrium constants K_1 and K_2 have been evaluated from pmr[8] and pH-titration[7] data[9]. The different pH dependence when the solution contains methylamine is due to the formation of a methylmercury-methylamine complex.

$$CH_3Hg^+ + RNH_2 \rightleftarrows CH_3HgNH_2R^+;$$

$$K_f = \frac{[CH_3HgNH_2R^+]}{[CH_3Hg^+]\,[RNH_2]} \qquad (3)$$

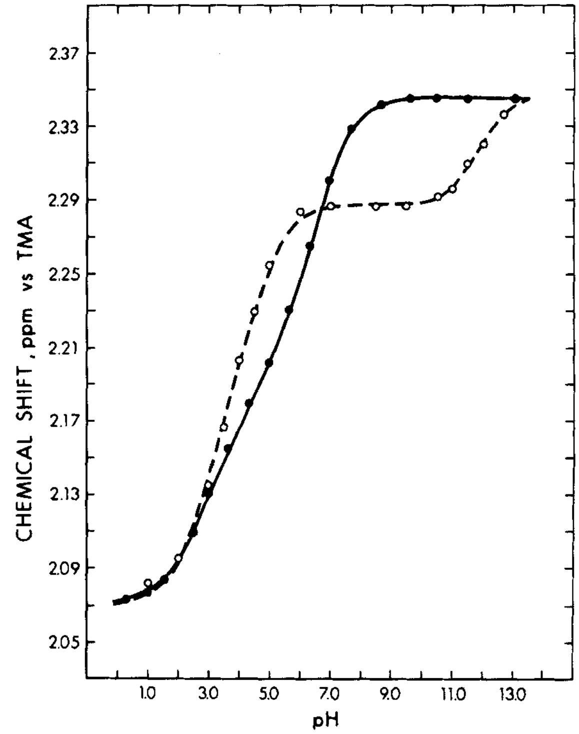

FIGURE 1 pH-dependence of the chemical shift of the methylprotons of methylmercury in an aqueous solution containing 0.190 *M* methylmercury (solid points) and in an aqueous solution containing 0.200 *M* methylmercury and 0.400 *M* methylamine (open points). The curves connecting the points are theoretical curves calculated using the constants given in the tables and the values reported in reference 8 for equilibrium constants K_1 and K_2. Approximately one-half of the actual experimental points are shown.

The observed chemical shift at a given pH is the sum of the chemical shifts of methylmercury in the free forms [CH_3Hg^+, CH_3HgOH, $(CH_3Hg)_2OH^+$] and in the complexed form, weighted according to the relative concentration of each species. Qualitatively, the data in Figure 1 indicate that the amine complex forms only at intermediate pH values; in acidic solution the proton competes with the methylmercury cation for the amine while in basic solution hydroxide ion competes with the amine for the methymercury cation. The predominant coordination number of methylmercury is one with higher complexes having comparatively small formation constants.[7]

The magnitude of the mercury-proton spin-spin coupling constant is pH dependent and also indicates complex formation, as illustrated by the data in Figure 2. Similarly, the chemical shift of the protons of the methyl group of methylamine is affected by complex formation, as shown in Figure 3.

