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(1,3-Dimethyluracil-5-yl)mercury(II): Preparative, Structural, and NMR Spectroscopic Studies of an Analog of CH_3Hg^{II}

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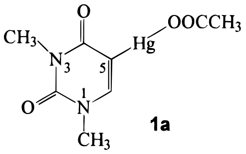
The solution behavior of (1,3-DimeU-*C5*)Hg(CH_3COO) (**1a**) (1,3-DimeU = 1,3-dimethyluracil) with regard to acetate replacement by anions X (Cl^-, Br^-, I^-, NO_3^-, SCN^-, CN^-) and by other model nucleobases (1-methylcytosine, 1-MeC, 1-methyluracil, 1-MeUH, 1-methylthymine, 1-MeTH, 9-ethylguanine, 9-EtGH, and 2-thiouracil, 2-ThioUH) has been studied, primarily by means of ^1H and ^{199}Hg NMR spectroscopy. Moreover, the bis(1,3-DimeU-*C5*) complex of Hg has been crystallized and studied by X-ray crystallography. **7a**: orthorhombic system, space group *Fdd*2, $a = 14.185(4)$ Å, $b = 25.275(7)$ Å, $c = 7.924(2)$ Å, $V = 2840(2)$ Å^3, $Z = 8$. The acetato ligand of **1a** is readily displaced by anions X, frequently followed by disproportionation reactions leading to HgX_2 and **7a**. The donor atom X *trans* to C(5) has an effect on ^3J coupling between ^{199}Hg and H(6) of the 1,3-DimeU ligand according to $NO_3^- > OAc^- > Cl^- \sim Br^- > I^- > SCN^- > CN^- >$ 1,3-DimeU-*C5* with extremes being 222 ($X = NO_3^-$) and 107 Hz (**7a**). In the presence of excess metal ions (Ag^+, Hg^{2+}), **1a** forms hetero- and homonuclear derivatives with the second metal ion probably sitting at O(4). The mixed nucleobase complexes have the second base bound to Hg via N(3) (1-MeU (**2a**), 1-MeT (**3a**)), N(4) (1-MeC$^-$ (**4a**), 1-MeC (**4b**)), N(1) (9-EtG (**5a**)), N(7) (9-EtGH (**5b**)), and N(1), N(7) (9-EtG (**5c**)), as well as S(2) (2-ThioU (**6a**)). With the exception of the 9-ethylguanine complexes **5b** and **5c**, all the other complexes are inert on the ^1H time scale. In several cases, e.g. **2a**, **3a**, **4a**, and **5a**, formation of dinuclear Hg or heteronuclear Ag and Pt derivatives has been established by multinuclear NMR spectroscopy.

Introduction

The chemistry of methylmercury(II), CH_3Hg^{II}, has been intensively studied, with regard both to its properties as a soft acid[2] and to its toxicity,[3] and related to it this, to its reactivity toward biomolecules.[4] Among the latter, reactions with nucleobases[5] and mechanisms of detoxification[6] have received particular attention.

We have recently prepared and structurally characterized (acetato) (1,3-dimethyluracil-5-yl)mercury(II), ($C_6H_7N_2O_2$)Hg(CH_3CO_2) (**1a**).[7] The compound was obtained upon direct reaction of the model nucleobase 1,3-dimethyluracil with Hg(CH_3CO_2)$_2$. An analogous complex with *trans*-(CH_3NH_2)$_2$Pt^{II}-Cl instead of the Hg(CH_3CO_2) entity was likewise obtained. Our findings confirmed previous reports on C(5) mercuration reactions of uracil and cytosine nucleobases.[8,9]



1a

The objective of the present was 2-fold. First, we wanted to establish basic NMR criteria (^1H, ^{199}Hg) on relevant solution species derived from (1,3-DimeU-*C5*)Hg^{II}. Second, by replacing the acetate anion by nucleobases we wanted to synthesize bis(nucleobase)complexes which were different from previously studied "metal-modified base pairs"[10] in that they also contained metal−carbon bonds instead of metal−nitrogen bonds only.

Experimental Section

Preparation of Starting Compounds. The starting materials (OAc)Hg(1,3-DimeU-*C5*)[7] (**1a**), *trans*-(NH_3)$_2$PdCl$_2$,[11] *trans*-(NH_2CH_3)$_2$-PtCl$_2$,[12] 1-methylcytosine (1-MeC),[13] 1-methyluracil (1-MeUH),[14] and 1-methylthymine (1-MeTH)[13] were prepared as previously described.

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1,3-Dimethyluracil (1,3-DimeU) was purchased from Sigma, 9-ethylguanine (9-EtGH) from Chemogen, and 2-thiouracil (2-ThioUH) and Hg(OAc)$_2$ from Fluka.[15]

Preparation of the (1,3-dimethyluracil-*C5*)Hg^{II}X Compounds. (1,3-dimethyluracil-*C5*)Hg^{II}X (X = Cl(**1b**), Br (**1c**), I (**1d**), SCN (**1e**)) were prepared by reaction of **1a** (0.2 mmol) with either NaCl, KBr, KI or KSCN (0.2 mmol) in water (6 mL). The solid obtained was filtered off after precipitation, washed with water and dried at 40 °C overnight. Anal. Calcd (found) for $C_6H_7N_2O_2HgCl$ (**1b**): C, 19.2 (19.1); H, 1.9 (1.8); N, 7.6 (7.5). Yields 62%. Anal. Calcd (found) for $C_6H_7N_2O_2HgBr$ (**1c**): C, 17.2 (17.2); H, 1.7 (1.7); N, 6.7 (6.7). Yield: 53%. Anal. Calcd (found) for $C_6H_7N_2O_2HgI$ (**1d**): C, 15.4 (15.8); H, 1.5 (1.7); N, 6.0 (6.2). Yield: 86%. Anal. Calcd (found) for $C_7H_7N_3O_2HgS$ (**1e**): C, 21.1 (21.4); H, 1.8 (2.1); N, 10.6 (10.6). Yield: 61%.

