dernier tableau montrent que presque toujours ce sont les deux isoméries, *cis-trans* et *endo-exo* qui sont responsables des différences dans les abondances relatives. Dans certains cas cependant, comme par exemple pour les ions *m/e* 103 à 70 eV et *m/e* 116 à 12 eV et 70 eV, l'isomérie *endo-exo* n'a pas d'influence; dans d'autres cas, plus rares, c'est l'isomérie *cis-trans* qui n'intervient pas, comme c'est par exemple le cas pour les ions *m/e* 99 de **IIa** et **IIb** à 70 eV et *m/e* 103 de **IIc** et **IId** à 12 eV.

Tableau 5. *Différences entre les spectres des O-isopropylidène-1,2*-thréo- *et* -érythro-*furannoses méthylés en C(4)*

m/e	12 eV				70 eV			
	IIa	**IIb**	**IIc**	**IId**	**IIa**	**IIb**	**IIc**	**IId**
	abondance relative (%)							
57	4	2	1	4	18	11	9	17
99	28	19	30	16	19	19	25	13
103	23	31	28	28	7	12	9	12
116	2	4	2	4	1	3	1	3
141	4	3	8	4	–	–	–	–
159	72	40	41	23	21	15	16	10

Ce travail a été financé en partie par le *Fonds National Suisse de la Recherche Scientifique* auquel nous exprimons notre gratitude (subside n° 2.478.71). Nous remercions également Mme *F. Kloeti* et Mlle *B. May* pour leur collaboration.

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149. Chelate Complexes with Methylmercury and Phenylmercury Cations

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(30. I. 74)

Summary. The complex formation of Hg^{2+}, CH_3Hg^+ and $C_6H_5Hg^+$ with eight substituted quinolines, α,α'-bipyridyl and 1,10-phenanthroline has been investigated in water and 75(v)% dioxane by pH and pHg methods. Hg^{2+} forms mercurated products with 8-hydroxyquinolines, if the 5- or 7-positions are unsubstituted. The formation of chelates by CH_3Hg^+ and $C_6H_5Hg^+$ is postulated.

1. Introduction. – *Schwarzenbach & Schellenberg* [1] have found similar values for the equilibrium constant of (I) and (II).

$$CH_3Hg^+ + L^{\mu-} \rightleftharpoons CH_3HgL^{(1-\mu)+} \qquad (I)$$

$$HgL^{(2-\mu)+} + L^{\mu-} \rightleftharpoons HgL_2^{(2-2\mu)+} \qquad (II)$$

Hg^{2+} shows its ability to form strong linear complexes L–Hg–L and CH_3–Hg–L. Further coordination can occur for $HgL_2^{(2-2\mu)+}$ but for $CH_3HgL^{(1-\mu)+}$ the tendency to increase the coordination number even with bidentate ligands is very small [2]. The data of [1] show for example, that in the complex of methylmercury and ethylendiamine chelation can be excluded.

In this investigation some results indicate that during the formation of the complexes between substituted 8-hydroxyquinolines and organomercury cations, chelates can be formed. For this reason ligands which favour strong chelation, such as 1,10-phenanthroline and α,α'-bipyridyl were also studied [3].

The following substances have been investigated: (1) 8-Hydroxyquinoline (HL) = HQ; (2) 8-Hydroxyquinoline-5-sulfonic acid (H_2L) = HQS; (3) 7-Iodo-8-hydroxyquinoline-5-sulfonic acid (H_2L) = IHQS; (4) 5-Chloro-7-iodo-8-hydroxyquinoline (HL) = CIHQ; (5) 4-Hydroxyquinoline-2-carboxylic acid (H_2L) = HQC; (6) 4,8-Dihydroxyquinoline-2-carboxylic acid (H_3L) = DHQC; (7) Quinoline (L) = Q; (8) Quinoline-2-carboxylic acid (HL) = QC; (9) α,α'-Bipyridyl (L) = DIP; (10) 1,10-Phenanthroline (L) = PHEN.

The symbols in parenthesis indicate the number of protons bonded to the ligand L in the neutral substance.

