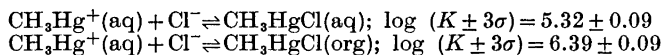


Solvent Extraction Studies on Complex Formation between Methylmercury(II) and Chloride Ions

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Complex formation between $\text{CH}_3\text{Hg}(\text{II})$ and Cl^- ions in the two-phase system *o*-xylene/1 M (Na,H)(ClO₄,Cl) has been studied by measuring the distribution of methylmercury(II) as a function of chloride concentration. The distribution of $\text{CH}_3\text{Hg}(\text{II})$ between the two phases has been studied by a radiometric method using Hg-203 labelled $\text{CH}_3\text{Hg}(\text{II})$ and also by a spectrophotometric titration method for the analysis of non-radioactive methylmercury(II). The distribution data have been analyzed with the computer program LETAGROP-DISTR.¹⁻⁵ The results of the analysis give evidence to the formation of the complex CH_3HgCl in both the aqueous and organic phases with the following equilibrium constants:



No extraction of $\text{CH}_3\text{HgClO}_4$ into *o*-xylene was found. The extracted CH_3HgCl was found predominantly as undissociated species.

Organic mercury compounds, *e.g.* methylmercury salts, being effective pesticides, have been widely used for seed disinfection⁶⁻¹⁰. Great interest has arisen in the solution chemistry of such organomercurial compounds during the past few years because of their polluting effects in natural water. Microbiological processes are believed to lead to the formation of methylmercury(II) from industrial waste containing inorganic mercury¹¹⁻¹³. Numerous studies have also been devoted to the clarification of their metabolism, since the organomercurials were found to be a hazard to the health of man and animals.¹⁴⁻²⁰

Organomercurials are normally found in natural waters in tracer concentrations only. Studies of their chemical state at low concentration levels are

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therefore of importance for the understanding of their distribution in nature. Solvent extraction using radiometric techniques is quite appropriate for this purpose, since it has proven to be a fruitful method for the study of chemical equilibria at very low concentration levels.²¹

In this paper we report solvent extraction studies of complex formation between methylmercury(II) and chloride ions in the two-phase systems $\text{CH}_3\text{Hg(II)} - 1 \text{ M (Na, H) (ClO}_4, \text{Cl)}/o\text{-xylene}$. The present work is part of a larger project in this laboratory concerned with studies of the solution chemistry of methylmercury(II) in particular and other heavy metal ions in general, primarily at the low concentration levels as found in natural waters.

The knowledge of the extraction properties of methylmercury(II)-chloride complexes has subsequently been used in studies of the complex equilibria between methylmercury(II) and other ligands.²² This work also illustrates the possibility and advantages of using solvent extraction techniques for accurate studies of complex equilibria. The preliminary results have been reported elsewhere.²³ The present studies were initiated by one of us (O.B.) who did the preliminary work using spectrophotometric and titration methods. The work has been continued and extended by F. I. and D. H. L. who applied both radiometric and spectrophotometric methods to the distribution studies.

Previous work. The distribution of methylmercuric chloride between toluene and water has previously been studied by Simpson²⁴ who reported the following value for the distribution constant $K_D = [\text{CH}_3\text{HgCl}]_{\text{org}}[\text{CH}_3\text{HgCl}]^{-1} = 11$. However, this result may not be taken as conclusive since for the calculation of K_D the author has only a single experimental point available and thus gives no evidences as to the CH_3HgCl species assumed to be formed.

Solubility studies as well as potentiometric studies on the formation of CH_3HgCl have previously been reported by Waugh *et al.*²⁵ However, their results are open to question, since these authors did not use a defined ionic medium in their studies and thus did not control the activity factors of the species studied. Results of potentiometric studies on the formation of CH_3HgCl in 0.1 M KCl medium have also been reported by Schwarzenbach and Schellenberg²⁶⁻²⁸ and in 0.1 M KNO_3 by Zanella *et al.*²⁹ These authors²⁵⁻²⁹ all found evidence for the formation of CH_3HgCl species in the aqueous solution. However, the values given for the formation constant for CH_3HgCl varied between $\log K = 4.90$ and 6.60 for the various media studied. Moreover no detailed studies on the possible formation of polynuclear methylmercuric species in two-phase systems have been reported. Thus further studies in the solution chemistry of $\text{CH}_3\text{Hg(II)}$ species are well motivated.

Barbieri and Bjerrum,³⁰ using a polarographical method, studied the solubility of organomonohalogeno and organomonothiocyanato mercury(II) complexes in 1 M salt solution ($\text{NaX} + \text{NaClO}_4$) or in a 50 vol % methanol-water solvent. They found evidence for the formation of distinct negatively charged complexes RHgX_n^{1-n} ($\text{R} = \text{C}_2\text{H}_5$ and 2-butyl; $n = 1, 2, 3$) only in the thiocyanate and iodide systems. Rizzardi *et al.*³¹ by ion-exchange studies found indications of the formation of $\text{C}_2\text{H}_5\text{HgCl}$ and probably also $\text{C}_2\text{H}_5\text{HgCl}_2^-$ and $\text{C}_2\text{H}_5\text{HgCl}_3^{2-}$ in aqueous solutions at high ligand concentrations. Eigen *et al.*³² studied the kinetics of the formation of $\text{CH}_3\text{HgX}^{1-n}$ from CH_3HgOH for $\text{X}^{n-} = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{SCN}^-, \text{and } \text{SO}_3^{2-}$.

Symbols and equilibrium constants

[] = equilibrium concentration in the aqueous phase.
 []_{org} = equilibrium concentration in the organic phase.

- C_{Cl} = initial total concentration of chloride ion in the aqueous and organic phase.
 C_{MeHg} = initial total concentration of methylmercury(II) ion in the organic phase.
 $K_{pqr,\text{org}}$ = $[(\text{H}^+)_p(\text{MeHg}^+)_q(\text{Cl}^-)_r]_{\text{org}}[\text{H}^+]^{-p}[\text{MeHg}^+]^{-q}[\text{Cl}^-]^{-r}$, formation constant of the complex $(\text{H}^+)_p(\text{MeHg}^+)_q(\text{Cl}^-)_r$ in the organic phase.
 $K_{klm,\text{aq}}$ = $[(\text{H}^+)_k(\text{MeHg}^+)_l(\text{Cl}^-)_m][\text{H}^+]^{-k}[\text{MeHg}^+]^{-l}[\text{Cl}^-]^{-m}$, formation constant of the complex $(\text{H}^+)_k(\text{MeHg}^+)_l(\text{Cl}^-)_m$ in the aqueous phase.
 $I_{\text{aq}}, I_{\text{org}}$ = gamma-activity of Me^{203}Hg in the aqueous and organic phase, cpm for equal volumes of samples.
 $N_{\text{aq}}, N_{\text{org}}$ = number of moles of $\text{MeHg}(\text{II})$ in equal volumes of equilibrated aqueous and organic phases analyzed by spectrophotometric titration.
 D = $\frac{\sum[\text{MeHg}]_{\text{org}}}{\sum[\text{MeHg}]} = I_{\text{org}}/I_{\text{aq}}$ or $N_{\text{org}}/N_{\text{aq}}$, net distribution ratio of $\text{CH}_3\text{Hg}(\text{II})$.
 MeHg = CH_3Hg , methylmercury(II).
 $\sigma(y)$ = standard deviation in y (cf. Ref. 3, eqn. 17).