Identification of (1,3-DimeU-*C5*)Hg^{II}X, Homo- and Heterobimetallic Compounds Derived from (1,3-DimeU-*C5*)Hg(OAc) by NMR Spectroscopy. Compounds (1,3-DimeU-*C5*)HgX, (X = NO$_3$(**1f**), CN (**1g**)), (1,3-DimeU-*C5,O4*)[Hg(OAc)]$_2$ (**1h**), and (1,3-DimeU-*C5,O4*)Hg(OAc)$_2$AgNO$_3$ (**1i**) were identified by ^{1}H and ^{199}Hg NMR spectroscopy only, yet were not isolated (cf. Results and Discussion).

Preparation of the (1,3-Dimethyluracil-*C5*)Hg^{II} Nucleobase Compounds. (1,3-DimeU-*C5*)Hg(1-MeU-*N3*) (**2a**) was obtained by reacting a solution of **1a** (0.2 mmol in 10 mL of water) with 1-MeUH (0.2 mmol in 10 mL of water) for 24 h at 22 °C in a stoppered flask (pH 6.5). The white solid was filtered off, washed with water, and dried at 40 °C overnight. Anal. Calcd (found) for $C_{11}H_{12}N_4O_4Hg$: C, 28.4 (28.6); H, 2.6 (2.6); N, 12.1 (12.3). Yield: 83%.

(1,3-DimeU-*C5*)Hg(1-MeT-*N3*)·3H$_2$O (**3a**) was obtained by the method used for preparation of compound **2a** (pH 5.0). Anal. Calcd (found) for $C_{12}H_{21}N_4O_7Hg$: C, 27.0 (27.3); H, 3.9 (3.1); N, 10.5 (10.6). Yield: 81%.

(1,3-DimeU-*C5*)Hg(1-MeC$^-$-*N4*)·2H$_2$O (**4a**) was obtained by mixing a solution of **1a** (0.15 mmol in 8 mL of water) with a solution of 1-MeC (0.15 mmol in 3 mL of water) and adjusting the pH of the solution to ca. 12 with KOH (1M). The solid formed was filtered off, washed with water, and dried at 40 °C overnight. Anal. Calcd (found) for $C_{11}H_{18}N_5O_5Hg$: C, 26.5 (25.5); H, 3.6 (2.9); N, 14.0 (13.6). Yield: 57%.

[(1,3-DimeU-*C5*)Hg(1-MeC-*N4*)](OAc)·3H$_2$O (**4b**) was obtained by the method used for preparation of compound **2a** at pH 5.5. Anal. Calcd (found) for $C_{13}H_{23}N_5O_8Hg$: C, 27.0 (27.1); H, 4.0 (3.3); N, 12.1 (12.1). Yield: 25%.

(1,3-DimeU-*C5*)Hg(9-EtG-*N1*)·3H$_2$O (**5a**) was obtained by the method used for preparation of compound **2a** at pH 5.5. Anal. Calcd (found) for $C_{13}H_{21}N_7O_6Hg$: C, 27.0 (27.3); H, 3.7 (3.4); N, 17.1 (17.2). Yield: 58%.

[(1,3-DimeU-*C5*)Hg(9-EtGH-*N7*)](NO$_3$)·2H$_2$O (**5b**) was prepared by reaction of a solution of **1a** (0.2 mmol in 10 mL of water) at pH ca. 2.7 (by addition of HNO$_3$, 1M) with 9-EtGH (0.2 mmol). After 1h at 22 °C the white solid formed was filtered off, washed with water and dried at 40 °C overnight. Anal. Calcd (found) for $C_{13}H_{20}N_8O_7Hg$: C, 26.0 (25.9); H, 3.3 (3.0); N, 18.6 (18.6). Yield: 34%; IR: 1341cm^{-1} (NO$_3^-$).

(1,3-DimeU-*C5*)Hg(2-ThioU) (**6a**) was obtained at pH 4.0 by the method used for preparation of compound **2a**. Anal. Calcd (found) for $C_9H_{10}N_4O_3SHg$: C, 23.8 (23.6); H, 2.2 (2.5); N, 12.3 (11.1). Yield: 88%.

