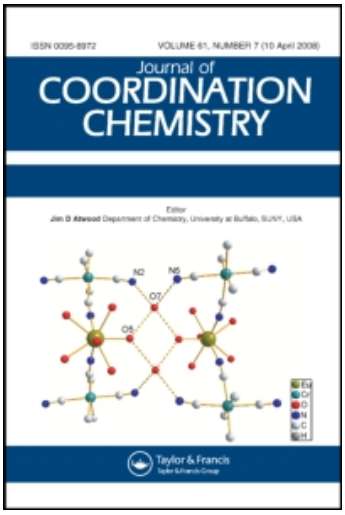

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COMMUNICATION

COMPLEXATION OF METHYLMERCURY(II) BY DL-SELENOMETHIONINE

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INTRODUCTION

The complexation of metal ions by methionine [Met] has attracted considerable interest.[1–3] However, the coordination chemistry of selenomethionine [Se-Met] has received much less attention despite the fact that it is one of the few naturally occuring selenoaminoacids and a component of at least one bacterial selenoenzyme.[4] It has been shown by ^{1}H NMR spectroscopy[1] that the prototypical 'soft' metal ion, methylmercury(II), binds to Met above pH 7 *via* the amino group and binds to the thioether group at low pH. A single crystal X-ray diffraction study has confirmed amino coordination in a complex isolated from alkaline solution.[5]

To our knowledge, no X-ray structural studies have been reported for group IIB metal complexes with Se-met, and in fact no equilibrium constants have been determined for the complexation of Se-Met by any metal ion,[6] although we have recently reported the interaction of Hg^{2+} and Au^{3+} with Se-Met followed by ^{1}H NMR spectroscopy.[7,8] We report here the formation constants for the binding of CH_3Hg(II) by Se-Met. At pH 0.8, log Kf = 3.73 for selenoether binding, and at pH 9.0, log Kf = 7.63 for amino binding.

EXPERIMENTAL

A stock solution of CH_3HgOH was prepared by metathesis of CH_3HgI with Ag_2O in H_2O as described previously.[9] The stock solution was standardized by titration of aliquots with standard thiosulphate solution in 50% aqueous methanol at pH 4. The sharp endpoint was located visually using Michler's thioketone (Eastman Kodak, 4,4′-bis(dimethylamino)thiobenzophenone) as an indicator. The Se-Met (Nutritional Biochemicals) showed no significant impurities by ^{1}H NMR spectroscopy and was used as received.

Measurements of pH were made using an Orion 701A meter fitted with a Philips GAT130 glass electrode and a RH44/2-SD/12 glass-sleeve double-junction

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Ag/AgCl reference electrode. 0.3 M KNO_3 was used as the outer junction electrolyte to preclude chloride complexation of $CH_3Hg(II)$. It has been shown previously[10] that nitrate binds much less strongly to $CH_3Hg(II)$ than hydroxide or methionine.

Solutions for NMR measurements were prepared at pH 0.8 (0.3 M HNO_3) and pH 9.0 (0.3 M KNO_3) by titrating 20 cm^3 aliquots of 20 mM Se-Met with 0.751 M CH_3HgOH. All solutions contained 1% D_2O for field frequency lock, and 2 mM tert-butanol for chemical shift reference (1.2365 ppm down-field from 2,2-dimethyl-2-silapentane-5-sulphonate). ^1H NMR spectra were obtained on a Bruker WM-360 spectrometer. Since all spectra were measured in H_2O, the water resonance was suppressed using a homogated decoupling technique.

RESULTS AND DISCUSSION

The chemical shifts of the methyl and methine protons of Se-Met, which gives rise to a singlet and triplet, are shown as a function of pH in Figure 1 for a solution containing 20 mM Se-Met and for a solution containing 20 mM of Se-Met:$CH_3Hg(II)$ at a 1:1 ratio. Exchange-averaged resonances were observed throughout the pH range studied. At pH less than 4, the chemical shift of the methine proton of Se-Met is only slightly affected by the presence of $CH_3Hg(II)$ but the methyl protons are deshielded by some 0.65 ppm, indicating the preferential binding by the selenoether group under these conditions. In the pH range 6-9, $CH_3Hg(II)$ binds to the amino group and not to the selenoether group

