Binary and Ternary Interactions of Mercury(II) with Seven Pyrimidines and Ethylenediaminetetraacetic Acid

J. Chem. Research (S), 1997, 280–281
J. Chem. Research (M), 1997, 1917–1928

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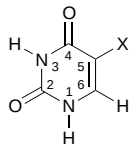
The introduction of an electronegative substituent at the C-5 position of a uracil ring leads to a decrease in the ring's complexation constants; the formation of mixed ligand complexes of mercury(II) takes place above pH 6 and gives [Hg(edta)(thymine)]-type species, the mixed coordination of which leads to enhanced stability.

It is well known that the metal complexes of pyrimidines and their nucleotides play a dominant role in many biochemical systems.[6,8] The present paper reports a study of the stability of mercury(II) complexes in aqueous solution with seven pyrimidines of biological interest. Our contribution tries to quantify the influence on the stability constants of the C-5 substitution on the one hand and the stability of the ternary complexes formed with thymine or uracil in the presence of ethylenediaminetetraacetic acid (edta) on the other hand.

Protometric studies on the pyrimidine analogues studied in the present work were performed according to the procedure previously described[9,10] by the usual approach of varying the ratio of total ligand to total metal concentration. Measurements were carried out at 25 °C and at a constant ionic strength of 0.1 M ($NaNO_3$), under a dynamic nitrogen atmosphere in order to avoid oxidation of the ligands.



I X = H **V** X = Cl
II X = OH **VI** X = Br
III X = Me **VIII** X = I
IV X = F

The acidity constants of the seven ligands had been determined previously[12] and the acid enhancement effect of the uracil halogenation was demonstrated. The complexation between a metal ion M and the two ligands L and L′ can be described by the general equilibrium:

$$pM + qH + rLsL' \rightleftarrows M_pH_qL_rL'_s$$

$$\beta_{pqrs} = \frac{[M_pH_qL_rL'_s]}{[M]^p \times [H]^q \times [L]^r \times [L']^s}$$

For simplicity, the charges of the species are omitted. The equilibrium constants β_{pqrs} were calculated by a method using the average number of H^+ ions bound per mole of ligand, $\bar{q}$, and a least-square refinement between the calculated average number of H^+ ions bound per mole of ligand, $\bar{q}_{cal}$, and the

Table 1 Logarithms of the protonation and stability constants of the mercury(II)–pyrimidine systems (T = 25 °C and I = 0.1 M $NaNO_3$)

Ligand (L)	*pqrs*	log β_{pqrs}	Species	pH
	0 1 1 0	9.17 ± 0.01[12]		
uracil (**I**)	1 −1 1 0	2.17 ± 0.04	$[HgH_{-1}(L)]$	6 < pH < 12
	1 −1 2 0	6.05 ± 0.08	$[HgH_{-1}(L)_2]^-$	8 < pH < 12
	0 1 1 0	8.12 ± 0.01[12]		
isobarbituric acid (**II**)	1 −1 1 0	1.98 ± 0.04	$[HgH_{-1}(L)]$	6 < pH < 12
	1 −1 2 0	5.88 ± 0.08	$[HgH_{-1}(L)_2]^-$	8 < pH < 12
	0 1 1 0	9.56 ± 0.01[12]		
thymine (**III**)	1 −1 1 0	2.25 ± 0.04	$[HgH_{-1}(L)]$	6 < pH < 12
	1 −1 2 0	6.32 ± 0.08	$[HgH_{-1}(L)_2]^-$	8 < pH < 12
	0 1 1 0	7.86 ± 0.01[12]		
5-fluorouracil (**IV**)	1 −1 1 0	1.49 ± 0.03	$[HgH_{-1}(L)]$	5 < pH < 12
	1 −1 2 0	4.92 ± 0.07	$[HgH_{-1}(L)_2]^-$	7 < pH < 12
	0 1 1 0	7.80 ± 0.01[12]		
5-chlorouracil (**V**)	1 −1 1 0	1.42 ± 0.03	$[HgH_{-1}(L)]$	5 < pH < 12
	1 −1 2 0	4.81 ± 0.06	$[HgH_{-1}(L)_2]^-$	7 < pH < 12
	0 1 1 0	7.83 ± 0.01[12]		
5-bromouracil (**VI**)	1 −1 1 0	1.55 ± 0.03	$[HgH_{-1}(L)]$	5 < pH < 12
	1 −1 2 0	5.01 ± 0.08	$[HgH_{-1}(L)_2]^-$	7 < pH < 12
	0 1 1 0	7.92 ± 0.01[12]		
5-iodouracil (**VII**)	1 −1 1 0	1.62 ± 0.04	$[HgH_{-1}(L)]$	5 < pH < 12
	1 −1 2 0	5.12 ± 0.08	$[HgH_{-1}(L)_2]^-$	7 < pH < 12