Table 1. List of Compounds and Numbering Scheme

compd	no.
(1,3-DimeU-*C5*)HgOAc	**1a**
(1,3-DimeU-*C5*)HgCl	**1b**
(1,3-DimeU-*C5*)HgBr	**1c**
(1,3-DimeU-*C5*)HgI	**1d**
(1,3-DimeU-*C5*)HgSCN	**1e**
(1,3-DimeU-*C5*)HgNO$_3$	**1f**[a]
(1,3-DimeU-*C5*)HgCN	**1g**[a]
(1,3-DimeU-*C5,O4*)[Hg(OAc)]$_2$	**1h**[a]
(1,3-DimeU-*C5,O4*)Hg(OAc)$_2$AgNO$_3$	**1i**[a]
(1,3-DimeU-*C5*)Hg(1-MeU-*N3*)	**2a**
[(1,3-DimeU-*C5*)Hg(1-MeU-*N3,O4*)]$_2$AgNO$_3$	**2b**
[(1,3-DimeU-*C5*)Hg(1-MeU-*N3,O4*)Hg(OAc)]$^+$	**2c**[a]
(1,3-DimeU-*C5*)Hg(1-MeT-*N3*)·3H$_2$O	**3a**
[(1,3-DimeU-*C5*)Hg(1-MeT-*N3,O4*)Hg(OAc)]$^+$	**3b**[a]
[(1,3-DimeU-*C5*)Hg(1-MeT-*N3,O4*)Ag]$^+$	**3c**[a]
(1,3-DimeU-*C5*)Hg(1-MeC$^-$-*N4*)·2H$_2$O	**4a**
[(1,3-DimeU-*C5*)Hg(1-MeC-*N4*)](OAc)·3H$_2$O	**4b**
[(1,3-DimeU-*C5*)Hg(1-MeC$^-$-*N3,N4*)Hg(OAc)]$^+$	**4c**[a]
(1,3-DimeU-*C5*)Hg(9-EtG-*N1*)·3H$_2$O	**5a**
[(1,3-DimeU-*C5*)Hg(9-EtGH-*N7*)]NO$_3$·2H$_2$O	**5b**
{[(1,3-DimeU-*C5*)Hg]$_2$(9-EtG-*N1,N7*)}$^{3+}$	**5c**[a]
[(1,3-DimeU-*C5*)Hg(9-EtG-*N1,N7*)Pt(NH$_2$CH$_3$)$_2$Cl]$^+$	**5d**[a]
(1,3-DimeU-*C5*)Hg(2-ThioU)	**6a**
(2-ThioU)$_2$Hg	**6b**
(1,3-DimeU-*C5*)$_2$Hg	**7a**

[a] Not isolated.

Hg(2-ThioU)$_2$ (**6b**) was obtained by reaction of a solution of Hg(OAc)$_2$ (0.72 mmol in 20 mL of water) with 2-ThioUH (1.44 mmol). The suspension (pH 3.0) was stirred for 1 d at 22 °C, and the solid formed was filtered off, washed with water, and dried at 40 °C overnight. Anal. Calcd (found) for $C_8H_6N_4O_2S_2Hg$: C, 21.0 (21.1); H, 1.3 (1.3); N, 12.3 (12.3). Yield: 91%.

Hg(1,3-DimeU-*C5*)$_2$ (**7a**) was prepared as follows: To a solution of **1a** (0.2 mmol in 10 mL of water) was added an equimolar amount of KCN, and the mixture was stirred for 30 min. The white solid formed was filtered off, washed with water, and dried at 40 °C overnight. Anal. Calcd (found) for $C_{12}H_{14}N_4O_4Hg$: C, 30.1 (30.0); H, 3.0 (3.4); N, 11.7 (11.1). Yield: 72%.

Identification of Several Homo- and Heterobimetallic Compounds from (1,3-DimeU-*C5*)Hg^{II}(nucleobase) by NMR Spectroscopy. A number of mixed nucleobase complexes with several metals were prepared on an NMR scale only and identified by ^{1}H, ^{199}Hg, and ^{195}Pt NMR when possible, yet were not isolated, e.g. [(1,3-DimeU-*C5*)Hg(1-MeU-*N3,O4*)]$_2$AgNO$_3$ (**2b**), [(1,3-DimeU-*C5*)Hg(1-MeU-*N3,O4*)Hg(OAc)]$^+$, **2c**; [(1,3-DimeU-*C5*)Hg(1-MeT-*N3,O4*)Hg(OAc)]$^+$ (**3b**), [(1,3-DimeU-*C5*)Hg(1-MeT-*N3,O4*)Ag]$^+$ (**3c**), [(1,3-DimeU-*C5*)Hg(1-MeC$^-$-*N3,N4*)Hg(OAc)]$^+$ (**4c**), {[(1,3-DimeU-*C5*)Hg]$_2$(9-EtG-*N1,N7*)}$^{3+}$ (**5c**), and [(1,3-DimeU-*C5*)Hg(9-EtG-*N1,N7*)Pt(NH$_2$CH$_3$)$_2$Cl]$^+$ (**5d**).

Table 1 provides a list of compounds prepared.

Instrumentation. IR spectra (KBr pellets) were recorded on a Perkin-Elmer 580B spectrometer. ^{1}H, ^{195}Pt, ^{199}Hg NMR spectra (200.13, 42.95, 35.79 MHz) were recorded on a Bruker AC200 instrument. Chemical shifts are given in ppm and are referenced to internal TSP (D$_2$O), the residual undeuterated DMSO signal (DMSO-*d*$_6$; 2.50 ppm from TMS) (^{1}H), external Na$_2$PtCl$_6$ (^{195}Pt), and external HgCl$_2$ in D$_2$O (^{199}Hg; to recalculate data referred to HgMe$_2$ add +1228 ppm), respectively. $J(^{199}\text{Hg}-^1\text{H})$ values in complexes were determined with help of nondecoupled ^{199}Hg NMR spectra and/or taken directly from ^{1}H NMR spectra. p*K*$_a$ values (in D$_2$O) were determined by plotting ^{1}H NMR chemical shifts vs the uncorrected pH (pH*).

