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Complexes of Mercury(II) with Thiamine

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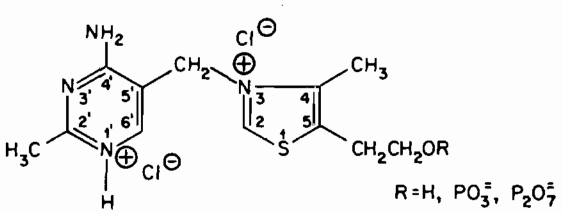
The reaction of mercuric chloride with thiamine has been explored. Two distinct salts, $[ThH]^{2+}[HgCl_3]_2^-$ *and* $[ThH]^{2+}[HgCl_4]^{2-}$ *(ThH = thiaminium = protonated thiamine), were isolated at pH 3.5. The structure of the latter compound was solved with X-ray methods and shows the presence of discrete thiaminium and tetrachloromercurate ions. At a higher pH (5.5), a third compound, not yet fully characterized, was isolated having the empirical formula* $(Hg_2Cl_5)(Th)$*. Crystal details on* $[ThH]^{2+}[HgCl_4]^{2-}\cdot H_2O$*: space group* $P2_1/c$ *(monoclinic);* $a = 17.189(17)$ Å, $b = 8.817(5)$ Å, $c = 13.971(6)$ Å, $\beta = 106.21(6)°$, $V = 2033(2)$ Å^3, $Z = 4$*. Final R factor = 7.3% for 2013 reflections.*

Introduction



I

The interaction of thiamine (*I*; vitamin B_1) and its derivatives with metals has been the subject of various investigations in recent years [1–11]. The pyrophosphate ester of thiamine (TPP), which is a coenzyme in many biological reactions, is known to act in the presence of bivalent metals like Mg(II) [12]. The role of the bivalent metals is not completely understood, but it has been proposed that the metal may form covalent bonds during the enzymatic action, either with the N(1′) of the pyrimidine moiety [13] or the pyrophosphate group of TPP [14].

^{1}H NMR studies on interactions of TPP with metals have shown that Co(II) or Ni(II) may approach the N(1′) atom of the ligand directly [6] or through a water molecule [7]. ^{31}P NMR studies, on the other hand, have shown that Mn(II) binds TPP through its pyrophosphate group [8]. However, most of the isolated metal–thiamine complexes in the solid state are ionic salts of the type $[ThH]^{2+}[MX_4]^{2-}$ [1–5] (the difficulty of thiamine and its phosphate esters to form metal complexes with direct metal–ligand bonds has been attributed to its net positive charge [12]). Exceptions, however, are found in the Pd(II) and Pt(II) complexes $M(Th)X_3$ (X = Cl, Br) [9], and the Cd(II) complex $Cd(Th)Cl_3$ [10]. These compounds contain a direct metal–N(1′) bond, as shown in the case of the Cd complex by an X-ray crystal structure determination [10]. From ^{1}H and ^{13}C NMR studies of DMSO-d_6 solutions of Hg(II) with thiamine, a direct Hg(II)–N(3′) interaction was also recently proposed [11].

Recently, we reported reactions of K_2MX_4 [M = Pt(II), Pd(II) and X = Cl, Br] with di- and tetrahydrogenated thiamine derivatives [15, 16], in which we compared the donor properties of pyrimidine, thiazoline and thiazolidine towards these metals. In order to further investigate the possibility of the formation of direct metal-thiamine bonds, we now report on complexes of mercury(II) chloride with thiamine. We show that, unlike Pt(II) and Pd(II), Hg(II) does not appear to coordinate directly with thiamine, as the crystal structure of thiaminium tetrachloromercurate monohydrate indicates.