2. Definitions and general remarks [4]. – H = proton or hydrogen ion; pH = – log [H]; RHg^+ = organomercury ion; L = ligand; H_pL = p-protonated ligand; I = ionic strength; [], $[]_t$ = concentration resp. total concentration (molarity) of the species symbolized in the brackets; a = degree of neutralisation obtained starting from the protonated ligand, *i.e.* total concentration of the strong base added divided by the total concentration of the ligand: $a = [OH]_t/[L]_t$; K_p = protonation constant = $[H_pL]/([H_{p-1}L][H])$; χ_p = overall protonation constant = $[H_pL]/([H]^p[L])$; β_n = overall stability constant = $[ML_n]/([M][L]^n)$.

To avoid confusion with K_p only β_n is used for the stability constant. For the protonated complex RHgLH: β_1 (HL) = [RHgLH]/([RHg][HL]) and for $RHgLH_2$: β_1 (H_2L) = $[RHgLH_2]/([RHg][H_2L])$ are given.

If unnecessary the charges of the particles are omitted. The error of the constants is given as three times the standard deviation obtained from at least three different titration curves. For some systems no precipitation occurs only in 75(v)% dioxane.

3. The investigated equilibria. – a) *Protonation of the ligands and hydrolysis of RHg^+.* The protonation constants are given in Table 1. The values of log K_1 for RHgOH (R = CH_3 or C_6H_5) of Table 1 are equal to the pK of RHg^+ cations. For 75% dioxane solutions the dimerisation equilibrium

$$RHg^+ + RHgOH \overset{K_D}{\rightleftharpoons} (RHg)_2OH^+ \qquad (III)$$

(III) is significant also for millimolar solutions of the cations: $K_D = 10^{3.7 \pm 0.05}$ (R = CH_3) and $K_D = 10^{3.85 \pm 0.05}$ (R = C_6H_5). In aqueous solution only the value for R = CH_3 ($K_D = 10^{2.37}$ [1]) is known, whereas C_6H_5HgOH is too insoluble for measurements.

Table 1. *Protonation constants* K_p *of the ligands and of RHgOH at 25° and ionic strength 0.1*

Base L of	in water with KNO_3 as inert salt		in 75% dioxane and $NaClO_4$ as inert salt		
	log K_1 (± 0.05)	log K_2 (± 0.05)	log K_1 (± 0.1)	log K_2 (± 0.1)	log K_3 (± 0.1)
HQ	9.63	4.95	11.9	3.7	
HQS	8.37	3.95			
IHQS	7.10	2.50			
CIHQ			9.8	3.0	
HQC	11.0	2.65	12.7	4.1	
DHQC			13.0	9.63	4.0
Q	4.97				
QC	4.79	1.9			
DIP	4.44				
PHEN	4.92				
CH_3HgOH	4.56		5.2		
C_6H_5HgOH	4.03		4.5		

b) *Complex formation with* RHg^+. The titration curves pH *vs.* degree of neutralisation a of acidic solutions of organomercury cation and ligand are particularly simple if the ligand can only form the protonated species HL (Fig. 1).

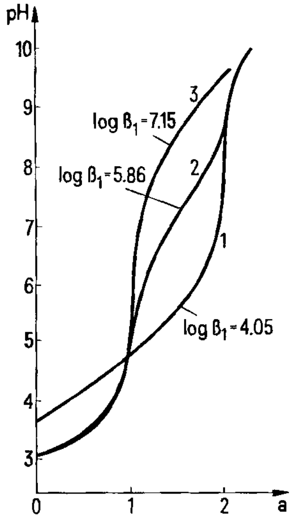

Fig. 1. *Titration of monoprotonated quinoline (1), α,α'-bipyridyl (2) and 1,10-phenanthroline (3) in presence of an equal amount of methylmercury ion*

For $0 < a < 1$ reaction (IV) takes place:

$$CH_3Hg^+ + HL^{(\mu-1)-} \longrightarrow CH_3HgL^{(\mu-1)-} + H^+ \qquad (IV)$$

After a = 1 the complex begins to decompose according to (V):

$$CH_3HgL^{(\mu-1)-} + H_2O \longrightarrow CH_3HgOH + L^{\mu-} + H^+ \qquad (V)$$