X-ray Crystal Structure Determinations. X-ray measurement of compound **7a** were carried out on a Rigaku AFC6S diffractometer using Mo Kα radiation (λ = 0.710 69 Å). Calculations were performed on a VAX station 3500 computer by using the TEXSAN 5.0 software[16] and in the later stages on a Silicon Graphics Personal Iris 4D35 computer with the teXsan 1.7 package.[17]

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(15) Abbreviations used: 1,3-DimeU = free base; 1,3-DimeU-*C5* = 1,3-dimethyluracil deprotonated at C(5) and metalated at this site; 1-MeUH = free base; 1-MeU-*N3* = monoanion coordinated to metal via N(3); 1-MeC = free base; 1-MeC$^-$-*N4* = monoanion coordinated to metal via N(4); 1-MeC-*N4* = rare iminooxo tautomer form of 1-MeC with metal at N(4) and proton at N(3); 1-MeC-*N3* = base coordinated to metal via N(3); 1-MeTH = free base; 1-MeT-*N3* = monoanion coordinated to metal via N(3); 9-EtGH = free base; 9-EtG-*N1* = monoanion coordinated to metal via N(1); 9-EtGH-*N7* = neutral base coordinated to metal via N(7); 2-ThioUH = free base; 2-ThioU = monoanion. In mixed nucleobase complexes, protons and metal binding sites of the second nucleobase are primed.

(16) TEXSAN 5.0: Single Crystal Structure Analysis Software. Molecular Structure Corp., The Woodlands, TX, 1989.

Table 2. Crystalographic Data for **7a**

formula	$C_{12}H_{14}N_4O_4Hg$	Z	8
fw	476.86	μ(Mo Kα), cm^{-1}	108.51
cryst dimens, mm	0.18 × 0.16 × 0.34	temp, °C	−100
cryst syst	orthorhombic	$2\theta_{max}$, deg	50
space group	*Fdd*2 (No. 43)	tot. no. of reflcns measd	727
a, Å	14.185(4)	no. of indep reflcns ((I) > 3σ(I))	563
b, Å	25.275(7)	no. of variables	95
c, Å	7.924(2)	final *R*; R_w	0.020; 0.025
V, Å^3	2840(2)	goodness of fit	0.83
d(calcd), g cm^{-3}	2.24	max peak in final diff map, e/Å^3	0.56

Table 3. Positional Parameters and *B*(eq)

atom	*x*	*y*	*z*	*B*(eq)
Hg	0	0	0.1100	1.45(2)
O(2)	−0.1101(5)	0.2333(2)	0.122(1)	1.8(3)
O(4)	0.0950(5)	0.1040(3)	−0.038(1)	2.3(4)
N(1)	−0.1410(6)	0.1488(3)	0.198(1)	1.6(3)
N(3)	−0.0094(6)	0.1686(4)	0.039(1)	2.1(4)
C(2)	0.0884(6)	0.1865(4)	0.119(2)	1.5(4)
C(4)	0.0213(8)	0.1161(4)	0.031(1)	2.0(5)
C(5)	−0.0415(7)	0.0779(4)	0.108(2)	1.7(4)
C(6)	−0.1199(7)	0.0963(5)	0.189(2)	2.2(5)
C(7)	−0.222(1)	0.1666(5)	0.299(2)	2.5(5)
C(8)	0.049(7)	0.2091(4)	−0.048(2)	3.1(5)

Relevant crystallographic data are listed in Table 2. Unit cell dimensions were determined by applying the setting angles of 25 high-angle reflections. Three standard reflections were monitored during the data collection showing ψ scans of several reflections with the transmission factor ranging 0.82−1.00.

The structure was solved by direct methods in SIR88.[18] Full-matrix least-squares refinement was carried out with anisotropic thermal displacement parameters for all the non-hydrogen atoms. The final difference Fourier map was featureless.

Crystallographic data and experimental details are reported in Table 2 and final positional and thermal parameters are listed in Table 3.

Results and Discussion

Substitution of Acetate. The acetate ligand in **1a** undergoes replacement by direct reaction with halogen and pseudohalogen anions such as Cl^-, Br^-, I^-, SCN^-, CN^-, and (**1b**−**1e** and **1g**) to give the corresponding compounds. These reactions proceed quickly (less than 1 min) and it is necessary to isolate the compounds obtained as soon as possible to avoid subsequent disproportionation reactions, which are observed with time:

$$2(1,3\text{-DimeU-}C5)\text{HgX} \rightarrow (1,3\text{-DimeU-}C5)_2\text{Hg} + \text{HgX}_2$$

Disproportionation leading to the formation of **7a** is observed when an excess of anion is added to replace the acetate from **1a** (in H_2O) or when complexes **1b**−**1e** and **1g** are dissolved in DMSO-d_6. In **1b**−**1d** formation of the corresponding mercury(II) salt, HgX_2 (X = Cl, Br, I), is also verified by ^{199}Hg NMR spectroscopy. Thus, while a 5%- disproportionation of **1b** takes place in DMSO-d_6, **1c** and **1d** undergo a 50% and quantitative disproportionation, respectively, under analogous conditions. These findings are consistent with a previous report.[9]

Substitution of acetate by nitrate is not possible upon direct reaction of **1a** with KNO_3. Rather, formation of a new trinuclear mercury(II) compound, $\{[(1,3\text{-DimeU-}C5)\text{Hg}]_3\text{O}\}(\text{NO}_3)$, is observed in which unusual Hg−Hg interactions are seen in the X-ray study.[19]

Table 4. Selected ^{1}H- and ^{199}Hg-NMR Parameters of **1a**−**1g** and **7a**

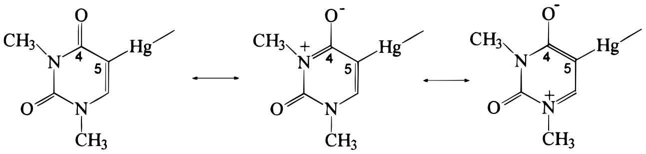
	^3J, Hz		δ(H(6))		δ(^{199}Hg)	
compd	*a*	*b*	*a*	*b*	*a*	*b*
1a	192	200	7.33	7.42	−2625	−2668
1b	183	187	7.38	7.44	−2352	−2412
1c	185	187	7.40	7.45	−2476	−2534
1d	174		7.42			
1e	143	177	7.39	7.46	−2245	
1f		222		7.40		−2640
1g		153		7.39		
7a	107		7.48		−1999	

[a] DMSO-d_6. [b] D_2O.