EXPERIMENTAL

Reagents. HClO_4 (*p.a.* Merck, Darmstadt) was used without further purification. NaClO_4 was prepared from Na_2CO_3 (*p.a.* Merck, Darmstadt) and HClO_4 (*p.a.*) as described in Ref. 34. *o*-Xylene (*puriss.*, Kebo) was purified by washing it with dilute NaOH solution, distilled water, dilute mineral acid (*e.g.* HClO_4) solution and finally several times with distilled water. Benzene (*p.a.* Merck, Darmstadt) was purified in the same way as *o*-xylene. Chloroform (*p.a.* Merck, Darmstadt) was purified by washing it several times with an equal volume of distilled water to remove any traces of ethanol. Dithizone (*p.a.* Merck, Darmstadt) was purified according to a procedure described by Irving and Cox³⁵ and the stock solution so prepared was stored under a layer of dilute sulfuric acid and kept in a refrigerator.³⁶

Non-radioactive methylmercuric hydroxide solution was prepared by shaking an aqueous suspension of methylmercuric bromide with freshly prepared $\text{Ag}_2\text{O}(\text{s})$ at about pH 12 for 10–12 h, centrifuging the mixture and pipetting the clear CH_3HgOH solution. The CH_3HgBr used was prepared from commercial methylmercuric bromide (Casco) which had been recrystallized twice from absolute alcohol.

Radioactive $\text{CH}_3^{203}\text{Hg}(\text{II})$ was purchased from the Radiochemical Centre, Amersham, England, in the form of $(\text{CH}_3^{203}\text{Hg})_2\text{O}$ and from the Swedish Atomic Energy Company, Studsvik, as $\text{CH}_3^{203}\text{HgNO}_3$ in aqueous solution. The $\text{Me}^{203}\text{Hg}(\text{II})$ was purified from the small amount of inorganic $^{203}\text{Hg}(\text{II})$ present by the following procedure which is a somewhat improved modification of the method described by Östlund:²⁰ The radioactive $\text{Me}^{203}\text{Hg}(\text{II})$ was first converted into $\text{Me}^{203}\text{HgCl}$ by the addition of an excess of HCl and the solution obtained then evaporated nearly to dryness in order to decompose any HNO_3 present. The residual solution was finally adjusted to 0.5 M with respect to HCl and was shaken several times with equal volumes of benzene, which extracted MeHgCl into the organic phase. Afterwards the benzene phase was shaken several times with 0.5 M HCl solution to remove any coextracted HgCl_2 . The MeHgCl benzene solution obtained was found to be free from inorganic $\text{Hg}(\text{II})$ as shown by the thin-layer chromatographic analysis method described by Östlund.²⁰ The purified $\text{MeHg}(\text{II})$ in the benzene phase

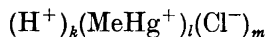
was used as the stock solution for the distribution experiments. In those experiments in which radioactive $\text{Me}^{203}\text{HgCl}$ was used, $C_{\text{Me}^*\text{HgCl}} = 8.2 \times 10^{-6}$ M, the *o*-xylene solvent contained 0.1 vol. % benzene. By comparison with the experiments in which pure *o*-xylene was used this small percentage of benzene was found not to affect the distribution of MeHg(II) .

Analysis of methylmercury(II). Non-radioactive methylmercury(II) was analyzed using a spectrophotometric titration method developed for this purpose by Ingman.³⁷

Distribution experiments. Equal volumes of aqueous and organic phases were equilibrated for at least 2 h in glass-stoppered centrifuge tubes using a rotating shaker. The two phases were afterwards separated from each other by centrifugation at approximately 3500 rpm. Samples of the solutions were pipetted out and the γ -radioactivity of the ^{203}Hg measured in a Tracerlab SC-57 low background well scintillation counter with a Tl-activated NaI crystal in conjunction with a Tracerlab SC-70 Compu/Matic V scaler. In the case of non-radioactive methylmercury(II) the amounts of MeHg(II) in the two phases were analyzed as described by Ingman.³⁷ All experiments were carried out in rooms thermostated at $25 \pm 0.3^\circ\text{C}$.

CHEMICAL MODEL

The methylmercury(II) species in the aqueous phase will be represented by the general formula:



in which complex formation with other ions and molecules present in the ionic medium, such as ClO_4^- , Na^+ , and H_2O has been disregarded. For example the species $\text{CH}_3\text{HgCl(aq)}$ and $\text{CH}_3\text{HgOH(aq)}$ will be denoted as the (0,1,1) and (-1,1,0) species in the aqueous phase. Similarly the general formula $(\text{H}^+)_p(\text{MeHg}^+)_q(\text{Cl}^-)_r$ will be used to represent the extractable $\text{CH}_3\text{Hg(II)}$ species in the organic phase, *e.g.* (0,1,1) species in the organic phase for $\text{CH}_3\text{HgCl(org)}$. As usual we make the assumption that only uncharged $\text{CH}_3\text{Hg(II)}$ species are extractable into the organic phase. The calculated distribution ratio for $\text{CH}_3\text{Hg(II)}$ in the two-phase system may be expressed by the following relationship:

$$D_{\text{calc}} = \frac{\sum q[(\text{H}^+)_p(\text{MeHg}^+)_q(\text{Cl}^-)_r]_{\text{org}}}{\sum l[(\text{H}^+)_k(\text{MeHg}^+)_l(\text{Cl}^-)_m]} = \frac{\sum qK_{pqr, \text{org}}[\text{H}^+]^p[\text{MeHg}^+]^q[\text{Cl}^-]^r}{\sum lK_{klm, \text{aq}}[\text{H}^+]^k[\text{MeHg}^+]^l[\text{Cl}^-]^m} \quad (1)$$