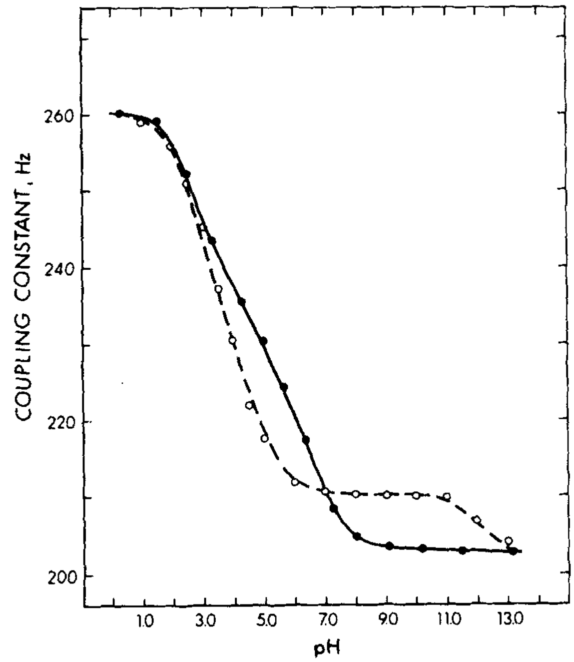

FIGURE 2 pH-dependence of the mercury-proton spin-spin coupling constant of methylmercury in an aqueous solution containing 0.190*M* methylmercury (solid points) and in an aqueous solution containing 0.200 *M* methylmercury and 0.400 *M* methylamine (open points). The curves connecting the points are theoretical curves calculated using the constants given in the tables and the values reported in reference 8 for equilibrium constants K_1 and K_2. Approximately one-half of the experimental points are shown.

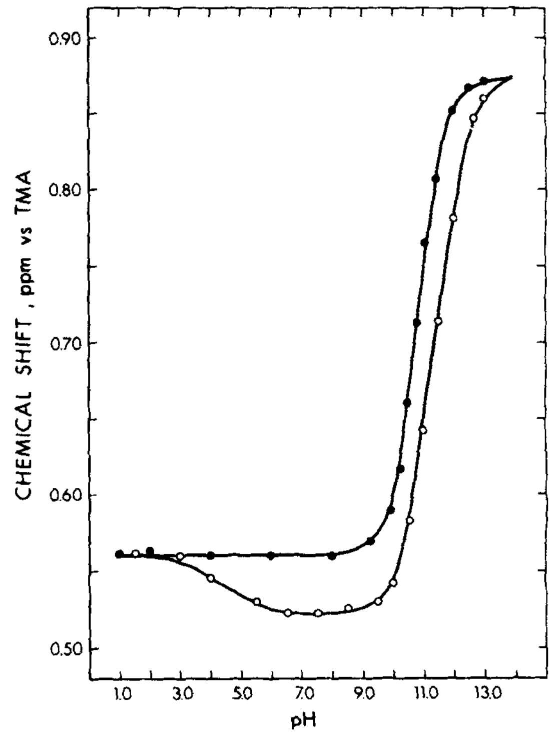

FIGURE 3 pH-dependence of the methyl resonance of methylamine in an aqueous solution containing 0.400 *M* methylamine (solid points) and in an aqueous solution containing 0.400 *M* methylamine and 0.200 *M* methylmercury (open points). The curves connecting the points are theoretical curves calculated using the constants given in the tables and the values reported in reference 8 for equilibrium constants K_1 and K_2. Approximately one-half of the actual experimental points are shown.

The formation constants of the methylmercury complexes of ammonia and selected amines were evaluated from the pH-dependence of the chemical shift of the protons of methylmercury, the mercury-proton coupling constant, and the chemical shifts of the ligand protons using methods described previously.[8] From each of these parameters some 15 to 20 values of the formation constant were calculated for a given methylmercury-amine system. The averages of all the values so obtained are given in Table 1. For comparison, Schwarzenbach and Schellenberg[7] reported the logarithm of the formation constant of the methylmercury complex of ammonia to be 7.60 (20°, 0.1 *M* KNO_3), while Simpson[6] reported a value of 8.4 (25°, variable medium). These are the only literature values available for comparison with the formation constants determined in this work although because of the different conditions direct comparison is difficult.

TABLE I

Formation constants of the methylmercury complexes and acid ionization constants of ammonia and selected amines[a]

	pK_A		
	This Work[b,c]	Literature[d]	$\log K_f$[h]
Ammonia	9.32[e]	9.24	7.25 ± 0.05
Methylamine	10.81	10.74	7.57 ± 0.04
Ethylamine	10.82	10.81	7.64 ± 0.07
Isopropylamine	10.76[f]	10.63	7.56 ± 0.06
tert-butylamine	10.81	10.45[g]	7.52 ± 0.08
Dimethylamine	11.02	10.86, 11.07	6.76 ± 0.05
Trimethylamine	10.05	9.91	5.05[i]

[a] 25°.