IR spectra of complexes **1b**−**1e** and **7a** show characteristic changes as compared to free 1,3-DimeU due to the C(5)-coordination of mercury. The two intense bands in 1,3-DimeU spectrum at 1705 and ca. 1650 cm^{-1} corresponding to υ(C=O) and υ(C=C)[20] are shifted to lower energies, appearing between 1700−1679 and 1642−1630 cm^{-1}. These changes are primarily a consequence of nucleobase deprotonation.[7] In the range 820−750 cm^{-1} the two strong bands for 1,3-DimeU at 815 and 755 cm^{-1}, assigned to δ_{oop}CH(5) and δ_{oop}CH(6) modes,[21] are lost and replaced by two weaker ones at ca. 760 cm^{-1}. All these complexes show a band at ca. 530 cm^{-1} which is tentatively assigned to υ(Hg−C).[22] On the other hand, compound **1e** exhibits two bands at 2138 and 2127 cm^{-1} which are indicative of SCN coordination to Hg(II) through S.[23]

^{1}H NMR spectra of **1a**−**1g** show the uracil H(6) resonance shifted upfield relative to the free ligand, with ^{199}Hg satellites (^3J) between 107 and 222 Hz (Table 4). The magnitude of the coupling constant depends upon the ligand in *trans* position to 1,3-DimeU-*C5*. Thus $^3J(^1\text{H}-^{199}\text{Hg})$ decreases as a function of the ligand as follows: NO_3^- > OAc^- > Cl^- ~ Br^- > I^- > SCN^- > CN^- > 1,3-DimeU-*C5*. Similar trends have been found in CH_3Hg^{II} complexes.[22,24] A similar effect is also seen in the ^{199}Hg NMR chemical shifts (Table 4).

Di- and Heteronuclear Derivatives of 1a. Displacement of the proton at the N(3′) position of an uracil or thymine nucleobase by a metal ion such as Pt^{II},[25] Pd^{II},[26] or CH_3Hg^{II} [5g,27] increases the basicity of the adjacent exocyclic oxygens, thereby allowing additional metal ions or a proton[28] to bind to this/these site(s). On the basis of the IR spectroscopic changes that occur on Hg^{II} binding to C(5) of 1,3-DimeU (see above), it appears that mercuration at C(5) has a similar effect on O(4) and hence reduces the double bond character of C(4)−O(4) and increases the basicity of O(4):



However, unlike in complexes with N(3)-bound Pt^{II}, where this increase in basicity is clearly evident from pH*-dependent

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[17] teXsan 1.7: Single Crystal Structure Analysis Software. Molecular Structure Corp., The Woodlands, TX, 1995.

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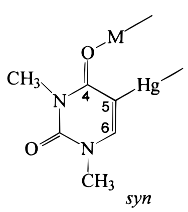
^{1}H NMR and UV spectroscopy as well as potentiometric titration,[28] the effect of C(5) bound to Hg^{II} appears to be considerably smaller. It almost certainly does not exceed 2 log units considering the pK_a of the protonated free ligand 1,3-DimeUH$^+$ (-3.25[29]) and the fact that pH*-dependent ^{1}H NMR spectra do not reveal any protonation at least down to pH$^* = 0$. The only effect to be seen in the ^{1}H NMR spectra with decreasing pH* is a gradual broadening of the H(6) resonance and a concomitant loss of the ^{199}Hg satellites. There is, however, no shift of this resonance, and CH_3 resonances remain sharp. At pH* ca. 0.6, the H(6) resonance becomes sharper again and a minor new species (H(6) at 7.59 ppm) grows in.

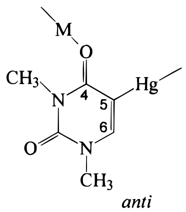
If $AgNO_3$ is titrated to an aqueous solution of **1a**, a slight downfield shift of H(6) is seen only with Ag$^+$ present in excess: At Ag$^+$:**1a** = 5:1, this shift is 0.1 ppm. Since the ^{199}Hg coupling is affected (a decrease from 200 Hz in **1a** to 187 Hz) we feel that the observed effect is real and indicative of formation of an Hg^{II}, Ag^{I} heteronuclear complex (**1i**), with Ag^{I} most likely binding to O(4) of the 1,3-DimeU. Complex stability must be low, considering the weak response on addition of Ag$^+$. The ^{199}Hg resonance is affected very little only (a shift from -2668 to -2634 ppm).

When $Hg(OAc)_2$ is added to an aqueous solution of **1a**, the original H(6) resonance broadens, with ^{199}Hg coupling retained, albeit reduced (to 186 Hz with Hg^{II}:**1a** = 5:1). In the ^{199}Hg NMR spectrum, resonances due to free $Hg(OAc)_2$ and the complex **1h** are observed, with the latter shifted to -2365 ppm (from -2668 ppm for **1a**). In both cases the hetero/dinuclear complexes formed are labile on the ^{1}H NMR time scale, since only averaged resonances of original and new species are observed. As with Ag$^+$, binding of a second metal Hg^{2+} to **1a** is suggested to occur via an exocyclic oxygen atom (**1h**).



syn

or



anti

The effect of the second metal on the H(6) resonance is too small to decide if the second metal is *syn* or *anti* with respect to Hg^{II} at C(5). With N(3) platinated pyrimidine nucleobases we have evidence that the orientation of the second metal at the exocyclic 4-position has a markedly different effect on H(5) and H(6) resonances.[7,30,31] However, in these systems, considerable downfield shifts are observed in both cases.