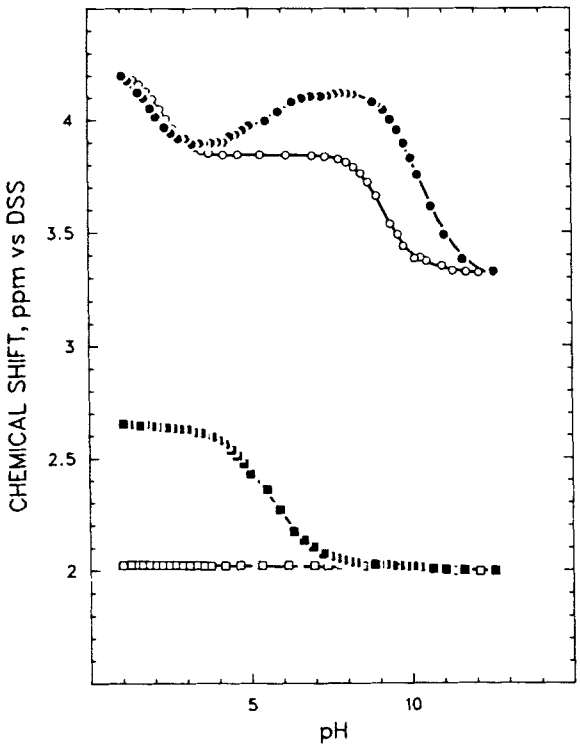

FIGURE 1 pH dependence of the chemical shift of the methine (upper curves) and methyl (lower curves) protons of selenomethionine in aqueous solutions containing 20 mM seleno-methionine (open points) and 20 mM (1:1) of $CH_3Hg(II)$:selenomethionine (closed points).

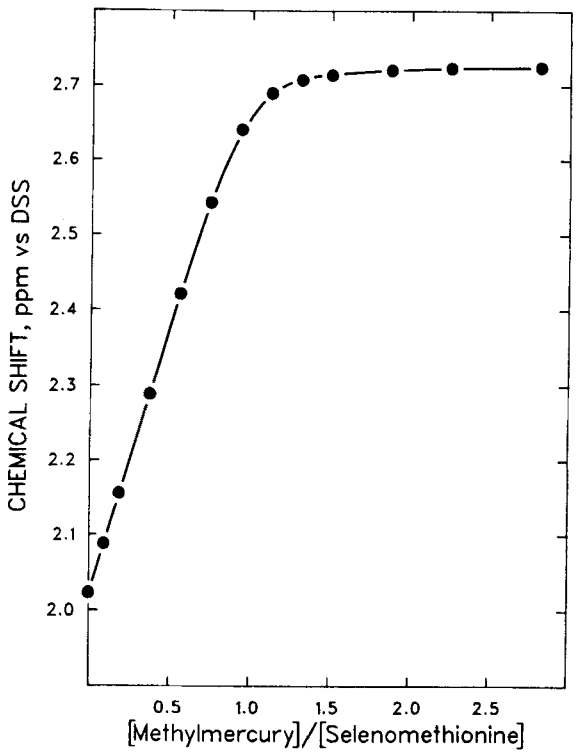

FIGURE 2 Chemical shifts of the concentration-dependent exchange-averaged resonance of the methyl protons on the ratio $[CH_3Hg(II)]/[Se\text{-}Met]$ at pH 0.8.

as indicated by the coincidence chemical shifts of the methyl protons of the ligand and complex. The methine proton is however deshielded by 0.2–0.3 ppm. At higher pH, the complex dissociates under the influence of hydroxide competition and the methine proton chemical shift approaches that of the free ligand.

Figure 2 shows the dependence of the chemical shifts of the exchange-averaged resonance of the methyl protons upon the ratio $[CH_3Hg(II)]/[Se\text{-}Met]$ at pH 0.8. At this pH, uncomplexed $CH_3Hg(II)$ exists predominantly as the aquated cation.[1] The equilibrium constant for the reaction, (*1*),

$$CH_3SeCH_2CH_2\underset{\displaystyle +NH_3}{\underset{|}{C}}HCOOH + CH_3Hg(II) \rightleftarrows CH_3\overset{+}{\underset{\displaystyle HgCH_3}{\underset{|}{S}}}eCH_2CH_2\underset{\displaystyle +NH_3}{\underset{\backslash}{C}}HCOOH \qquad (1)$$