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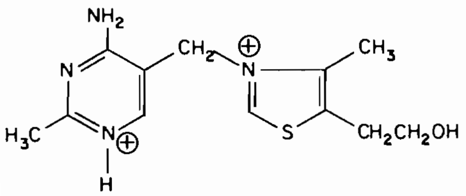
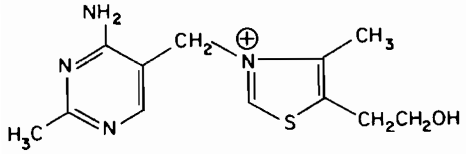
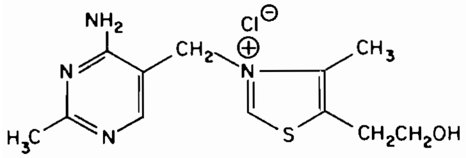


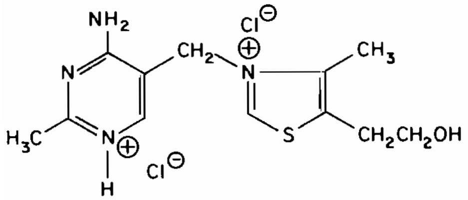
$[ThH]^{2+}$
(thiaminium cation)



$[Th]^{+}$
(thiamine cation)



ThCl*
(thiamine)



ThCl•HCl
(thiamine chloride hydrochloride)

Scheme 1. Abbreviations used in this paper.

*In some papers, this compound is called thiamine chloride, and given the abbreviation Th•HCl.

Results and Discussions

Our original aim was to prepare compounds having direct mercury–thiamine covalent bonds. Since thiamine is not stable in neutral or alkaline media [9, 12], we first chose to carry out a reaction at pH ~ 3.5 in aqueous solutions, in analogy with our earlier Pt(II) and Pd(II) experiments [9]. More acidic conditions were avoided, since at lower pH values N(1′) would be strongly protonated, thereby enhancing the possibility for the formation of unwanted metal salts of thiamine of the type $[ThH]^{2+}[MX_4]^{2-}$ [9]. Another reason for avoiding large amounts of HCl is the fact that high chloride concentrations also enhance the possibility of forming ionic species such as $[HgCl_3]^-$ and $[HgCl_4]^{2-}$ [17].

Contrary to our expectations, however, Hg(II)–thiamine ionic salts did form. Unlike Pt(II) and Pd(II), which compete favorably with protons and become covalently attached to the N(1′) position of thiamine at pH ~ 3.5 [9], Hg(II) gives two different ionic salts having 1:2 and 1:1 ligand-to-metal ratios [(*II*) and (*III*), respectively]. the 1:2 salt is presumably formed as follows:

$$HgCl_2 + Cl^- \rightarrow [HgCl_3]^- \xrightarrow{[ThH]^{2+}} [ThH]^{2+}[HgCl_3]_2^- \qquad (II)$$

After the 1:2 salt (*II*) is removed by filtration, the 1:1 salt (*III*) is obtained when the filtrate is allowed to stand for a few days in a refrigerator:

$$[HgCl_3]^- + Cl^- \rightarrow [HgCl_4]^{2-} \xrightarrow{[ThH]^{2+}} [ThH]^{2+}[HgCl_4]^{2-} \qquad (III)$$

Once again, in order to increase the chances of forming a covalent Hg–N bond, we decided to repeat the reaction at a less acidic pH (5.5), so that N(1′) would be less strongly protonated. This produced a third species, $(Hg_2Cl_5)(Th)$ (*IV*), which is still incompletely characterized. Although conductivity measurements suggest that $(Hg_2Cl_5)(Th)$ has ionic properties, infra-red data provide some evidence for the presence of covalent bonding (*vide infra*).

$$2[HgCl_3]^- + [ThH]^{2+} \rightarrow HCl + (Hg_2Cl_5)(Th) \qquad (IV)$$

The corresponding TPP complex having the formula $(Hg_2Cl_5)(TPP)$ (*V*) was also isolated at pH ~ 5.5.

The analytical data on all four compounds (*II–V*) are consistent with the assigned formulae (Table I). Conductivity measurements show that the complex $[ThH]^{2+}[HgCl_3]_2^-$ is a 1:2 electrolyte, while the other two {*i.e.*, $[ThH]^{2+}[HgCl_4]^{2-}$ and $(Hg_2Cl_5)(Th)$} behave as 1:1 electrolytes in DMF solution.