Much stronger binding of a second metal is to be expected if bonded in a chelating fashion between two O(4) sites, e.g. with **7a**. However, the poor solubility of **7a** in water did not permit this aspect to be studied.

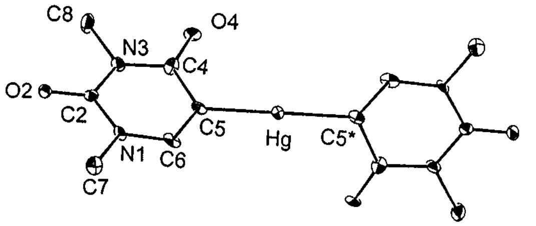


Figure 1. View of Hg(1,3-DimeU-*C5*)$_2$ (**7a**), with atom numbering scheme.

Table 5. Bond Lengths (Å) and Angles (deg) in **7a**

(a) Bonds			
Hg−C(5)	2.05(1)	N(1)−C(7)	1.46(2)
N(3)−C(2)	1.37(1)	O(2)−C(2)	1.22(1)
N(3)−C(4)	1.40(1)	O(4)−C(4)	1.22(1)
N(3)−C(8)	1.48(1)	N(1)−C(2)	1.36(1)
C(4)−C(5)	1.45(2)	N(1)−C(6)	1.36(2)
C(5)−C(6)	1.36(2)		
(b) Angles			
C(5)−Hg−C(5)	179.2(8)	N(1)−C(2)−N(3)	115.6(8)
C(2)−N(1)−C(6)	122(1)	O(4)−C(4)−C(3)	122(1)
C(2)−N(1)−C(7)	117.6(8)	O(4)−C(4)−C(5)	123(1)
C(6)−N(1)−C(7)	120(1)	N(3)−C(4)−C(5)	115(1)
C(2)−N(3)−C(4)	126(1)	Hg−C(5)−C(4)	117.7(8)
C(2)−N(3)−C(8)	116.5(9)	Hg−C(5)−C(6)	124(1)
C(4)−N(3)−C(8)	117.4(9)	C(4)−C(5)−C(6)	118(1)
O(2)−C(2)−N(1)	122(1)	N(1)−C(6)−C(5)	122(1)
O(2)−C(2)−N(3)	122(1)		

X-ray structure of Hg(1,3-DimeU-*C5*)$_2$ (7a). The molecule **7a** with atom numbering scheme is shown in Figure 1. Selected interatomic distances and angles are presented in Table 5. Complex **7a** contains two 1,3-DimeU rings bound to a single Hg. The metal has a linear coordination sphere, but the two nucleobase rings are not coplanar (dihedral angle 64.9°). The molecule is chiral and both enantiomers are present in the crystal lattice (cf. Supporting Information), consistent with the nonpolar space group (*Fdd*2) of the compound. The Hg−C(5) bond length (2.05(1) Å) is in the expected range for organomercurials[32] and agrees in particular with our previous findings[7] and that of chloro(2-deoxyuridin-5-yl)mercury.[33] Hg is to be considered 2-coordinate, since the O(4) oxygens are too far removed (3.180(8) Å) for any substantial bonding, very much as in Hg(1-MeT-*N3*)$_2$ (2.98 Å).[34]

A weak intermolecular contact (2.901(8) Å) exists between Hg and O(2) of a neighboring molecule ($^1/_4 + x$, $^1/_4 - y$, $^1/_4 + z$), but has no effect on the linearity of the C−Hg−C bond. The geometry of the 1,3-DimeU rings is normal. The rings are planar within 0.029 Å as far as endocyclic atoms are concerned. Exocyclic groups deviate by as much as 0.085 Å (O(4)), and the Hg is out by 0.096 Å.

Mixed Nucleobase Complexes: Reaction of 1a with 1-MeUH and 1-MeTH. Compounds **2a** and **3a** are obtained upon reaction of **1a** with the corresponding nucleobase (1:1) in water, pH ca. 5−6.5. According to ^{1}H NMR spectroscopy (DMSO-d_6) the two nucleobases are present in a 1:1 ratio (Figure 2). Furthermore, a similar ^3J coupling with ^{199}Hg (Table 6) is observed in both complexes. The ^{199}Hg NMR spectra of **2a** and **3a** confirm a C−Hg−N arrangement. We note that the H(5′) resonance of 1-MeU in **2a** has undergone a downfield shift of 0.17 ppm relative to the free ligand 1-MeUH. This is unusual in that, in Pt^{II} ammine complexes with this ligand, H(5′)

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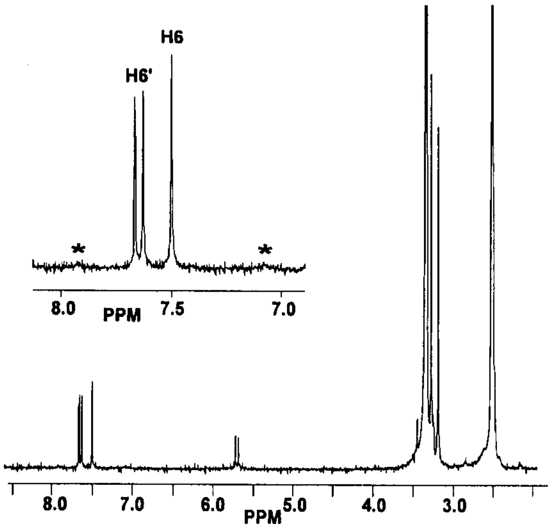


Figure 2. ^1H NMR spectrum (200 MHz, DMSO-d_6) of **2a**, with ^{199}Hg satellites indicated (∗).