[b] Ionic strength 0.4–0.6 *M*.

[c] Determined by nmr unless otherwise indicated.

[d] From L. G. Sillen and A. E. Martell, 'Stability Constants of Metal-Ion Complexes,' The Chemical Society, London, 1964, unless otherwise indicated.

[e] Determined from pH titration data.

[f] From the methyl resonance of isopropylamine.

[g] N. F. Hall and M. R. Sprinkle, *J. Amer. Chem. Soc.*, 54, 3469 (1932).

[h] The average of the formation constants determined from the chemical shift of the methyl group of methylmercury, the mercury-proton coupling constant and the chemical shift of the ligand protons. The uncertainty indicates the range of the values from the three different parameters.

[i] Precise values for the formation constant with trimethylamine could not be obtained from the methylmercury pmr data due to the effects from complexation being very small.

The chemical shift of the methyl group and the mercury-proton spin-spin coupling constant of methylmercury in the methylmercury-amine complexes were also obtained from the above calculations and are given in Table II. The dashed curves drawn through the experimental points in Figures 1 and 2 are theoretical curves calculated from the results given in Tables I and II, and are representative of the fits obtained. Precise values for the formation constant of the trimethylamine complex could not be obtained from the pmr data for methylmercury because the pH dependence of the chemical shift and coupling constant of methylmercury is almost the same for a solution of methylmercury and for a solution of trimethylamine and methylmercury.

Mixed-mode acid ionization constants for the protonated amines, defined by Equation 4

$$RNH_3^+ \rightleftarrows RNH_2 + H^+;$$

$$K_A = \frac{[RNH_2]a_{H^+}}{[RNH_3^+]} \qquad (4)$$

where a_{H+} represents the activity of the hydrogen ion, were determined from the pH dependence of the chemical shifts of selected carbon-bonded protons of the amines in solutions containing no coordinating metal ions.[13] The mixed-mode constants so obtained are listed in Table I. The chemical shifts of the

TABLE II
Chemical shifts and coupling of methylmercury

Species	δ_{CH_3}[a]	$\lvert J_{^1H} - {^{199}Hg}\rvert$[b]
CH_3Hg^+	2.072	260.0
$(CH_3Hg)_2OH^+$	2.188	232.5
CH_3HgOH	2.345	203.0
$CH_3HgNH_3^+$	2.285	214.1
$CH_3HgNH_2CH_3^+$	2.279	211.5
$CH_3HgNH_2CH_2CH_3^+$	2.263	211.0
$CH_3HgNH_2CH(CH_3)_2^+$	2.244	209.0
$CH_3HgNH_2C(CH_3)_3^+$	2.226	210.2
$CH_3HgNH(CH_3)_2^+$	2.250	216.6
$CH_3Hg\overset{+}{N}H_2CH_2CO_2^-$	2.294	216.0
$CH_3Hg\overset{+}{N}H_2(CH_2)_2CO_2^-$	2.287	213.9
$CH_3Hg\overset{+}{N}H_2(CH_2)_3CO_2^-$	2.264	211.9
$CH_3Hg\overset{+}{N}H_2(CH_2)_4CO_2^-$	2.264	211.2
$CH_3Hg\overset{+}{N}H_2(CH_2)_5CO_2^-$	2.268	211.8
$CH_3Hg\overset{+}{N}H_2CH(CH_2C_6H_5)CO_2^-$	2.800(c)	
$CH_3HgO_2C(CH_2)_2\overset{+}{N}H_3$	2.167	230.5
$CH_3HgO_2C(CH_2)_3\overset{+}{N}H_3$	2.175	230.0
$CH_3HgO_2C(CH_2)_4\overset{+}{N}H_3$	2.179	230.2
$CH_3HgO_2C(CH_2)_5\overset{+}{N}H_3$	2.177	230.4

[a] In units of ppm relative to the central resonance of TMA.