Infra-red Spectra

The IR spectra of the complexes (Table I) show strong bands in the region 2900–3500 cm^{-1}, which are assigned to $\nu(OH)$, $\nu(NH_2)$, $\nu(NH^+)$, $\nu(CH)$ (aliphatic and aromatic), or combinations of these bands. In the 1600 cm^{-1} region, thiamine chloride hydrochloride (ThCl•HCl; see Scheme I) shows two strong bands at 1658 and 1608 cm^{-1}, which were assigned to the coupling of $\delta(NH_2)$ with the $\nu(C{=}N)$ motion of the pyrimidine moiety, protonated at N(1′) [9]. Of the four isolated mercury/thiamine salts in this study, two, namely $[ThH]^{2+}[HgCl_3]_2^-$ (*II*) and $[ThH]^{2+}[HgCl_4]^{2-}$ (*III*), show bands at

TABLE I. Analytical, Conductivity and IR Data of the Complexes.

Compound	C (%)		H (%)		N (%)		Cl (%)		S (%)	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$[ThH]^{2+}[HgCl_3]_2^- \cdot 2H_2O$ (*II*)	15.72	15.64	2.40	2.38	6.11	6.03	23.25	22.89	3.49	3.79
$[ThH]^{2+}[HgCl_4]^{2-} \cdot H_2O$ (*III*)	22.97	22.39	3.19	3.28	8.93	9.21	22.66	22.39	–	–
$(Hg_2Cl_5)(Th)$ (*IV*)	17.07	17.18	2.01	2.38	6.63	6.73	21.01	20.77	3.80	4.12
$(Hg_2Cl_5)(TPP)$ (*V*)	14.56	14.72	1.98	1.95	5.67	5.64	17.98	18.05	3.24	3.13

Compound	Molar Conductance (in DMF) (cm^{-1} ohm^{-1} M^{-1})	M. Pt. (°C)	IR Bands (KBr Pellet)		
			$\nu(NH)$, $\nu(OH)$, $\nu(CH)$ (cm^{-1})	$\delta(NH_2)$, $\nu(C{=}N)$ (cm^{-1})	$\nu(HgX)$ (cm^{-1})
$[ThH]^{2+}[HgCl_3]_2 \cdot 2H_2O$ (*II*)	128.6	95–98	3482, 3380, 3230, 3050, 2970	1660	272
$[ThH]^{2+}[HgCl_4]^{2-} \cdot H_2O$ (*III*)	87.2	155–160	3520, 3370, 3320, 3205, 3090, 2942, 2915	1680, 1657, 1602	288
$(Hg_2Cl_5)(Th)$ (*IV*)	78.0	125[a]	3480, 3380, 3230, 2900	1642	345, 283 180
$(Hg_2Cl_5)(TPP)$ (*V*)	–	–	3420, 2960, 2920	1640, 1600	–

[a] With decomposition.

1660 cm^{-1} and at 1680 and 1657 cm^{-1} respectively, which are assigned, in analogy with ThCl·HCl [9], to indicate that thiamine is protonated at N(1′) in both compounds. The other two compounds show these bands at lower frequencies: 1642 cm^{-1} for $(Hg_2Cl_5)(Th)$ and 1640 and 1600 cm^{-1} for $(Hg_2Cl_5)(TPP)$, in accordance with a non-protonated N(1′). Lastly, the fact that the $\delta(NH_2)$ band did not shift to lower frequencies in the complexes (it is 1640 cm^{-1} in the free ligand [9]) indicates that the NH_2 group is not involved in bonding to the metal atom.

The ν(Hg–X) stretching frequency is a function of the Hg–X distance and decreases as the distance increases [18]. It appears at 286 cm^{-1} in K_2HgCl_4 [19]. Similarly, it can be assigned to a band at 288 cm^{-1} in the complex $[ThH]^{2+}[HgCl_4]^{2-}$ (*III*) which we have subsequently shown to contain tetrahedral $[HgCl_4]^{2-}$ species. In the complex $[ThH]^{2+}[HgCl_3]_2^-$, it can be assigned to a medium-intensity broad band at 272 cm^{-1} in analogy with $[(CH_3)_3S]^+[HgCl_3]^-$, which has the ν(Hg–Cl) band at 263 cm^{-1} [20].

Finally, $(Hg_2Cl_5)(Th)$ may be similar to the compound (Hg_2Cl_5)(N-benzylpiperazine), whose crystal structure has been solved [18]. The latter complex contains a direct Hg–N bond and non-equivalent Hg–Cl bonds, which give rise to bands at 363, 280 and 178 cm^{-1}, assigned to Hg–Cl stretching modes [18]. In the complex $(Hg_2Cl_5)(Th)$, we observe bands at 345, 283 and 180 cm^{-1}, which may be assigned analogously, if a structure similar to (Hg_2Cl_5)(N-benzylpiperazine) is assumed.