For low values of $C_{\text{MeHg}} (< 9.5 \times 10^{-4}$ M) we may make the reasonable assumption that only mononuclear MeHg(II) species are formed in both the organic and aqueous phases, *i.e.* q and l may only have the values 0 or 1. As will be shown later, some experimental evidence seems to support this assumption for the extraction conditions used. Assuming the formation of only mononuclear methylmercury(II) species, D will be independent of $[\text{MeHg}^+]$ and (1) may be written in the form:

$$D_{\text{calc}} = \frac{\sum K_{pqr, \text{org}}[\text{H}^+]^p[\text{Cl}^-]^r}{\sum K_{klm, \text{aq}}[\text{H}^+]^k[\text{Cl}^-]^m} \quad (2)$$

The mass balances for $\text{CH}_3\text{Hg(II)}$ and Cl^- are given by the following equations:

$$C_{\text{MeHg}} = \sum qK_{pqr, \text{org}}[\text{H}^+]^p[\text{MeHg}^+]^q[\text{Cl}^-]^r + \sum lK_{klm, \text{aq}}[\text{H}^+]^k[\text{MeHg}^+]^l[\text{Cl}^-]^m \quad (3)$$

$$C_{\text{Cl}} = \sum rK_{pqr, \text{org}}[\text{H}^+]^p[\text{MeHg}^+]^q[\text{Cl}^-]^r + \sum mK_{klm, \text{aq}}[\text{H}^+]^k[\text{MeHg}^+]^l[\text{Cl}^-]^m \quad (4)$$

Given the values of C_{MeHg} , C_{Cl} , $[\text{H}^+]$ for each point and the equilibrium constants $K_{pqr, \text{org}}$, $K_{klm, \text{aq}}$ for the formation of the $\text{CH}_3\text{Hg(II)}$ species in the organic and aqueous phase, we may calculate $[\text{CH}_3\text{Hg}^+]$ and $[\text{Cl}^-]$ from (3) and (4) and D_{calc} from (1) or (2).

ANALYSIS OF THE DATA

The distribution data given in Table 1 were analyzed using the computer program LETAGROP-DISTR,¹⁻⁵ which is a version of LETAGROP (=pit-mapping) for the analysis of distribution data. This program is used to find from the data the "best" set of constants $K_1, K_2 \dots K_N$ for the formation of the species $(\text{H}^+)_p(\text{MeHg}^+)_q(\text{Cl}^-)_r$, in both phases by, *e.g.*, minimizing the error-square sum $U = \sum_1^{Np} (\log D_{\text{calc}} - \log D_{\text{exp}})^2$, where Np represents the number of experimental points available. The program also allows the choice of minimizing the error-squares sums of other types of errors. *i.e.* $Fel[2] = (D_{\text{exp}}D_{\text{calc}}^{-1} - 1)$ or $Fel[3] = (D_{\text{calc}}D_{\text{exp}}^{-1} - 1)$, (Fel = error). The results of the computer analysis of the data in this work, assuming the same chemical model but minimizing different types of error-squares sums, are given in Table 3. Their comparison will be discussed further below. The input data for the computer are: (1) I_{aq} , I_{org} or N_{aq} , N_{org} (2) C_{MeHg} in mol/l; (3) C_{Cl} in mol/l, and (4) $\log [\text{H}^+]$.

Table 1. The distribution of $\text{CH}_3\text{Hg(II)}$ between 1 M (Na,H)(ClO₄,Cl) and *o*-xylene at 25°C. Data given as C_{Cl} M, $\log D_{\text{exp}}$, $\log [\text{Cl}^-]$ and $\log (D_{\text{calc}}D_{\text{exp}}^{-1})$. $-\log [\text{H}^+] = 1.699$.

$C_{\text{MeHg(II)}} = 2.358 \times 10^{-4} \text{ M}^a$
6.916 $\times 10^{-5}$, -0.407, -6.809, -0.025; 1.089 $\times 10^{-4}$, -0.038, -6.495, -0.094; 1.333 $\times 10^{-4}$, 0.101, -6.315, -0.068; 1.582 $\times 10^{-4}$, 0.244, -6.123, -0.039; 1.831 $\times 10^{-4}$, 0.434, -5.898, -0.044; 2.089 $\times 10^{-4}$, 0.667, -5.581, -0.047; 2.363 $\times 10^{-4}$, 0.891, -5.023, 0.002; 2.588 $\times 10^{-4}$, 0.982, -4.580, 0.017; 3.107 $\times 10^{-4}$, 1.039, -4.119, 0.006; 3.627 $\times 10^{-4}$, 1.053, -3.894, 0.002; 4.627 $\times 10^{-4}$, 1.080, -3.643, -0.018; 7.547 $\times 10^{-4}$, 1.055, -3.285, 0.012; 1.282 $\times 10^{-3}$, 1.064, -2.980, 0.005; 6.356 $\times 10^{-3}$, 1.102, -2.213, -0.031; 1.000, 1.082, -0.000, -0.010.
$C_{\text{MeHg(II)}} = 5.900 \times 10^{-4} \text{ M}^a$
1.333 $\times 10^{-4}$, -0.578, -6.961, -0.003.
$C_{\text{MeHg(II)}} = 9.432 \times 10^{-4} \text{ M}^b$
5.638 $\times 10^{-5}$, -1.212, -7.623, -0.022; 1.589 $\times 10^{-4}$, -0.699, -7.119, -0.037; 2.596 $\times 10^{-4}$, -0.437, -6.847, -0.032; 3.589 $\times 10^{-4}$, -0.282, -6.638, 0.014; 4.836 $\times 10^{-4}$, -0.061, -6.404, 0.012; 5.635 $\times 10^{-4}$, 0.087, -6.255, 0.000; 6.656 $\times 10^{-4}$, 0.250, -6.048, 0.018; 7.685 $\times 10^{-4}$, 0.474, -5.787, 0.002; 8.704 $\times 10^{-4}$, 0.734, -5.375, 0.008; 1.016 $\times 10^{-3}$, 1.013, -4.112, 0.033; 1.524 $\times 10^{-3}$, 1.018, -3.236, 0.049.

^a Distribution of $\text{CH}_3\text{Hg(II)}$ measured by a radiometric method. Initial total concentration of radioactive $\text{CH}_3^{203}\text{HgCl}$ in the organic phase was $8.2 \times 10^{-6} \text{ M}$.

^b Distribution of $\text{CH}_3\text{Hg(II)}$ measured by a spectrophotometric method.