[b] In units of Hz; the sign of the coupling constant is negative: F. A. L. Anet and J. L. Sudmeier, *J. Mag. Res.*, 1, 124 (1969); H. F. Henneike, *J. Amer. Chem. Soc.*, 94, 5945 (1972).

[c] Shieldedby the ring current of the phenyl group.

TABLE III
Chemical shifts of carbon-bonded amine protons[a]

	$\delta_{RNH_3^+}$	δ_{RNH_2}	$\delta_{Complex}$
Methylamine	0.560	0.873	0.474
Ethylamine	0.117 [b]	0.528 [b]	0.023 [b]
	1.910 [c]	2.132 [c]	1.872 [c]
Isopropylamine	1.882 [d]	2.142 [d]	1.869 [d]
Tert-Butylamine	1.812	2.062	1.807
Dimethylamine	0.450	0.900	0.387
Trimethylamine	0.280	0.997	0.375

[a] In units of ppm relative to the central resonance of TMA.
[b] For the methylene protons.
[c] For the methyl protons.
[d] For the methyl protons.

carbon-bonded amine protons of the protonated, ionized and methylmercury-complexed amines are given in Table III.

The extent of formation of methylmercury-amine complexes is pH-dependent, as illustrated in Figure 4 by the pH-dependence of the methylmercury-containing species in the methylmercury-methylamine system. At pH 1, virtually all the methylmercury is in the form of the aquated cation due to dissociation of the complex through protonation of the amine. As the pH is increased, the dimeric species $(CH_3Hg)_2OH^+$ and the complex $CH_3Hg(NH_2CH_3)^+$ start to form. The maximum fractional concentration of the complex occurs over the pH range 7.5 to 9.5, with further increases in pH resulting in dissociation of the complex due to displacement of the methylamine by hydroxide ion.

The formation constants of the methylmercury complexes of amines are somewhat larger than those of carboxylic acids.[8] However, the proton association constants of the carboxylic acids are less, making it possible for the methylmercury cation to compete effectively for the carboxylate ligand at lower pH values. For comparison, the fractional concentrations of the methylmercury-containing species in the methylmercury-acetic acid systems are also given as a function of pH in Figure 4. The pK_A of acetic acid is 4.65 and the logarithm of the formation constant of its methylmercury complex is 3.18.

The results in Figure 4 indicate that, in multidentate ligands containing amino and carboxylate donor groups, the site to which coordination occurs will be strongly pH dependent. This is shown to be the case by the chemical shift data in Figure 5 for 5-aminovaleric acid. The chemical shift of the protons of the methylene group bonded to the carboxylate group is most sensitive to protonation and complexation at this site, while protonation and complexation of the amine dentate are indicated by the chemical shift of the carbon-bonded protons adjacent to the amine group. From pmr data at pH values less than 5 and greater than 9, formation constants were determined for coordination of methylmercury by the carboxylate dentate and the amino dentate, respectively. The results are given in Table IV. The formation constant for binding of methylmercury to the carboxylate group of phenylalanine could not be determined, because kinetic phenomena, observable between pH 1 and 7 in all these solutions, broadens the resonances. The pmr parameters for the methyl group of methylmercury in the amino acid complexes are given in Table II. No attempt was made to determine formation constants for complexes of the type $(CH_3Hg)_2L^+$ in which each of the amino acid dentates is bonded to a methylmercury cation.