NMR Spectra

The ^1H NMR chemical shifts of the ligand and the complexes are included in Table II. If there were a direct Hg(II)–thiamine bond, down-field chemical shifts of the protons near the bonding site would be expected. This, for example, has been the case for the Pt(II) and Pd(II) complexes of thiamine, where complexation at N(1′) of the pyrimidine ring causes a down-field shift of 0.50–0.65 ppm of the nearby C(6′)–H protons [9]. This does not appear to be the case in the complexes of the present study. The free ligand (thiamine) was reported to give a C(6′)–H signal at 8.47 ppm in DMSO–d_6 [11], while $[ThH]^{2+}[HgCl_3]_2^-$ and $[ThH]^{2+}[HgCl_4]^{2-}$ show the C(6′)–H resonance at 8.18 and 8.34 ppm respectively (Table II). These shifts are not sufficiently large to indicate

TABLE II. ^{1}H NMR Data of the Complexes (in ppm).

Compound	C(2)–H	C(6′)–H	N(4′α)–H$_2$	C(3,5′)–H$_2$	C(5β)–H$_2$	C(5α)–H$_2$	C(4α)–H$_3$	C(2′α)–H$_3$	Solvent
thiamine (in D_2O)	9.62	8.00	–	5.53	3.79	3.10	2.56	2.50	D_2O
thiamine[a] (in DMSO-d$_6$)	10.08	8.47	9.33	5.70	3.10	3.10	2.60	2.57	DMSO-d$_6$
$[ThH]^{2+}[HgCl_3]_2^-$ (*II*)	9.65	8.18	8.85	5.40	3.69	3.07	2.62	2.62	DMSO-d$_6$
$[ThH]^{2+}[HgCl_4]^{2-}$ (*III*)	9.86	8.34	8.99	5.49	3.63	2.98	2.52	2.52	DMSO-d$_6$
$(Hg_2Cl_5)(Th)$[b] (*IV*)	9.60	8.00	–	5.55	3.85	3.20	2.65	2.56	0.1 N DCl

[a] For thiamine, the DMSO-d$_6$ values are taken from reference 11. [b] In 0.1 *N* DCl solution, it is possible that $(Hg_2Cl_5)(Th)$ may in fact be $[ThH]^{2+}[HgCl_3]_2^-$ (see text).

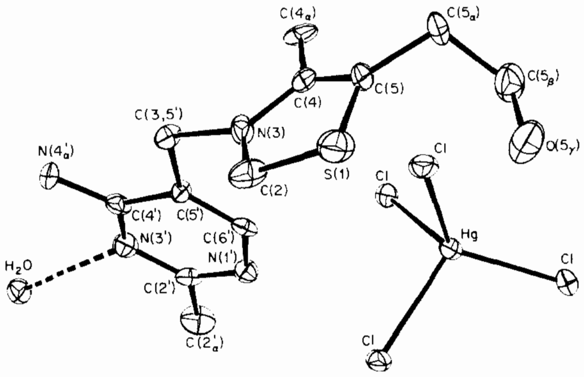


Fig. 1. Molecular structure of $[ThH]^{2+}[HgCl_4]^{2-}$.

direct metal–ligand bonding in either case. (To quote another example, when a direct metal–ligand bond is formed between Hg(II) and guanosine, downfield shifts of 0.6–0.7 ppm in the ^{1}H NMR spectrum and 2.0–3.0 ppm in the ^{13}C NMR spectrum are expected [21, 22]).

Other workers, however, in studying the Hg(II)/thiamine system, have reached the opposite conclusion. In a study of a mercury–thiamine complex whose ^{1}H NMR spectrum is very similar to the one we find for $[ThH]^{2+}[HgCl_4]^{2-}$, Gary and Adeyemo [11] concluded, using ^{1}H NMR, ^{13}C NMR and IR evidence, that a direct Hg–N(3′) bond existed in their compound. It is possible that the observed chemical shift of the 4′–NH$_2$ group reported by those investigators [11] may be a result of hydrogen-bonding interactions rather than metal coordination through N(3′). In our crystal structure analysis of $[ThH]^{2+}[HgCl_4]^{2-}$ we do find that N(3′) engages in H-bonding, and it is reasonable to suppose that this H-bonding could persist in solution.