RESULTS

The data given in Table 1 are represented as $\log D$ versus $\log C_{\text{Cl}}$ in Fig. 1. The distribution curve obtained shows clearly the following characteristics for the extraction system studied. The levelling of the curve to a limiting value of $\log D$ ($\approx +1.06$) with increasing total concentration of chloride indicates the formation of MeHg(II) species with the same chloride composition in both the aqueous and the organic phase for $C_{\text{Cl}} > 3.107 \times 10^{-4}$ M.

The results of the Letagrop analysis of the data ($Np=27$ points) are summarized in Table 2. Assuming the formation of only mononuclear

Table 2. Equilibrium constants $\log \beta_{pqr}$ for the formation of $(\text{H}^+)_p(\text{MeHg}^+)_q(\text{Cl}^-)_r$ species in the system MeHg(II) - 1 M (Na,H)(ClO₄,Cl)/*o*-xylene for various assumptions of chemical models which minimize the error-square sum $U = \sum_1^{27} (\log D_{\text{calc}} - \log D_{\text{exp}})^2$.

Model	$(\text{H}^+)_p(\text{MeHg}^+)_q(\text{Cl}^-)_r(\text{aq})$	$(\text{H}^+)_p(\text{MeHg}^+)_q(\text{Cl}^-)_r(\text{org})$	U_{min}	$\sigma(\log D)$
I		(0,1,1) 4.18, max. 4.58	13.672	0.725
II ^b	(0,1,1) 5.32, max. 5.65	(0,1,1) 6.39, max. 6.71	0.029	0.034
III	(0,1,2) 3.64, max. 4.19	(0,1,1) 4.54, max. 4.80	2.953	0.344
IV	(0,1,1) 5.32, max. 5.66; (0,1,2) $\beta=0$, max. 4.58	(0,1,1) 6.39, max. 6.72	0.029	0.034
V	(0,2,2) 14.17, max. 14.66	(0,1,1) 6.02, max. 6.29	0.443	0.133
VI	(0,1,1) 5.32, max. 5.51	(0,1,1) 6.39, max. 6.61; (0,2,2) $\beta=0$, max. 14.72	0.029	0.033
VII	(0,1,1) 5.26, max. 5.56; (0,2,2) 13.67, max. 14.19	(0,1,1) 6.37, max. 6.65	0.024	0.031
VIII	(0,1,1) $\beta=0$, max. 5.40; (0,2,2) 15.99, $\sigma(\beta)$ undetd.	(0,1,1) 5.80, max. 6.05; (0,2,2) 15.94, $\sigma(\beta)$ undetd.	0.021	0.030

^a The equilibrium constant $\beta_{pqr} = [(\text{H}^+)_p(\text{MeHg}^+)_q(\text{Cl}^-)_r]_i [(\text{H}^+)]^{-p} [(\text{MeHg}^+)]^{-q} [(\text{Cl}^-)]^{-r}$, where the lower index i indicates the phase referred to in the reaction. The limits given (=max.) correspond approximately to $\log(\beta + 3\sigma(\beta))$.

^b The "best" model assumed.

CH₃Hg(II) species in both the aqueous and organic phase and minimizing the square-sum of the error $Fel[1] = \log(D_{\text{calc}} D_{\text{exp}}^{-1})$, model II clearly gives the lowest value for the minimized error-square sum U ($U_{\text{min}} = 0.029$ and $\sigma(\log D) = 0.034$) compared with the other chemical models tried. A slight improvement of U_{min} and $\sigma(\log D)$ is obtained when additional dimeric CH₃Hg(II) species in the aqueous phase or in both phases are assumed to be formed (*cf.* models VII and VIII). However, for these latter models the standard deviations found for the formation constant β are greater than those

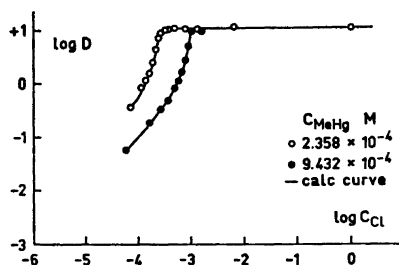


Fig. 1. Distribution of MeHg(II) between *o*-xylene and 1 M (Na,H)(ClO₄,Cl) aqueous solutions as a function of the initial total concentration of chloride, C_{Cl} M, for $-\log [H^+] = 1.699$ and different constant values of initial total concentration of MeHg(II), $C_{MeHg} = 2.358 \times 10^{-4}$ M (O) and 9.432×10^{-4} M (●). The full-drawn lines have been calculated using the equilibrium constants given in model II (Tables 2 and 3) for the formation of the $(H^+)_p(MeHg^+)_r(Cl^-)_s$ species: MeHg⁺(aq), MeHgCl(aq) and MeHgCl(org). The data are given in Table 1.

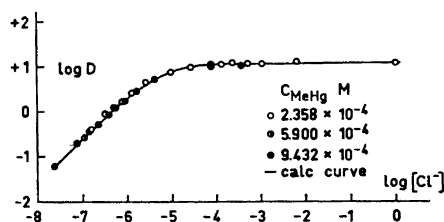


Fig. 2. The distribution of MeHg(II) in the system 1 M (Na,H)(ClO₄,Cl)/*o*-xylene as a function of the equilibrium concentration of chloride ions in the aqueous phase, $[Cl^-]$ M, for $-\log [H^+] = 1.699$ and different constant values of initial total concentration of MeHg(II), $C_{MeHg} = 2.358 \times 10^{-4}$ M (O); 5.900×10^{-4} M (●) and 9.432×10^{-4} M (●). The full-drawn line has been calculated assuming the set of MeHg(II) - Cl⁻ species and the equilibrium constants given in model II (Tables 2 and 3). The data are given in Table 1.

