Reactions of THTH (Tetrahydrothiamine) with HgX_2 (X = Cl, Br, I)

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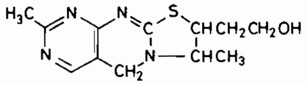
Recently, we reported the reactions of K_2MX_4 (M = Pt(II) and Pd(II) and X = Cl, Br) with di- and tetrahydrothiamine [1, 2], in order to compare the donor properties of pyrimidine, thiazoline and thiazolidine, towards these metals. In the present report, we present preliminary results on the reactions of tetrahydrothiamine (THTH) with mercury halides. The reactions were carried out in mixtures of ethanol:chloroform = 1:1 solutions and lead to the formation of 1:1 and 1:2 metal complexes, as follows:

$$HgX_2 + THTH \longrightarrow [HgX(LH)]^+X^- \qquad (1)$$

and

$$2HgX_2 + THTH \longrightarrow [HgX(LH)]^+HgX_3^- \qquad (2)$$

where X = Cl, Br, I and L a possible rearrangement product of THTH, of the formula,



The 1:1 complex could not be isolated in the case of iodine. In these complexes the mercury atom is believed to be in the (I) oxidation state, as will be evident in the ensuing discussion.

The analytical results agree with the assigned formulae (Table I). The conductivity of the complexes in DMF solutions, indicates that they are all 1:1 electrolytes (Table I).

In the ir spectra of the complexes, the highest band in the region 4000–2000 cm^{-1} occurs at 3220 cm^{-1} for all the complexes, except $[HgI(LH)]^+HtI_3^-$, where it is found at 3335 cm^{-1} (Table I). This band cannot be assigned to a ν_{NH} vibration of an NH_2

TABLE I. Analytical Conductivity and I.r. Data of the Complexes.

Compound		C%	H%	N%	X%	S%	Λ_M (in DMF) (cm^{-1} ohm^{-1} M^{-1})	M.P.[a] (°C)	IR bands (KBr pellet)	
									ν_{NH}, ν_{OH}, ν_{CH} (cm^{-1})	δ_{NH_2}, $\nu_{C=N}$ (cm^{-1})
$[HgCl(LH)]^+Cl^-$ [b]	Calc	26.8	3.5	10.4	13.2	6.0	35.7	155–160	3400–3220	1660, 1603
	Found	27.3	3.9	10.7	13.0	6.3			3080, 2920	1580, 1540
$[HgBr(LH)]^+Br^-$	Calc	23.0	2.9	8.9	–	5.1	41.5	155	3400, 3220	1658, 1608
	Found	22.4	2.7	8.7		5.2			3080, 2985 2920	1578, 1540
$[HgCl(LH)]^+[HgCl_3]^-$	Calc	17.8	2.2	6.9	–	–	50.2	145	3460, 3225	1660, 1603
	Found	17.8	2.3	6.7					3080, 2978 2930	1560, 1545
$[HgBr(LH)]^+[HgBr]^-$	Calc	14.6	1.8	5.7	32.4	3.2	47.3	155	3510, 3220	1656, 1609
	Found	14.7	2.0	5.8	32.4	3.2			3080, 2920	1600, 1580 1543
$[HgI(LH)]^+[HgI_3]^-$	Calc	12.3	1.5	4.8	43.2	2.7	57.2	163–165	3335, 3060	1651, 1615
	Found	12.4	1.7	5.1	43.3	2.4			2970, 2880	1570, 1543

[a] Decomposition points. [b] The ligand L is the rearranged product of tetrahydrothiamine (see text).

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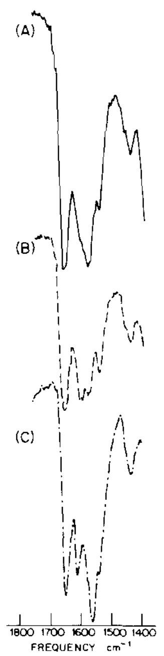


Fig. 1. Ir spectra in 1600 cm^{-1} region of the complexes, (A) $[HgCl(LH)]^+[HgCl_3]^-$, (B) $[HgBr(LH)]^+[HgBr_3]^-$ and (C) $[HgI(LH)]^+[HgI_3]^-$.

group [1, 2], due to its low value. It is rather assigned to an NH^+ vibration of the pyrimidine ring [1–3]. The absence of massive absorptions near 2500 cm^{-1} indicates the absence of strong hydrogen bonding in these compounds [3]. The ν_{CH} aromatic and aliphatic vibrations occur at 3080 cm^{-1} and near 2900 cm^{-1} for all the compounds.