The last compound, having the formula (Hg_2Cl_5)-(Th), might be expected (from IR evidence) to have a direct metal–ligand bond, like the analogous (Hg_2X_5)(N-bzpipzH) [18]. However, this cannot be proved unambiguously from ^{1}H NMR studies, due to the insolubility of $(Hg_2Cl_5)(Th)$ in suitable solvents. Its ^{1}H NMR spectrum, which was recorded in 0.1 *N* DCl, is virtually identical to that $[ThH]^{2+}[HgCl_3]_2^-$ in D_2O (see Table II). Thus, $(Hg_2Cl_5)(Th)$ may be decomposing in HCl solution, according to the equation below. Such a process would break the original metal–ligand bond, if present.

$$(Hg_2Cl_5)(Th) + HCl \rightarrow [ThH]^{2+}[HgCl_3]_2^-$$

Structure of $[ThH]^{2+}[HgCl_4]^{2-}$

The crystal structure of the complex $[ThH]^{2+}$-$[HgCl_4]^{2-}$ (*III*), which has been solved with X-ray diffraction, proves unambiguously the absence of any direct Hg–ligand interaction in this salt. The

TABLE III. Distances in [Thiaminium]$^{2+}$ [HgCl$_4$]$^{2-}$·H$_2$O (in Angstroms).

(A) Bond Distances	
Hg–Cl(1)	2.395(6)
Hg–Cl(2)	2.477(6)
Hg–Cl(3)	2.514(6)
Hg–Cl(4)	2.553(5)
S(1)–C(2)	1.633(23)
S(1)–C(5)	1.770(21)
C(2)–N(3)	1.425(28)
N(3)–C(4)	1.354(26)
C(4)–C(5)	1.331(31)
C(4)–C(4_α)	1.521(31)
C(5)–C(5_α)	1.475(30)
C(5_α)–C(5_β)	1.533(34)
C(5_β)–O(5_γ)	1.343(32)
C(3,5')–C(5')	1.558(25)
C(5')–C(6')	1.323(26)
C(5')–C(4')	1.408(26)
C(6')–N(1')	1.358(24)
N(1')–C(2')	1.310(26)
C(2')–N(3')	1.353(26)
C(2')–C($2'_\alpha$)	1.510(32)
N(3')–C(4')	1.351(25)
C(4')–N($4'_\alpha$)	1.347(24)

(B) Hydrogen-Bonding Interactions	
N($4'_\alpha$)···H$_2$O	2.892(21)
N(3')···H$_2$O	2.936(22)
O(5_γ)···S(1)	3.121(21)
Cl(4)···N(1')	3.140(20)

molecular structure (Fig. 1) shows the presence of discrete [ThH]$^{2+}$ and [HgCl$_4$]$^{2-}$ ions, the latter having the expected tetrahedral geometry. Distances and angles in the molecule are listed in Tables III and IV. The molecular parameters of the thiaminium cation are normal, and fall within expected ranges for thiamine derivatives [4, 5, 10, 23]. Probable H-bonding interactions are found between the protonated N(1') atom of the pyrimidinium ring and one of the chlorines [Cl(4)] of the [HgCl$_4$]$^{2-}$ anion; and between the sulfur atom of the thiazolium ring [S(1)] and the terminal hydroxyl group of the CH$_2$-CH$_2$OH chain [O(5_γ)]. Additionally, hydrogen-bonding interactions link the water molecule to the N(3') atom and the H$_2$N($4'_\alpha$) group of adjacent thiaminium cations (Fig. 2). The torsion angles, ϕ_P = N(3)–C(3,5')–C(5')–C(4') = 179° and ϕ_T = C(5')–C(3,5')–N(3)–C(2) = –103°, correspond to the rare S conformation of the thiamine molecule and are in qualitative agreement with the values ϕ_P = –167° and ϕ_T = 93° found in 2-(α-hydroxybenzyl)thiamine chloride·HCl·3H$_2$O [24].

TABLE IV. Angles in [Thiaminium]$^{2+}$[HgCl$_4$]$^{2-}$·H$_2$O (in degrees).