Table 3. Comparison of equilibrium constants $\log \beta_{pqr}$ for the formation of $(H^+)_p(MeHg^+)_q(Cl^-)_r$ species in the two-phase system MeHg(II) - 1.0 M (Na,H)(ClO₄,Cl)/*o*-xylene which minimize the error-square sum

$$U = \sum_{i=1}^{27} Fel[i]^2, \text{ where } Fel[1] = \log(D_{calc}D_{exp}^{-1}); \quad Fel[2] = (D_{exp}D_{calc}^{-1} - 1) \text{ and } Fel[3] = (D_{calc}D_{exp}^{-1} - 1).$$

Model (cf. Table 2)	$(H^+)_p(MeHg^+)_q(Cl^-)_r(aq)$	$(H^+)_p(MeHg^+)_q(Cl^-)_r(org)$	Choice of error $Fel[i]$	U_{min}	$\sigma(y)$
II	(0,1,1) 5.32, max. 5.65	(0,1,1) 6.39, max. 6.71	$Fel [1]$	0.029	0.034
	(0,1,1) 5.32 ± 0.09	(0,1,1) 6.40 ± 0.09	$Fel [2]$	0.171	0.083
	(0,1,1) 5.32 ± 0.09	(0,1,1) 6.39 ± 0.09	$Fel [3]$	0.138	0.074
IV	(0,1,1) 5.32, max. 5.66; (0,1,2) $\beta = 0$, max. 4.58	(0,1,1) 6.39, max. 6.72	$Fel [1]$	0.029	0.034
	(0,1,1) 5.33, max. 5.66; (0,1,2) $\beta = 0$, max. 4.72	(0,1,1) 6.40, max. 6.73	$Fel [2]$	0.171	0.084
	(0,1,1) 5.32, max. 5.69; (0,1,2) $\beta = 0$, max. 4.81	(0,1,1) 6.39, max. 6.75	$Fel [3]$	0.138	0.076

The equilibrium constant $\beta_{pqr} = [(H^+)_p(MeHg^+)_q(Cl^-)_r]_l [H^+]^{-p} [MeHg^+]^{-q} [Cl^-]^{-r}$, where the lower index indicates the phase referred to in the reaction. The limits given correspond approximately to $\log(\beta \pm 3\sigma(\beta))$ and if $\sigma(\beta) > 0.2\beta$, the maximum value $\log(\beta + 3\sigma(\beta))$ is given.

found for model II. Within the experimental accuracy these three models all give a satisfactory description of the available data. Since in these experiments the total concentration of MeHg(II) was always kept rather low ($C_{\text{MeHg}} < 9.432 \times 10^{-4}$ M), it seems reasonable to assume the formation of only mononuclear MeHg(II) species in both phases. This assumption is supported by the fact that the experimental points describing the extraction of MeHg(II) for different initial total concentrations of methylmercury ($C_{\text{MeHg}} = 2.358 \times 10^{-4} - 9.432 \times 10^{-4}$ M) as a function of $[\text{Cl}^-]$ (cf. Fig. 2) practically all fall on the same line. From Table 3 it can be seen that practically the same values for the formation constant of β_{pqr} are found for the set of $(\text{H}^+)_p(\text{MeHg}^+)_q(\text{Cl}^-)_r$ species in model II and model IV even if other types of error square sums are minimized, *i.e.* the square sums of the errors $FeI[2] = (D_{\text{exp}} D_{\text{calc}}^{-1} - 1)$ or $FeI[3] = (D_{\text{calc}} D_{\text{exp}}^{-1} - 1)$. This indicates that for the set of data available, the assumption made in the data analysis that equal weight may be given to the different experimental points, *i.e.* weight factor = 1, is not unreasonable.

In Fig. 3 are illustrated some data from Ref. 22, which show the distribution of MeHg(II) at $C_{\text{Cl}} = 1.27 \times 10^{-3}$ M with varying values of $[\text{H}^+]$ (pH = 1.26–2.55). The practically constant value of $\log D$ as a function of $\log [\text{H}^+]$ indicates that the hydrolysis of MeHg(II) is negligible in the pH range studied. This agrees with the results reported by Schwarzenbach and Schellenberg.^{26–28}

TEST FOR THE EXTRACTION OF METHYLMERCURIC PERCHLORATE

To test whether MeHgClO_4 species may also be extractable in *o*-xylene the following two sets of experiments were performed:

(a) The distribution of MeHg(II) was studied at constant values of $C_{\text{MeHg}} = 5.90 \times 10^{-4}$ M and $\log [\text{H}^+] = -1.699$, while varying the concentration of the perchlorate ions ($C_{\text{ClO}_4} = 2.5, 1.0$ and 0.5 M). Within this series of experiments the distribution of MeHg(II) increased with increasing $[\text{ClO}_4^-]$ (cf. Fig. 4). This effect may be interpreted as being due to the extraction of either MeHgClO_4 or of MeHgCl complex due to the presence of chloride ion impurities in the NaClO_4 medium used.

(b) Five solutions, each containing 1 M $(\text{Na,H})\text{ClO}_4$ and 1.18×10^{-4} M, 2.36×10^{-4} M, 4.72×10^{-4} M, 5.90×10^{-4} M, and 9.34×10^{-4} M $\text{CH}_3\text{Hg(II)}$ (added as non-radioactive CH_3HgOH), respectively, were equilibrated with equal volumes of *o*-xylene. The organic phases were then analyzed for $\text{CH}_3\text{Hg(II)}$ using the photometric titration method. In all cases, the organic phase was found to contain the same concentration of methylmercury(II), namely $C_{\text{MeHg(org)}} = 4.70 \times 10^{-6}$ M.

Table 4. The distribution of methylmercury(II) between NaClO_4 solutions and *o*-xylene at 25°C. $-\log [\text{H}^+] = 1.699$.

(a) $C_{\text{MeHg(II)}} = 5.895 \times 10^{-4}$ M
C_{ClO_4} M ($\log D$): 0.50 (–2.407); 1.00 (–2.095); 2.0 (–1.690).
(b) $C_{\text{ClO}_4} = 1.0$ M.
$C_{\text{MeHg(II)}} \text{ M } (\log D)$: 1.18×10^{-4} (–1.381); 2.36×10^{-4} (–1.691); ¹ 4.72×10^{-4} (–1.998); 5.90×10^{-4} (–2.095); 9.43×10^{-4} (–2.300).

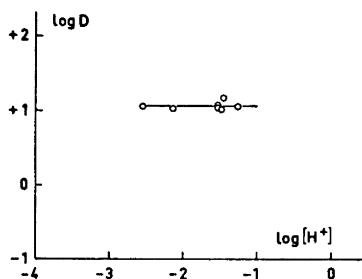


Fig. 3. The distribution of MeHg(II) in the system MeHg(II)–1 M (Na,H) (Cl,ClO₄)/*o*-xylene as a function of [H⁺] for $C_{Cl} = 1.27 \times 10^{-3}$ M and $C_{MeHg(II)} = 4.15 \times 10^{-5} - 5.349 \times 10^{-4}$ M. The full-drawn line has been calculated assuming the formation of the species MeHg⁺(aq), MeHgCl(aq) and MeHgCl(org) with equilibrium constants given in Table 2 (model II). The data are taken from Ref. 25.