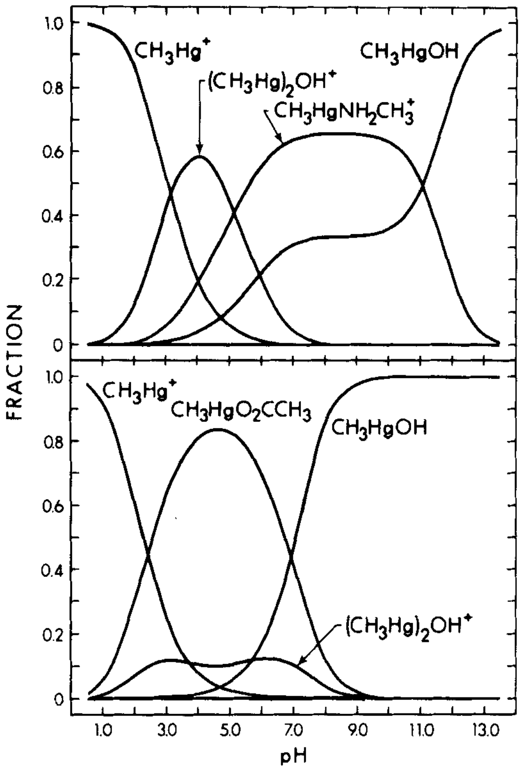

FIGURE 4 Upper half: Fractional concentrations of the methylmercury-containing species in an aqueous solution containing 0.200 *M* methylmercury and 0.200 *M* methylamine as a function of pH. Fractional concentrations were calculated from the constants given in Table I and the values reported in reference 8 for equilibrium constants K_1 and K_2. Lower half: Fractional concentrations of the methylmercury-containing species in an aqueous solution containing 0.200 *M* methylmercury and 0.200 *M* acetic acid as a function of pH. Fractional concentrations were calculated from previously reported constants (8).

DISCUSSION

One purpose of the present work was to determine if any relationship exists between the magnitudes of the formation constants of methylmercury-amine complexes and the basicity of the nitrogen, as reflected by the magnitude of the acid ionization constant of the amine.[14] The primary amines listed in Table I are of similar pK_A, and their formation constants are of approximately the same magnitude, but slightly less than the formation constants for coordination of CH_3Hg^+ to the amino group of fully ionized 5-aminovaleric acid- and 6-aminohexanoic acid, both of which have pK_A's similar to those of the primary amines. For ammonia and the series of methylamines, however, the pK_A values increase in the order

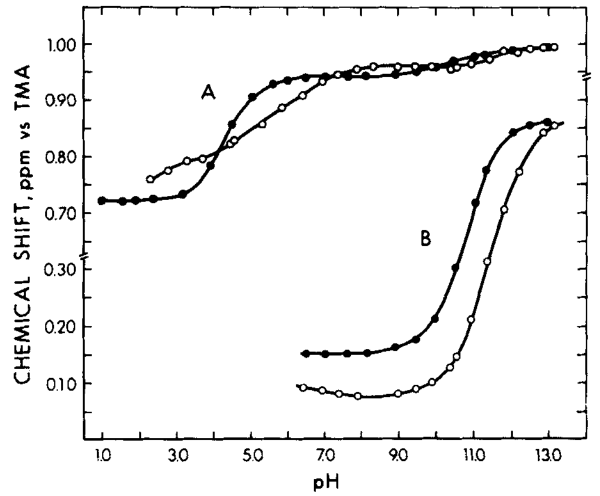

FIGURE 5 pH-dependence of the chemical shift of the protons of the methylene groups bonded to the carboxylate (A) and amino (B) dentates of 5-aminovaleric acid. The closed points are for a solution containing 0.10 *M* 5-aminovaleric acid; the open points are for a solution containing 0.10 *M* 5-aminovaleric acid and 0.10 *M* methylmercury.