Cl(1)–Hg–Cl(2)	120.1(2)
Cl(1)–Hg–Cl(3)	117.0(2)
Cl(1)–Hg–Cl(4)	109.4(2)
Cl(2)–Hg–Cl(3)	102.5(2)
Cl(2)–Hg–Cl(4)	102.8(2)
Cl(3)–Hg–Cl(4)	103.0(2)
C(2)–S(1)–C(5)	94.1(11)
N(3)–C(2)–S(1)	109.6(16)
C(4)–N(3)–C(2)	112.8(18)
C(4)–N(3)–C(3,5')	127.7(17)
C(2)–N(3)–C(3,5')	118.8(16)
C(5)–C(4)–N(3)	116.0(20)
N(3)–C(4)–C(4α)	117.3(19)
C(5)–C(4)–C(4α)	126.7(19)
C(4)–C(5)–C(5_α)	135.0(20)
C(4)–C(5)–S(1)	107.5(15)
C(5_α)–C(5)–S(1)	117.4(15)
C(5)–C(5_α)–C(5_β)	110.0(19)
C(5_α)–C(5_β)–O(5_γ)	110.4(20)
N(3)–C(3,5')–C(5')	110.3(15)
C(3,5')–C(5')–C(6')	126.6(16)
C(3,5')–C(5')–C(4')	114.7(15)
C(6')–C(5')–C(4')	118.6(17)
C(5')–C(6')–N(1')	121.0(17)
C(6')–N(1')–C(2')	119.6(16)
N(1')–C(2')–C($2'_\alpha$)	116.5(18)
N(1)–C(2')–N(3')	122.7(18)
N(3')–C(2')–C($2'_\alpha$)	120.8(19)
C(2')–N(3')–C(4')	118.1(17)
N(3')–C(4')–N($4'_\alpha$)	117.2(17)
C(5')–C(4')–N($4'_\alpha$)	123.2(17)
N(3')–C(4')–C(5')	119.7(17)
C(4')–N($4'_\alpha$)···H$_2$O	131.2(12)
N(3')···H$_2$O···N($4'_\alpha$)	92.6(6)

Experimental

Materials

The mercury halides were purchased from Merck Chemical Co., and thiamine and TPP from Fluka A.G.

Methods

IR spectra were recorded on a Perkin-Elmer 283 spectrophotometer as KBr pellets. Far-IR spectra were recorded on Beckman IR-11 and IR-12 spectrophotometers. ^{1}H NMR spectra were recorded on a Varian T60 spectrometer, using TMS or DSS as internal references. Conductivity measurements were performed on a Metrohm E-365 B conductoscope, Metrohm Ltd, Herisau, Switzerland. The melting points were determined in a Büchi melting point apparatus and are uncorrected. X-ray diffraction data were collected on a Nicolet (Syntex) P2$_1$ automated diffractometer.