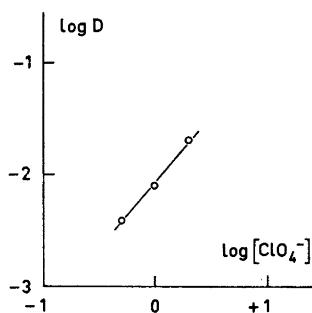


Fig. 4. The distribution of CH₃Hg(II) between (Na,H)ClO₄ solutions ($-\log [H^+] = 1.699$) and *o*-xylene as a function of [ClO₄⁻] M. The initial total concentration of MeHg(II), $C_{MeHg} = 5.895 \times 10^{-5}$ M. The data are given in Table 4.

Assuming the extraction of both MeHgCl and MeHgClO₄ in *o*-xylene we may write the following expression for the distribution ratio D :

$$\begin{aligned}
 D &= \frac{[MeHgClO_4]_{org} + [MeHgCl]_{org}}{[MeHg^+] + [MeHgCl]} = \\
 &= \frac{*K_{011,org}[ClO_4^-] + K_{011,org}[Cl^-]}{1 + K_{011,aq}[Cl^-]} = \\
 &\approx *K_{011,org}[ClO_4^-] + K_{011,org}[Cl^-] \quad (5)
 \end{aligned}$$

since for the low concentration range of $[Cl^-] < 10^{-7}$ M, $K_{011,aq}[Cl^-] \ll 1$.

From the equation for the mass balance of Cl⁻ we find the following expression for [Cl⁻]:

$$\begin{aligned}
 C_{Cl} &= [Cl^-] + [MeHgCl] + [MeHgCl]_{org} \approx [MeHgCl] + [MeHgCl]_{org} = (K_{011,aq} + \\
 &K_{011,org})[MeHg^+][Cl^-], \text{ and thus } [Cl^-] = C_{Cl}(K_{011,aq} + K_{011,org})^{-1} [MeHg^+]^{-1} \approx \\
 &C_{Cl}(K_{011,aq} + K_{011,org})^{-1} C_{MeHg(aq)}^{-1} \quad (6)
 \end{aligned}$$

Substituting (6) and the value $[ClO_4^-] = 1$ M into (5) gives the following relationship:

$$D = *K_{011,org} + K_{011,org}(K_{011,aq} + K_{011,org})^{-1} C_{Cl} C_{MeHg(aq)}^{-1} \quad (7)$$

According to (7) the plot $\log D$ versus $\log C_{MeHg(aq)}^{-1}$ will give two straight lines with limiting slopes equal 0 and +1 in the case when both MeHgClO₄ and MeHgCl species are extracted. As seen in Fig. 5 this plot gives only one straight line with a slope of +1, indicating that for the concentration of

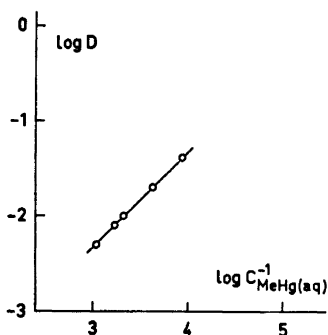


Fig. 5. The distribution of $\text{CH}_3\text{Hg}(\text{II})$ between 1.0 M $(\text{Na,H})\text{ClO}_4$ solutions ($-\log [\text{H}^+] = 1.699$) and *o*-xylene as a function of the total concentration of $\text{CH}_3\text{Hg}(\text{II})$ in the aqueous phase, $C_{\text{MeHg}(\text{aq})}$ M. The data are given in Table 4.

ClO_4^- studied ($C_{\text{ClO}_4} = 1.0$ M) no detectable extraction of MeHgClO_4 in *o*-xylene occurred. Goggin and Woodward³⁸ from Raman spectra studies found no evidence for the formation of a MeHgClO_4 complex in aqueous solution, which is not surprising in view of the present results.

Using the values found for D , $K_{011,\text{aq}} = 10^{5.32}$ M⁻¹, $K_{011,\text{org}} = 10^{6.39}$ M⁻¹, $*K_{011,\text{org}} = 0$ for the formation of MeHgClO_4 (org), and the given values of C_{MeHg} , the background concentration of Cl^- for the 1.0 M NaClO_4 medium used was calculated to be $C_{\text{Cl}} = 5.1 \times 10^{-6}$ M. The values of C_{Cl} given in Table 1 have been corrected for with this background chloride concentration.

Conclusion. We thus conclude that the simplest chemical model which gives a satisfactory description of the available data is the assumption of the formation of $\text{CH}_3\text{HgCl}(\text{aq})$ and $\text{CH}_3\text{HgCl}(\text{org})$ with the following equilibrium constants:

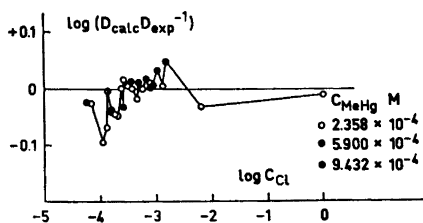
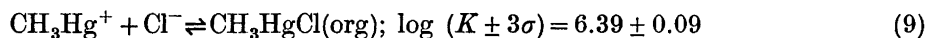
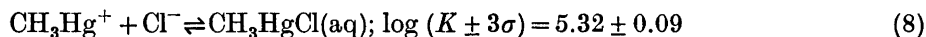


Fig. 6. The error $\log (D_{\text{calc}} D_{\text{exp}}^{-1})$ as a function of $\log C_{\text{Cl}}$ for the two-phase system $\text{MeHg}(\text{II}) - 1.0$ M $(\text{Na,H})(\text{ClO}_4, \text{Cl})/o$ -xylene, assuming the $(\text{H}^+)_p(\text{MeHg}^+)_q(\text{Cl}^-)_r$ species and equilibrium constants given in model II (Tables 2 and 3). The distribution data are given in Table 1.