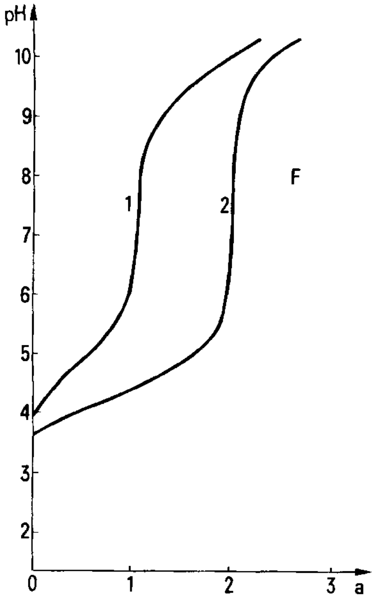

Fig. 2. *Titration of diprotonated 8-hydroxyquinoline (H_2L^+) alone (1) and in presence of an equal amount of methylmercury ion in water (2)*

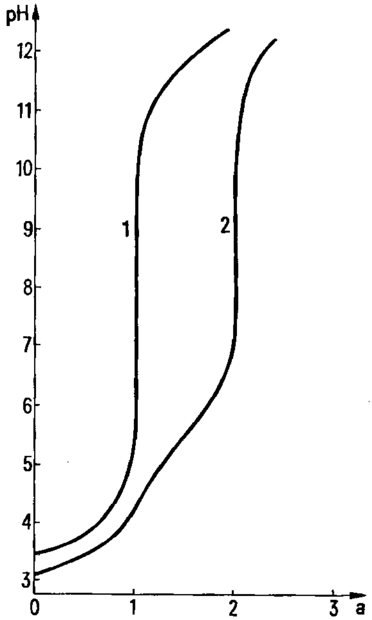

Fig. 3. *Titration of diprotonated 8-hydroxyquinoline (H_2L^+) alone (1) and in presence of an equal amount of methylmercury ion in 75% dioxane (2)*

The equilibrium constant of (V) K_V being equal to the inverse of the product K_1 (CH_3HgOH) times β_1, an increase of β_1 will produce a diminution of K_V and increase the pH of the hydrolysis (V). The curves are somewhat different for 8-hydroxyquinolines which may also form diprotonated species (Fig. 2). For $0 \leq a \leq 2$ not only $CH_3HgL^{(\mu-1)}$ but also appreciable amounts of CH_3HgOH and $HL^{(\mu-1)-}$ are formed and an exact evaluation of β_1 is no more possible. In 75% dioxane however the two buffer regions $0 \leq a \leq 1$ and $1 \leq a \leq 2$ corresponding to the reactions:

$$H_2L^{(2-\mu)+} + CH_3Hg^+ \longrightarrow CH_3HgLH^{(2-\mu)+} + H^+$$
$$CH_3HgLH^{(2-\mu)+} \longrightarrow CH_3HgL^{(1-\mu)+} + H^+$$

are well separated and an evaluation of the two stability constants is now possible. Between a = 2 and 3 (V) takes place as for the other systems. The relations for $[H]_t$, $[L]_t$ and $[RHg^+]_t$ [4] which contain $[H_pL]$ (p = 0, 1, 2), $[RHg^+]$, $[RHgL]$, $[RHgOH]$, the measured $[H^+]$ and $[OH^-]$ ($= K_W/[H^+]$) combined with the protonation constants of L and RHgOH leads to a system of three linear equations with the unknowns [L], $[RHg^+]$ and [RHgL]. From these values the constant β_1 is obtained (Table 2). The stability of the protonated complex $RHgLH^{(\mu-2)+}$ is obtained in a similar way using data for the pH region in which $L^{\mu-}$ and $RHgL^{(\mu-1)-}$ can be neglected.

c) *Miscellanea.* Additional measurements have also been performed to recognize the formation and the stability of the mercury(II) complexes using the pHg method [4] [5]. 8-Hydroxyquinolines are attacked by mercury(II) in the 5- and 7-position with formation of mercurated products [6]. It is possible to confirm this by addition of Na_2S to alkaline solutions of the mercury(II) complexes of 8-hydroxyquinoline and 8-hydroxyquinoline-5-sulfonic acid, the expected precipitate of HgS(s) does not appear [6]. For 7-iodo-8-hydroxyquinoline-5-sulfonic acid (H_2L) the stability constant for the 1:2 complex HgL_2^{2-} is $\beta_2 = 10^{21.2}$.