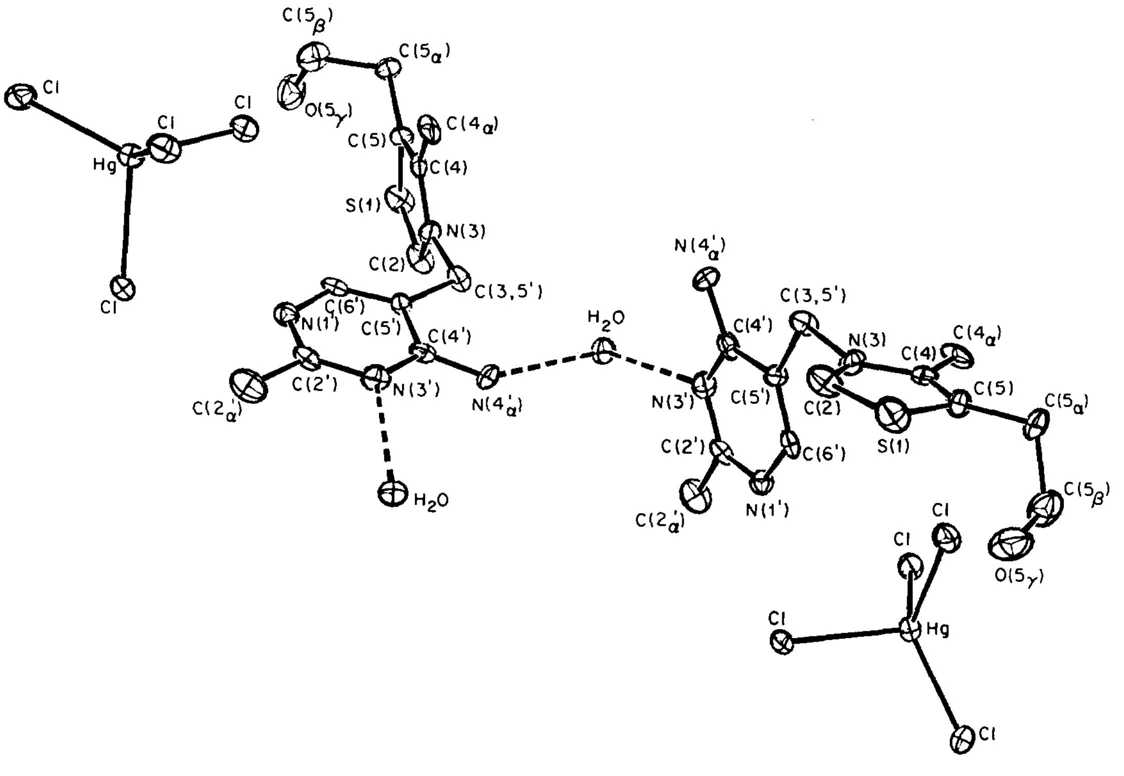


Fig. 2. A plot of two adjacent units of $[ThH]^{2+}[HgCl_4]^{2-}$, showing the water molecule forming a hydrogen-bonding bridge from the N(3') atom of one thiaminium cation to the $H_2N(4'_\alpha)$ group of another.

Elemental analyses were performed in the Laboratories of the National Hellenic Research Foundation in Athens, and the Alfred Bernhardt Microanalytisches Laboratorium, West Germany.

Preparation of the Complexes

$[ThH]^{2+}[HgCl_3]_2^{-}\cdot 2H_2O$

0.8 g (2.4 mmol) of thiamine chloride hydrochloride (ThCl•HCl) was dissolved in 25 ml of water and the pH adjusted to 3.5. A solution of $HgCl_2$ [0.64 g (2.4 mmol) in 15 ml of water] was then added to the solution of thiamine under stirring and the final pH adjusted to 3.5. The mixture was stirred for one day and filtered from any undissolved material. It was then evaporated to one-third of its initial volume and left in the refrigerator for 2–3 days to crystallize. The crystals formed were filtered and washed with acetone and ether and dried at 0 °C under vacuum. Yield 60%.

$[ThH]^{2+}[HgCl_4]^{2-}\cdot H_2O$

After the filtration of the complex $[ThH]^{2+}$-$[HgCl_3]_2^{-}$, the filtrate was kept in the refrigerator. After a few days, crystals of the complex are formed, filtered and washed with acetone and ether. Yield 30%.

$(Hg_2Cl_5)(Th)\cdot 2H_2O$

1.24 g (3.7 mmol) of thiamine were dissolved in 30 ml of water. A solution containing 1.0 g (3.7 mmol) $HgCl_2$ was then added under stirring to the first, and the pH of the mixture was then adjusted to ~5.5 using 0.1 *N* NaOH solution. A precipitate was immediately formed, filtered and washed with alcohol and ether. It was then dried under vacuum. Yield 75%. (Hg_2Cl_5)(TPP) was prepared similarly.

Structure Determination

$[Thiaminium]^{2+}[HgCl_4]^{2-}\cdot H_2O$ crystallizes in the monoclinic space group $P2_1/c$, with $a = 17.189(17)$, $b = 8.817(5)$, $c = 13.971(6)$ Å, $\beta = 106.21(6)°$, $V = 2033(2)$ Å^3, $Z = 4$. One quadrant of data was collected with MoKα radiation up to a 2θ maximum of 45°. Data processing (which included Lorentz, polarization and absorption corrections) reduced the 2745 independent reflections to a total of 2013 having $I > 3\sigma(I)$. The structure was solved by standard Patterson and heavy atom methods and refined to a conventional R factor of 7.3%.

Acknowledgements

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