In the 1600 cm^{-1} region, there is a strong band at 1650–1660 cm^{-1} for all the complexes, which is assigned to a skeletal stretching frequency of the pyrimidine ring [1–3] and decreases in the order $Cl^- < Br^- < I^-$ (Table I) (Fig. 1). This band disappears in a sample of the compound which was previously neutralized to pH 6.5, in water. A second medium intensity band appears at 1615 cm^{-1} in the complex $[HgI(LH)]^+HgI_3^-$ and can be assigned to the $\nu_{C=N}$ vibration, near the sulfur atom. This band appears as a shoulder in the other chloro- and bromo- compounds, at lower frequencies (Table I). The shift to lower frequencies is a function of the halogen and follows the order Cl > Br > I. With the assumption of a Hg–S bond, the decrease in the $\nu_{C=N}$ vibration follows the electronegativity of the halogens, since its double bond character should decrease in the same order. This band becomes strong and broad in the complex without HCl, coinciding with the $\nu_{C=N}$ motions (*i.e.*, the skeletal stretching frequency), of the non protonated pyrimidine ring.

In the ^{1}H nmr of the complex $[HgCl(LH)]^+HgCl_3^-$, there is a signal at 9.55 ppm (Fig. 2), which integrates for one proton and disappears upon the addition of a few drops of D_2O. This is assigned to an NH^+ group, of the protonated pyrimidine ring. The signal at 8.05 ppm in DMSO-d_6 (Fig. 2B) is assigned to the C_6'-H near the protonation site and it was found at 7.78 ppm (Fig. 2A), in the non protonated ligand tetrahydrothiamine [1, 2]. The other observed signals can be assigned according to THTH [1, 2]. (See the Scheme for the numbering of THTH): 1.05 ppm for the 4-CH_3 group, 2.53 ppm (coupled with the DMSO band) for the 2'-CH_3, 1.68 ppm for the C_5–CH_2. Finally, the multiplet at 3.53 ppm is assigned to the $-CH_2-O-$ group with the C_4–H, the 3.03 ppm to the C_5–H and the C_5'–CH_2 at 3.92 ppm.

The characteristic feature of the spectrum is the absence of any signal assignable to the amino protons of THTH. Only the three methyl protons of the 2'-CH_3 group occur under the DMSO signal and it is highly unlikely to have any other proton resonating at 2.5 ppm [2].

Finally, the ^{13}C nmr spectrum of the complex $[HgCl(LH)]^+HgCl_3^-$, in DMSO-d_6, again shows clearly that the pyrimidine moiety is protonated, most probably at N_1'. Thus, the signal at 138.2 ppm is assigned to the C_6' near the protonation site. It was found at