4-Hydroxyquinoline-2-carboxylic acid (H_2L) also forms a complex HgL_2^{2-} with $\beta_2 = 10^{22.8}$, stabilized by loss of the proton of the non coordinated OH group. In 75% dioxane 5-chloro-7-iodo-8-hydroxyquinoline and mercury(II) form an insoluble product. Quinoline-2-carboxylic acid (HL) gives weak complexes ML at 25° and I = 0.1 (KNO_3): $\log \beta_1 = 1(Ca^{2+})$; $3.50 \pm 0.05(Pb^{2+})$; $4.91 \pm 0.05(Ni^{2+})$; $4.35 \pm 0.05(Co^{2+})$ and $3.92 \pm 0.1(Cd^{2+})$.

4. Discussion. – Organomercury salts of 8-hydroxyquinoline have been introduced 20 years ago for their antifungal activity [7]. Some spectroscopic investigations with the method of continuous variation have shown, that ethylmercury and phenylmercury ions form 1:1 complexes with oxinate, which are stable between pH 6 and 10 [8]. For these complexes a chelate structure has been proposed by comparison of the spectra with those of other oxinate complexes with chelate structure [9].

The data of Table 2 show the greater stability of phenylmercury in comparison to the methylmercury complexes: the ratio of the stability constants remain for all ligands the same and is equal to 4. The decrease of the dielectric constant of aqueous dioxane compared to water, increases as expected the value of β_1. With 4-hydroxyquinoline-2-carboxyclic acid (H_2L) complex formation takes place only in dioxane; in water CH_3Hg^+ hydrolyses before the complex is formed. A simple calculation shows that with $pK(HL) = 11$, $[L]_t = [CH_3Hg]_t = 10^{-3}$, the formation of CH_3HgL can only be observed when $\beta_1 \geq 10^{8,4}$. The formation of protonated complexes with 8-oxinates in 75% dioxane can be explained by the higher basicity of the ligand L (8-phenolate group) with stabilization of RHgLH.

The chelate effect 'Chel' for some 1:1 metal 8-oxinates $ML^{(\nu-1)+}$ of Table 3 is the logarithm of the equilibrium constant of (VI), where A^{a-} and B^{b-} are the monodentate ligands [10].

$$MAB^{(\nu-a-b)+} + L^- \rightleftharpoons ML^{(\nu-1)+} + A^{a-} + B^{b-} \qquad \text{(VI)}$$

Table 2. *Stability constants of the complexes with RHg^+ ion* at 25 ± 0.1° and the ionic strength I = 0.1

Ligand L of	water, KNO_3 $\log \beta_1$		75(v)% dioxane, $NaClO_4$ (± 0.1)		
	R = CH_3	R = C_6H_5	R = CH_3		R = C_6H_5
			$\log \beta_1$ (HL)	$\log \beta_1$ (L)	$\log \beta_1$ (L)
HQ	8.8 ± 0.1[a]	↓	4.7	11.5	–
HQS	8.3 ± 0.1	8.9 ± 0.1	–	–	–
IHQS	8.1 ± 0.1	8.7 ± 0.1	–	–	–
ClHQ	↓	↓		9.2	9.8
HQC	8.4 ± 0.1	–	4.6	10.3	–
DHQC	↓	↓	6.6[b]	–	–
Q	4.05 ± 0.05	–	–	–	–
QC	5.75 ± 0.05	6.35 ± 0.05	–	–	–
DIP	5.86 ± 0.05	–	–	–	–
PHEN	7.15 ± 0.05	–	–	–	–

↓ Formation of precipitate; – not investigated.

[a] $\log \beta_1$ (HL) < 4.

[b] $\log \beta_1$ (H_2L) = 4.6 ± 0.1.

Table 3. *Values of log β_1 and of Chel*

	quinoline	phenolate	8-hydroxy-quinolinate	Chel
Cu^{2+}	2.65a)	5.4b)	12.1 [11]	~4
Pb^{2+}	≤ 0	4.5c)	9 [12]	4.5
La^{3+}	≤ 0	1.5 [13]	5.85 [14]	4.35
CH_3Hg^+	4.05^4	≤ 5d)	8.8^1	small

a) This work. b) Estimated from the stability constant of CuHL with tiron [15]. c) Estimated from the value with tiron [16]. d) In 0.1 M phenol no complexes have been detected: therefore $\beta_1 < 10^5$ 1)).