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Table 2 Protonation equilibrium and formation constants of the mercury(II)–pyrimidine and mercury(II)–edta–pyrimidine bases systems (T = 25 °C and I = 0.1 M $NaNO_3$)

System	*pqrs*	log β_{pqrs} (lit.)	pH
H_4edta	0 4 0 1	21.33 ± 0.08 (21.38 ± 0.18[13])	< 3,5
H_3edta	0 3 0 1	19.03 ± 0.04 (19.18 ± 0.05[13])	1 < pH < 5
H_2edta	0 2 0 1	16.29 ± 0.02 (16.41 ± 0.02[13])	2 < pH < 9
Hedta	0 1 0 1	10.07 ± 0.02 (10.25 ± 0.02[13])	> 8
$[HgH_{-1}]^+$	1 −1 0 0	−3.3 ± 0.2 (−3.1 ± 0.1[14])	
$[Hg(Hedta)]^-$	1 1 0 1	23.8 ± 0.2 (24.3 ± 0.1[13])	< 5
$[Hg(edta)]^{2-}$	1 0 0 1	20.4 ± 0.2 (21.6 ± 0.1[13])	> 2
$[Hg(edta)(thymine)]^{3-}$	1 0 1 1	25.6 ± 0.3	> 6
$[Hg(edta)(uracil)]^{3-}$	1 0 1 1	24.9 ± 0.3	> 6

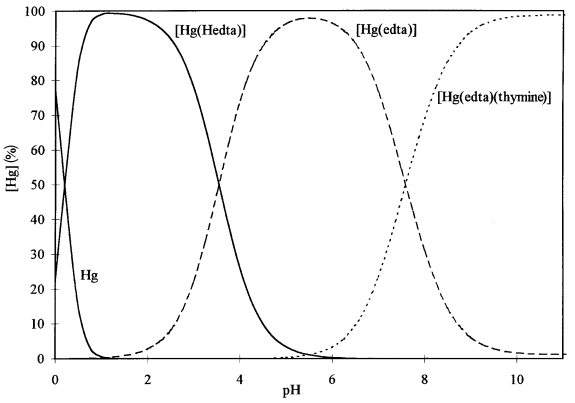

Fig. 4 Distribution curves for the mercury(II)–edta–thymine system: $C_M = 5 \times 10^{-5}$ M and $C_L = 10^{-4}$ M. The relative concentration of each species is given as a percentage of the total mercury(II) concentration C_M.

experimental average number of H^+ ions bound per mole of ligand, $\bar{q}_{exp}$.

Mercury(II)*–pyrimidine systems*. These systems were studied with low metal concentrations between 1.42 and 2.5×10^{-5} M with corresponding ligand to metal ratios of 4–7:1. In the acidic medium, the equilibrium constants (Table 1) were calculated by considering the presence of the $[HgH_{-1}]$ species (≡HgOH). From Table 1, it can be seen that the substitution of the uracil hydrogen atom in the C-5 position by a more electronegative substituent causes a decrease in the complex stability.

Mercury(II)*–edta system*. In order to ensure the homogeneity of our study, we determined the protonation equilibrium constants of edta and complexation equilibrium constants of the mercury(II)–edta system under the same conditions of temperature, ionic strength and concentration of ligand. The results, in good agreement with the bibliographic data, are summarised in Table 2. As expected, edta has a greater complexing ability than pyrimidine bases.

Mercury(II)*–edta–pyrimidine base systems*. The ternary systems showed the presence of the [Hg(edta)(thymine)] and [Hg(edta)(uracil)] ternary complexes (Fig. 4) in addition to [Hg(Hedta)] and [Hg(edta)] binary complexes. $[HgH_{-1}(uracil)]$, $[HgH_{-1}(uracil)_2]$, $[HgH_{-1}(thymine)]$ and $[HgH_{-1}(thymine)_2]$ were not present in the ternary systems.

By comparison of the stability constants of the ternary and binary systems, it is demonstrated that ternary complexation is responsible for the stabilisation of the mixed complexes.

Full text in French

Techniques used: Protometry

References: 15

Figures: 4

Received, 10th January 1997; Accepted, 30th April 1997
Paper F/7/03085A

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