TABLE I
Comparison of formation constants[a] of some aminoacids with $CH_3Hg(II)$ in aqueous solutions at 25°

ligand	Log Kf	pH	binding site	Ref.
L-methionine	1.94	0.5	thioether	1
	7.40	>8.0	amino	1
DL-selenomethionine	3.73	0.8	selenoether	this work
	7.63	9.0	amino	this work
valine	7.41	>8.0	amino	11
ß-alanine	7.56	>8.0	amino	11

[a]All the formation constants were measured in the presence of 0.2–0.3 M HNO_3 or KNO_3

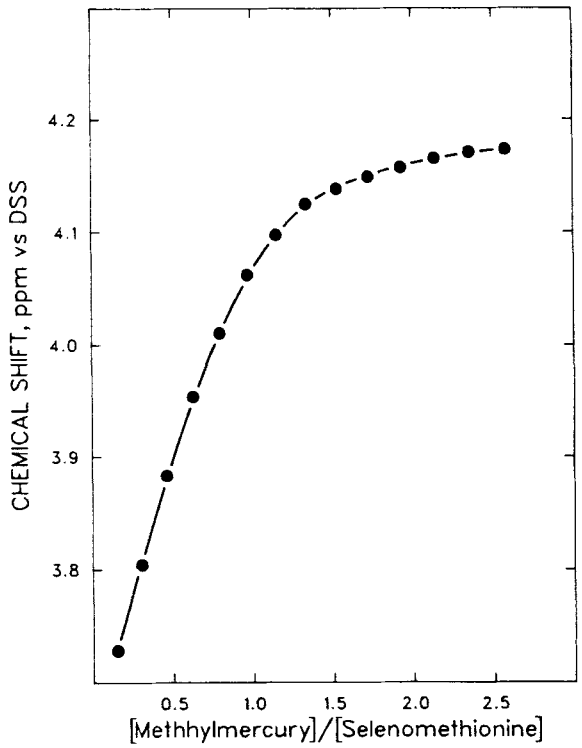

FIGURE 3 Chemical shifts of the concentration-dependent exchange-averaged resonance of the methine protons on the ratio $[CH_3Hg(II)]/[Se\text{-}Met]$ at pH 9.0.

was determined from this data by non-linear least-squares analysis as described previously.[1] The log Kf measured was 3.73 and δ_{comp} (which is the chemical shift of the resonance for the complexed form) was measured at 2.729 ppm. As shown in Table I, for Met, log Kf was reported as 1.94 and δ_{comp} as 2.863 ppm.

The conditional formation constant for amino-binding was similarly obtained from the pH 9.00 data (Figure 3) with respect to Equation (*2*). In this case, complexation by hydroxide was taken into account using the formation constant for CH_3HgOH obtained under similar conditions, to give log Kf = 7.63 and δ_{comp} = 4.205 ppm.

$$CH_3SeCH_2CH_2\underset{\displaystyle NH_2}{\underset{|}{C}}HCO_2^- + CH_3Hg(II) \rightleftarrows CH_3SeCH_2CH_2\underset{\displaystyle H_2NHgCH_3}{\underset{\diagdown}{C}}HCO_2^- \qquad (2)$$

By comparison, methionine has log Kf = 7.4 for complexation of the amino group. Similar log Kf values were obtained for the complexation of $CH_3Hg(II)$ by the amino group of other amino acids (see Table I).

These results indicate that the selenoether group forms more stable complexes with 'soft' $CH_3Hg(II)$ than an analogous thioether donor. In fact, the difference in binding strength (1.7 log Kf units) is greater than that between selenohydryl and sulfhydryl ligands (0.3–0.9 log Kf units[12]), reflecting the greater "softness" of the selenium donor in selenoethers than in selenols. Similar observations were made when Hg(II) was reacted with Se-Met,[7] and it was concluded that Se-Met forms more stable complexes than Met in acidic solution.

The specificity of the binding of $CH_3Hg(II)$ to the selenoether group in acidic solution may help to identify the Se-Met resonance in the ^1H NMR spectra of Se-Met-containing peptides and proteins by observing changes in the spectrum as the peptide or protein is titrated as a function of the concentration of $CH_3Hg(II)$ at low pH.

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