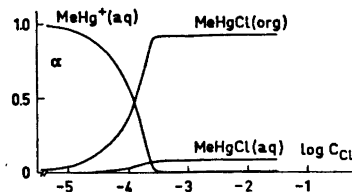


Fig. 7. The mol fraction of different $\text{MeHg}(\text{II})$ species in the two-phase system $\text{MeHg}(\text{II}) - 1.0$ M $(\text{Na,H})(\text{ClO}_4, \text{Cl})$ as a function of C_{Cl} for $C_{\text{MeHg}} = 2.36 \times 10^{-4}$ M and $-\log [\text{H}^+] = 1.699$. The curves have been calculated assuming the formation of $\text{MeHg}(\text{II}) - \text{Cl}^-$ species with the equilibrium constants given in model II (Tables 2 and 3).

and from (8) and (9) one finds for the distribution equilibrium of CH_3HgCl :

$$\text{CH}_3\text{HgCl}(\text{aq}) \rightleftharpoons \text{CH}_3\text{HgCl}(\text{org}); \log (K_D \pm 3\sigma) = 1.07 \pm 0.13.$$

In Fig. 6 the error, $\log (D_{\text{calc}} D_{\text{exp}}^{-1})$, found for the different experimental points when model II is assumed has been plotted as a function of $\log C_{\text{Cl}}$. Fig. 7 shows the mol fraction of the different $\text{MeHg}(\text{II})$ species as a function of C_{Cl} for $C_{\text{MeHg}} = 2.36 \times 10^{-4}$ M, calculated using the HALTAFALL program³⁹ and the values of the constants for model II.

The results of the present work have been used in studies of the complex formation of $\text{CH}_3\text{Hg}(\text{II})$ with other inorganic ligands,²² *e.g.* OH^- and HPO_4^{2-} . These have been carried out by studying the extraction of $\text{CH}_3\text{Hg}(\text{II})$ as a function of the concentration of the ligand in question at different constant values of chloride concentration.

DISCUSSION

The value found for the formation constant of $\text{CH}_3\text{HgCl}(\text{aq})$ is comparable with that reported by Waugh *et al.*²⁵ ($\log K = 5.38 - 6.06$, proposed mean value 5.45) in chloride medium and by Schwarzenbach and Schellenberg²⁶⁻²⁸ at ionic strength $I = 0.1$ ($\log K = 5.25$). This latter value was found by potentiometric titration of $\text{CH}_3\text{Hg}(\text{II})$ solution with HCl solution and thus the chloride and the hydrogen ion concentration of the solution varied. ($C_{\text{Cl}} = 0.1005 - 0.1019$ M and $-\log [\text{H}^+] = 9.35 - 8.17$.) Since the titration was performed for only one value of the total concentration of methylmercury ($C_{\text{MeHg}} = 2.34 \times 10^{-3}$ M) Schwarzenbach and Schellenberg's data cannot be used to test the possibility of the formation of polynuclear $\text{CH}_3\text{Hg}(\text{II})\text{-Cl}$ species. Zanella *et al.*²⁹ reported the value $K = 10^{4.90}$ M⁻¹ for the formation of MeHgCl in 0.1 M KNO_3 solution. Compared with the results found by the other authors this value is definitely too low, especially since no complex formation between CH_3Hg^+ and NO_3^- is expected.³⁸ In Table 5 we summarise

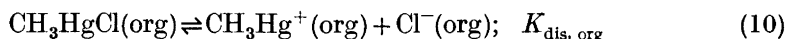
Table 5. Distribution constant K_D and equilibrium constant^a K_{011} for formation of CH_3HgCl complex in various systems.

System	$\log K_D$	$\log K_{011}$	Experimental method	Ref.
Water/toluene	1.04		Distr.	Simpson ²⁴
0-7 mM Cl^-		5.45	EMF	Waugh <i>et al.</i> ²⁵
0.1 M KCl		5.25	EMF	Schwarzenbach and Schellenberg ²⁶⁻²⁸
0.1 M KNO_3		4.90	EMF	Zanella <i>et al.</i> ²⁹
1.0 M $(\text{Na,H})\text{ClO}_4$ / <i>o</i> -xylene	1.07 ± 0.13	5.32 ± 0.09	Distr.	This work

^a The distribution constant $K_D = [\text{CH}_3\text{HgCl}]_{\text{org}}[\text{CH}_3\text{HgCl}]^{-1}$ and equilibrium constant $K_{011} = [\text{CH}_3\text{HgCl}][\text{CH}_3\text{Hg}^+]^{-1}[\text{Cl}^-]^{-1}$. The limits given correspond approximately to $\log (K \pm 3\sigma(K))$.

the results of work on the distribution and formation of CH_3HgCl species in various systems reported previously.

*Test for the dissociation of CH_3HgCl in *o*-xylene.* An interesting question which may be raised is whether or not the available data can indicate the formation of dissociated CH_3HgCl species in the organic phase. Assuming this to be the case the following additional equilibrium reaction must be taken into account:



The condition for electroneutrality in the organic phase requires that $[\text{CH}_3\text{Hg}^+]_{\text{org}} = [\text{Cl}^-]_{\text{org}}$, assuming that no other charged species are extracted.

From (9) and (10) the following relationship may be obtained:

$$[\text{CH}_3\text{Hg}^+]_{\text{org}} = (K_{\text{dis, org}} K_{011, \text{aq}} [\text{CH}_3\text{Hg}^+][\text{Cl}^-])^{\frac{1}{2}} \quad (11)$$

The distribution ratio D for $\text{CH}_3\text{Hg}(\text{II})$ may now be expressed as follows:

$$D = \frac{[\text{MeHgCl}]_{\text{org}} + [\text{MeHg}^+]_{\text{org}}}{[\text{MeHg}^+] + [\text{MeHgCl}]} = \frac{K_{011, \text{org}} [\text{MeHg}^+][\text{Cl}^-] + (K_{\text{dis, org}} K_{011, \text{aq}} [\text{MeHg}^+][\text{Cl}^-])^{\frac{1}{2}}}{K_{011, \text{aq}} [\text{MeHg}^+][\text{Cl}^-] + [\text{MeHg}^+]} \quad (12)$$

From (12) we now may derive the expression for D for the following two limiting cases when $[\text{Cl}^-]$ is varied:

$$\log D_{[\text{Cl}^-] \rightarrow 0} = \log (K_{011, \text{org}} [\text{Cl}^-] + (K_{\text{dis, org}} K_{011, \text{aq}} C_{\text{MeHg}}^{-1})^{\frac{1}{2}} [\text{Cl}^-]^{\frac{1}{2}}) \quad (13)$$

$$\log D_{[\text{Cl}^-] \rightarrow \infty} = \log (K_{011, \text{org}} K_{011, \text{aq}}^{-1} + K_{\text{dis, org}}^{\frac{1}{2}} K_{011, \text{aq}}^{-\frac{1}{2}} ([\text{MeHg}^+][\text{Cl}^-])^{-\frac{1}{2}}) \quad (14)$$

From eqn. (13) it follows that a plot of $\log D$ versus $\log [\text{Cl}^-]$ will give a straight line with a limiting slope of $+1$ in the region where undissociated CH_3HgCl predominates and the limiting slope $+\frac{1}{2}$ in case dissociated species of $\text{MeHg}(\text{II})$ predominate. Furthermore from eqn. (14) we will expect a limiting value of $-\frac{1}{2}$ with increasing value of $[\text{Cl}^-]$ for the extraction at a constant value of $\text{MeHg}(\text{II})$ concentration. The distribution data available, as seen in Fig. 2 where $\log D$ is plotted as a function of $\log [\text{Cl}^-]$ indicates only a limiting slope of $+1$ with decreasing $[\text{Cl}^-]$ and a limiting slope of 0 with increasing $[\text{Cl}^-]$. This gives evidence that under the condition of experiments the extracted MeHgCl species are predominantly in the undissociated form. This fact is not surprising considering the low value found for the dissociation constant in the aqueous solution $K_{\text{dis, aq}} = K_{011, \text{aq}}^{-1} = 10^{-5.32}$ M. The formation of dissociated MeHgCl in nonaqueous solvent thus may only be expected in rather polar solvents.