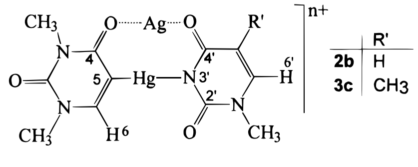
Table 6. Selected NMR Data for Mixed Nucleobase Complexes

compd	$\delta(^{199}Hg)$	$^3J(^{199}Hg-^1H(6))$, Hz	δ(H(6))
2a[a]	−2450	170	7.49
2b[b]		174	7.55
3a[a]	−2433	167	7.49
4a[a]	−2307	155	7.41
4b[b]	−2494	179	7.47
4b[a]	−2510	175	7.39
5a[a]	−2457	175	7.47
5b[a]	−2460	180	7.40
6a[a]	−2247	163	7.48
6b[a]	−2491		
7a[a]	−1999	107	7.48

[a] DMSO-d_6. [b] D_2O.

and H(6′) are always upfield from the corresponding resonances of free 1-MeUH. Whether this is an effect of the metal or the C-bound ligand remains to be studied.

Di- and Heteronuclear Derivatives of 2a and 3a. The neutral compounds **2a** and **3a** are virtually insoluble in water. However, when $AgNO_3$ is added to **2a** or $AgClO_4$ to **3a** in excess, they dissolve readily. In **2b** the H(5′) resonance of 1-MeU (in D_2O) undergoes a downfield shift of 0.17 ppm relative to the free 1-MeU, and a ^{199}Hg coupling with H(6) of the 1,3-DimeU of 174 Hz is observed for both **2b** and **3c**. We propose that binding of Ag^+ to exocyclic oxygens of the two nucleobases, 1,3-DimeU and 1-MeU (**2a**), 1-MeT (**3a**), accomplishes this solubilization.



	R′
2b	H
3c	CH3

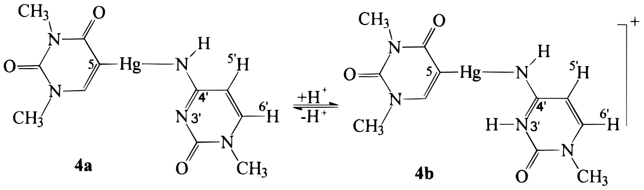
We have previously noted a similar phenomenon with insoluble *trans*-$(NH_3)_2Pt(1\text{-}MeU\text{-}N3)_2$ in the presence of Ag^+.[35] The separation of the two potential donor sites, O(4) or O(2) of 1-MeU, 1-MeT and O(4) of 1,3-DimeU should be very similar in the two systems, therefore allowing similar coordination patterns. $Hg(OAc)_2$ likewise solubilizes **3a**, although not to the same extent (some undissolved material still present). With **2a**, no solubilization is seen with $Hg(OAc)_2$ at room temperature. When kept at 40−50 °C for 2 h, some precipitate dissolves, which does not contain 1-MeU, however. In the ^1H NMR spectrum only 1,3-DimeU resonances are observed. The undissolved white material, on the basis of its IR spectrum, appears to be $Hg(1\text{-}MeU\text{-}N3)_2$.[36] The soluble part displays ^1H NMR resonances identical with those of **1a** in the presence of excess $Hg(OAc)_2$ (H(6) at 7.28 ppm (broad, no ^{199}Hg satellites resolved). These findings suggest the following reaction to take place:

$$2\ \mathbf{2a} + 3Hg(OAc)_2 \rightarrow Hg(1\text{-}MeU\text{-}N3)_2\downarrow + 2\ \mathbf{1h}$$

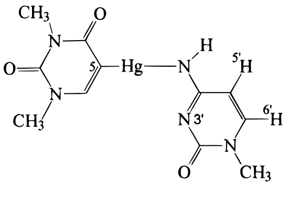
Reaction of 1a with 1-MeC. Two compounds (**4a**, **4b**) are isolated upon reaction of **1a** with 1-MeC. Depending on the pH applied, a neutral one (**4a**) is obtained at alkaline pH (12), and a cationic one (**4b**) at acidic pH (5.5). Both compounds differ by their protonation state, yet display identical metal coordination sites, as evident form ^1H NMR spectra obtained upon mixing **4a** and **4b**. pH*-dependent ^1H NMR spectra of **4a**/**4b** indicate a pK_a of 6.5 for the 1-MeC ligand in this

$$\mathbf{4a} \xrightleftharpoons[-H+]{+H+} \mathbf{4b}$$

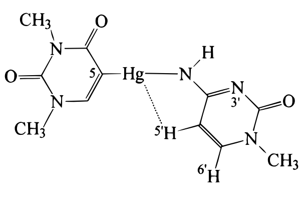
equilibrium (cf. Supporting Information). This pK_a value rules out a N(3′) metal binding site at the 1-MeC nucleobase, since any acidification of a $NH_2(4')$ proton by metal at N(3′) (pK_a = 16.7[37]) should not exceed 3−4 log units.[31] The data is, however, consistent with Hg binding to N(4′) of 1-MeC and with the following equilibrium:



From ^1H NMR spectra (cf. Supporting Information) we can draw firm conclusions neither concerning the distribution of rotamers about C(5)−Hg and/or Hg−N(4′) bonds nor about the C(4′)−N(4′) bond of 1-MeC. This latter rotation could lead to different species with N(3′) and Hg *syn* to each other or *anti*. We note, however, that H(5′) of **4b** shows a remarkable solvent dependence, 5.67 ppm in DMSO-d_6, yet is 6.22 ppm in D_2O. In contrast, H(6′) resonances differ less (7.46 in DMSO-d_6; 7.78 in D_2O), and CH_3 resonances in the two solvents are within 0.1 ppm.