$pK_{A,\text{ ammonia}} < pK_{A,\text{ trimethylamine}}$

$pK_{A,\text{ methylamine}} < pK_{A,\text{ dimethylamine}}$

whereas the log K_f values increase in the order log $K_{f,\text{trimethylamine}}$ < log $K_{f,\text{dimethylamine}}$ < log $K_{f,\text{ammonia}}$ < log $K_{f,\text{methylamine}}$. Similar behavior is observed for the coordination of CH_3Hg^+ to the amino group of the amino acids listed in Table IV. These results suggest that the magnitude of the formation constants for coordination of CH_3Hg^+ by amine dentates is governed by the degree of substitution on the nitrogen as well as the basicity of the nitrogen. The results in Tables I and IV suggest that the logarithms of the formation constants for coordination to the primary amino groups in peptides and proteins are in the range 7.5 ± 0.2. The binding to the amino group of phenylalanine is an exception, having a log K_f of 8.29. We propose that the greater stability of the phenylalanine complex results from an interaction, perhaps hydrophobic in nature, between the phenyl ring of the ligand and the methyl group of methylmercury. In support of this is the observation that the shift of the methyl group in the complex is 0.5 ppm upfield from that for the glycine complex, consistent with the methyl group lying close to and above the plane of the phenyl ring.

The formation constants for coordination to the carboxylate group of the zwitterionic form of the amino acid increase as pK_{A1} increases, however the observed formation constants are different by from

TABLE IV

Formation constants of the methylmercury complexes and acid ionization constants of selected amino acids[a]

Amino Acid	pK_{A1}[b,c]	pK_{A2}[b,c]	$\log K_{f,O}$[e,f]	$\log K_{f,N}$[f,g]
Glycine	2.34	9.69		7.88 ± 0.05
β-Alanine	3.61	10.25	2.52 ± 0.10	7.56 ± 0.07
4-Aminobutyric Acid	4.12[d]	10.48[d]	2.74 ± 0.13	7.54 ± 0.03
5-Aminovaleric Acid	4.33[d]	10.81[d]	2.98 ± 0.10	7.75 ± 0.05
6-Aminohexanoic Acid	4.46[d]	10.84[d]	3.10 ± 0.01	7.83 ± 0.02
8-Aminooctanoic Acid	4.56[d]	10.89[d]	3.15 ± 0.09	7.60 ± 0.04
Valine	2.29[i]	9.81[i]	2.7 ± 0.02[h]	7.41 ± 0.01[h]
Phenylalanine	-	9.16[j]	-	8.29 ± 0.05

[a] 25°

[b] Ionic strength 0.2–0.3 *M*.

[c] Determined by nmr unless otherwise indicated.

[d] Determined by pH titration.

[e] The average of the formation constants obtained from the three pmr parameters for coordination to the carboxylate group.

[f] The uncertainty represents the range of the values determined from the three pmr parameters.

[g] The average of the formation constants obtained from the three pmr parameters for coordination to the amino group.

[h] Obtained only from the chemical shift of the methylmercury protons. The uncertainty is the standard deviation of the individual values.

[i] From L. G. Sillen and A. E. Martell, 'Stability Constants of Metal-Ion Complexes,' The Chemical Society, London, 1964.

[j] Reference 16.

0.08 to 0.77 log $K_{f,o}$ units than those predicted by the relationship[14] reported previously for methylmercury-carboxylic acid complexes. This presumably is due, in part, to the positive charge on the protonated amino group.

The results in Table II indicate that the mercury-proton coupling constant when CH_3Hg^+ is complexed by an amine is 212 ± 4 Hz, while the coupling constant for CH_3Hg^+ bonded to the carboxylate oxygen of the zwitterionic form of amino acids is 230.3 ± 0.3 Hz. The coupling constant of CH_3Hg^+ coordinated to the carboxylate oxygen of simple carboxylic acids was found to range from 230.7 to 245.8 Hz,[8] while the coupling constant of sulf hydryl-coordinated CH_3Hg^+ has been found to be in the range 170 to 180 Hz in studies of binding to sulfur-containing amino acids and peptides.[15] These results suggest that the magnitude of the coupling constant reflects the stability of the complex.

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