The needed stability constant of $MAB^{(\nu-a-b)+}$ is obtained on the assumption that $M^{\nu+}$ and $MA^{(\nu-a)+}$ form equally stable complexes with B^{b-}, neglecting a statistical correction of 0.1 to 0.3, for the smaller number of available coordination sites of the latter cation. One obtains $[MAB]/([M][A][B]) = \beta_1(A) \cdot \beta_1(B)$. This should be a good approximation for the metal ions, but not for CH_3Hg^+, because of its very weak tendency for a coordination number two. The enhanced stability of the complexes with bidentate ligands can be discussed using Δ, which represents the difference of log β_1 with a bidentate ligand and an appropriate monodentate ligand. For DIP compared to pyridine (PYR) one obtains: $\Delta = \log \beta_1(\mathrm{DIP}) - \log \beta_1(\mathrm{PYR})$ and the values of Table 4. For ligands of similar basicity, as positive value of Δ would imply an interaction of both donor groups. The large value of Chel with Cu^{2+} becomes negative with Hg^{2+}, since with the latter ion the preferred linear geometry cannot be realised. More drastic is the situation with CH_3Hg^+, in which Δ is smaller than for mercury(II) ion. Some gain in stability with CH_3Hg^+ can only be achieved with rigid ligands such as 1,10-phenanthroline or 8-hydroxyquinoline, in which the central ion is forced to form a chelate ring. The increase Δ, relative to quinoline, amounts to 3.1 and 4.8 respectively and shows that chelate rings are presumably formed.

Table 4. *Calculation of Chel and Δ* [3] [18] [20]

	PYR		DIP	Chel	Δ
	log β_1	log β_2	log β_1		
Cu^{2+}	2.4	4.3	8	3.6	5.5
Hg^{2+}	5.1	10	9.64	–0.4	4.5
CH_3Hg^+	4.72		5.75	?	1

5. Experimental. – All the substances used were of the highest purity available and if necessary further recrystallized. Dioxane was purified according to *Freiser* [19]. The potential of the cell (Glass electrode; sample with $I = 0.1$; Bridge with 0.1 M KNO_3 ($NaClO_4$); 0.01 M KCl (NaCl) + 0.09 M KNO_3 ($NaClO_4$); Hg_2Cl_2(s); Hg) was measured with an *Orion* digitalvoltmeter 801. Eventual potentials between sample solution/bridge were calculated with the equation of *Henderson* [5] [21] and used to correct the experimental results. The standardization of the cell was

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1) From the shift of the polarographic half-wave potential *Simpson* [17] puts log $\beta_1 = 6.5$. As mentioned by the authors '... phenolate... did not give the same value of the association constant at various ligand concentrations... The cause of the discrepancies are not clear'.

done with solutions of strong acids with $I = 0.1$ (KNO_3 or $NaClO_4$) with $pH = -\log [H^+]$. The limited concentration range for $[L]_t$ and $[RHg]_t$ ($0.5:2.10^{-3}$ M) is due to the low solubility of the substances and of complications for the dimerization equilibrium of the cations.

Support by *Ciba-Geigy* S.A., Basle, is gratefully acknowledged. I thank Mr. *P. Corbat* for experimental assistance.

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150. Stereoselective Ring Closure of Methyl-5-hexenyl-aluminium Systems[1])

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(8. V. 74)

Summary. A remarkable intramolecular stereoselectivity was observed in the ring closure reactions of 1-, 2-, 3-, and 4-methyl-5-hexenyl-aluminium systems. The possible relationship between this stereoselectivity and the relative thermodynamic stabilities of the conformers involved in the cyclization reactions, is discussed.

The persisting controversy on the mechanism of the *Ziegler-Natta* α-olefin polymerization, after two decades of extensive debating[2]), is far from being settled, and

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[1]) The kind of stereoselectivity discussed in the present paper can be considered, in our opinion, as a case of intramolecular asymmetric induction, even if it concerns racemic mixtures. However, in acceptance of the opinion of the Editorial Committee, we avoid for historical reasons the use of the term 'asymmetric induction', which is conventionally used only in the case of optically active materials.

[2]) For a full discussion of the matter see [1].