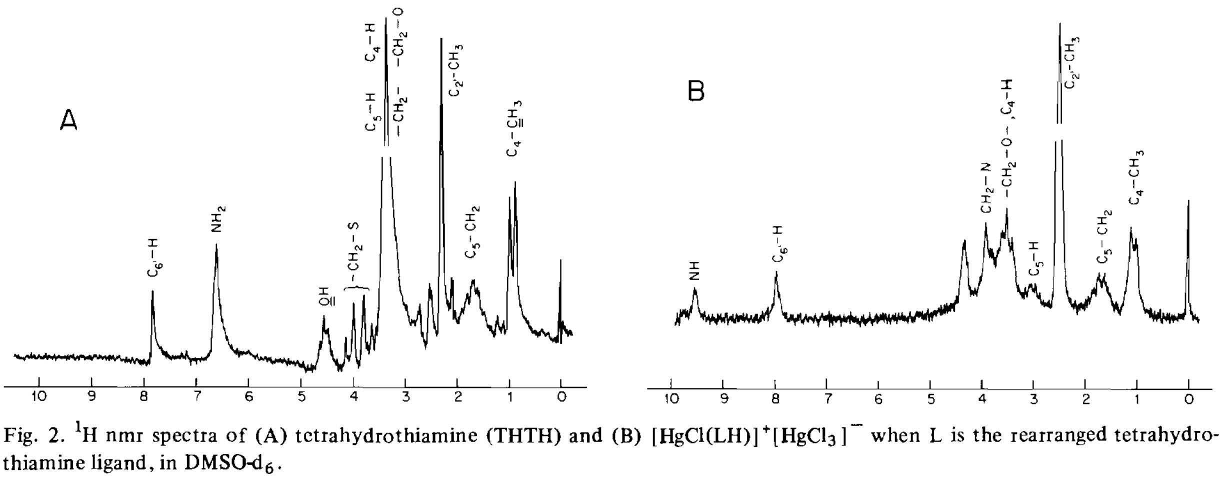
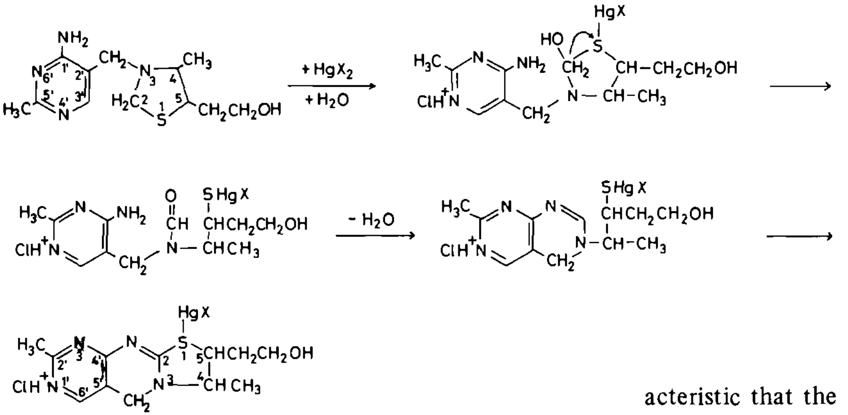


Fig. 2. ^{1}H nmr spectra of (A) tetrahydrothiamine (THTH) and (B) $[HgCl(LH)]^+[HgCl_3]^-$ when L is the rearranged tetrahydrothiamine ligand, in DMSO-d_6.

154.3 ppm in the non protonated ligand THTH and it was shifted upfield by about 10 ppm in THTH• HCl [2]. The other aromatic carbon resonances appear at 159.5 ppm for C'_4, 159.7 ppm for C'_2 and 107.5 ppm for C'_5. The remaining observed bands are at 44.2 for C_5 and 55.1 for C_4 appearing as doublets in the off resonance spectra. The 5-CH_2 occurs at 45.6 ppm, 5'-CH_2 (bridge) at 58.4 ppm and the OCH_2 at 58.7 ppm. They are all shown as triplets in the off resonance. Finally, the 4-CH_3 and 2'-CH_3 carbons appear at 10.1 and 20.6 ppm, respectively.

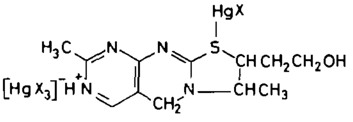


Scheme 1.

With all the above experimental data and the fact that thiazoline and thiazolidine derivatives are known to hydrolyze in alkaline solution or in the presence of metal ions, like Hg(II) and Ag(I) [4–6], it is reasonable to assume that Hg(II) attacks first the sulfur atom of the thiazolidine moiety in the present system. This is followed by the production of HX and protonation of the N'_1 of pyrimidine. On the other hand, thiamine itself is known to produce thiochrome at pH $\geqslant$ 11, upon oxidation [7]. A structure similar to that of thiochrome most probably forms in the present case, and this implies a reduction of Hg(II) to Hg(I), as is shown in Scheme 1.

A redox titration with Ce^{+4} showed the presence of Hg(I) in the complexes.

When an excess of HgX_2 was used, the bulky anion $[HgX_3]^-$ was produced, resulting in the precipitation of the complexes. Similarly, the 1:2 ligand to metal complexes may correspond to the following structure.



In fact the 1:1 and 1:2 complexes have similar spectra and the presence of the second metal does not appear to affect the ligand further. It is characteristic that the 1:1 complex of HgI_2 could not be isolated, even when an excess of the ligand was used. It seems that the less easily solvated I^- ions may more easily produce the less soluble $[HgI_3]^-$ species, thus resulting in the precipitation of the 1:2 complexes.

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