Acknowledgements. The authors are obliged for the interest shown by the late Professor Lars Gunnar Sillén during the course of the work. The financial support given by the *Statens Naturvårdsverk* (The Swedish National Environment Protection Board) and the *Swedish Natural Science Research Council* is gratefully acknowledged. Dr. Derek Lewis has kindly revised the English of the manuscript.

REFERENCES

1. Liem, D. H. *Acta Chem. Scand.* **25** (1971) 1521.
2. Ingri, N. and Sillén, L. G. *Arkiv Kemi* **23** (1964) 97.
3. Sillén, L. G. and Warnqvist, B. *Arkiv Kemi* **31** (1969) 315.
4. Sillén, L. G. and Warnqvist, B. *Arkiv Kemi* **31** (1969) 341.
5. Arnek, R., Sillén, L. G. and Wahlberg, O. *Arkiv Kemi* **31** (1969) 353.
6. a. Lindström, O. *Trans. Royal Inst. Technol. Stockholm* **1968** 185; b. Ulfvarson, U. *Svensk Kem. Tidskr.* **73** (1961) 553.
7. Torgeson, D. C. *Fungicides*, Academic, New York 1967, Vol. I.
8. Grewal, J. S. and Vir, D. *Indian Phytopathol.* **14** (1961) 213; *Chem. Abstr.* **62** (1968) 3339c.
9. Schmutterer, H. Z. *Pflanzenkrankh. Pflanzenschutz* **68** (1961) 479; *Chem. Abstr.* **56** (1962) 738b.
10. Schuhmann, G. *Nachtbl. Deut. Pflanzenschutzdienstes (Brunswick)* **15** (1963) 37; *Chem. Abstr.* **59** (1965) 10707e.
11. Jensen, S. and Jernelöv, A. *Biocidinformatio* **10** (1967) 4.
12. Jensen, S. and Jernelöv, A. *Biocidinformatio* **14** (1968) 3.
13. Wood, J. M., Kennedy, F. S. and Rosén, C. G. *Nature* **220** (1968) 173.
14. Borg, K., Wanntorp, H., Erne, K. and Hanko, E. *Viltrevy (Swedish Wildlife)* **6** (1969) 301; *J. Appl. Ecol.* **3** (1966) 171.
15. Borg, K. *Proc. VIII Nord. Veterinärmötet*, Helsingfors 1968, p. 394.
16. Westöö, G. *Acta Chem. Scand.* **20** (1966) 2131; **21** (1967) 1790.
17. Westöö, G. and Rydäl, M. *Vår Föda* **7-8** (1971) 1; *Report on Mercury in Foods*, by the Joint FAO/WHO Expert Committee on Food Additives, 1970.
18. Norén, K. and Westöö, G. *Vår Föda* **19** (1967) 13.
19. a. Boetius, J. *Medd. Komm. Danmarks Fiskeri Havundersøgelser* **3** (4) (1960) 93; *Chem. Abstr.* **61** (1967) 6311b; b. *FAO Fisheries Reports*, No. 99, Rome 1971.
20. Östlund, K. *Acta Pharmacol. Toxicol.* **27** (1969) 1.
21. a. Rydberg, J. *Svensk Kem. Tidskr.* **67** (1955) 499; b. Dyrssen, D. *Svensk Kem. Tidskr.* **68** (1956) 212; c. Liem, D. H. *Inaugural Dissertation*, Royal Institute of Technology, Stockholm 1971 (available on request).
22. Liem, D. H. and Ingman, F. *To be published; Proc. 15th Int. Conf. Coord. Chem.*, Moscow 1973.
23. Budevsky, O., Ingman, F. and Liem, D. H. *Proc. 14th Nordic Chem. Conf.*, Umeå 1971.
24. Simpson, R. B. *J. Am. Chem. Soc.* **83** (1961) 4711.
25. Waugh, T. D., Harold, F. W. and Laswick, J. A. *J. Phys. Chem.* **59** (1955) 395.
26. Schellenberg, M. *Diss. ETH*, Zürich 1963.
27. Schellenberg, M. and Schwarzenbach, G. *Proc. 7th Int. Conf. Coord. Chem.*, Stockholm 1962, p. 157.
28. Schwarzenbach, G. and Schellenberg, M. *Helv. Chim. Acta* **48** (1965) 28.
29. Zanella, P., Plazzogna, G. and Tagliavini, G. *Inorg. Chim. Acta* **2** (3) (1960) 340.
30. Barbieri, R. and Bjerrum, J. *Acta Chem. Scand.* **19** (1965) 469.
31. Rizzardi, G., Pietropaolo, R. and Barbieri, R. *Gazz Chim. Ital.* **96** (1965) 1371.
32. Eigen, M., Geier, G. and Kruse, W. *Experientia* **9** (1964) 164.
33. Sillén, L. G. *Acta Chem. Scand.* **16** (1962) 159.
34. Some laboratory methods in current use at the Department of Inorganic Chemistry, Royal Institute of Technology, Stockholm, Mimeograph 1959.
35. Irving, H. M. N. H. and Cox, J. J. *J. Chem. Soc.* **1961** 1470.
36. Irving, H. M. N. H. and Kiwan, A. M. *Anal. Chim. Acta* **45** (1969) 243.
37. Ingman, F. *Talanta* **18** (1971) 744.
38. Goggin, P. L. and Woodward, L. A. *Trans. Faraday Soc.* **58** (1962) 1495.
39. Ingri, N., Kakolowicz, W., Sillén, L. G. and Warnqvist, B. *Talanta* **14** (1967) 1261.

Received October 16, 1972.