Hg,N(3′) *syn*



Hg,N(3′) *anti*

We have previously demonstrated that DMSO-d_6 and D_2O can stabilize rotamers in bis(nucleobase) complexes of *trans*-a_2Pt^{II} differently.[38] Although H(5′) has undergone a remarkable downfield shift in water, thereby pointing toward an *anti* orientation of Hg and N(3′), the effect is smaller than in *trans*-$[Pt(NH_3)_2(1\text{-}MeC\text{-}N4)_2]^{2+}$ and *trans*-$Pt(NH_3)_2(1\text{-}MeC^-\text{-}N4)_2$.[31]

Dinuclear Derivative of 4a. When the poorly soluble **4a** is treated with an excess of $Hg(OAc)_2$ (1:2) in D_2O, it dissolves, giving spectra identical with those of **4b** in the presence of extra $Hg(OAc)_2$. At pD 6.5, only H(5′) is affected, shifted downfield by 0.13 ppm as compared to **4a**/**4b** at the same pH. There is clear evidence from the H(5′) signal of 1-MeC for a second,

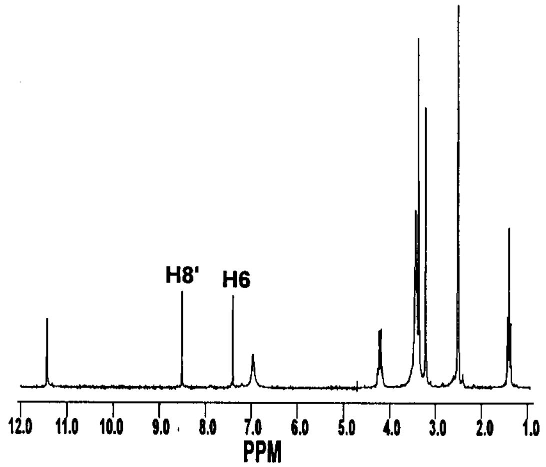
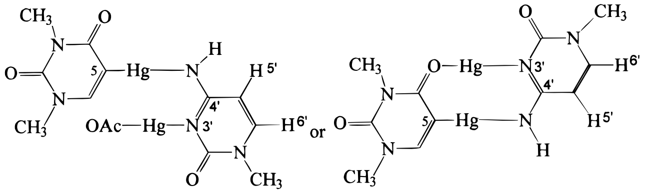


Figure 3. ^1H NMR spectrum (200 MHz, DMSO-d_6) of **5b**.

minor species, which could be due to another rotamer (cf. Supporting Information). We interpret this finding in terms of binding of a second Hg^{II} to **4a** via the cytosine N(3′) position. A similar binding pattern has been established for CH_3Hg^{II} by X-ray crystallography.[5f]



4c

With long reaction times (weeks), the original H(5′), H(6′) doublets of 1-MeC are completely lost and two singlets of H(6) of 1,3-DimeU (ca. 7.45 ppm) and of an unidentified species at 7.50 ppm are left. The latter resonance is tentatively assigned to H(6′) of 1-MeC. It is unclear at present whether this spectroscopic simplification is due to an isotopic exchange of H(5′) by ^2D, or due to migration of the second Hg^{II} to the C(5′) position of 1-MeC.

Reaction of 1a with 9-EtGH. Depending upon pH, two different mixed nucleobase complexes are also obtained upon reaction of **1a** with 9-ethylguanine: **5a**, isolated at pH 5.5 and assigned to (1,3-DimeU-*C5*)Hg(9-EtG-*N1*) and **5b**, isolated at pH 2.7 and assigned to $[(1,3\text{-DimeU-}C5)Hg(9\text{-EtGH-}N7)]^+$. A third compound, $\{[(1,3\text{-DimeU-}C5)Hg]_2(9\text{-EtG-}N1,N7)\}^{3+}$, **5c**, was not isolated. N(7′) metal binding in **5b** is indicated by a considerable downfield shift of guanine H(8′) (0.8 ppm relative to the free ligand, DMSO-d_6) and the presence of N(1′)H (11.41 ppm) and $N(2)H_2$ resonances (6.95 ppm) (Figure 3). The compound, which is soluble both in water and DMSO-d_6, is labile on the ^1H NMR time scale, as evident from signal averaging with free 9-EtGH added. ^{199}Hg-H(6) coupling is affected upon addition of excess 9-EtGH to a solution of **5b** in DMSO-d_6 (increase from 180 Hz to 200 Hz), indicating a shift of the following equilibrium toward the left side.

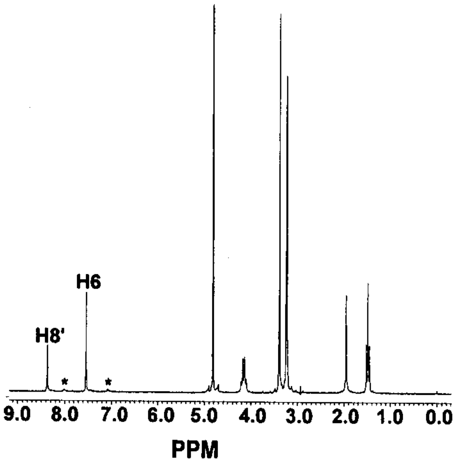


Figure 4. ^1H NMR spectrum (200 MHz, D_2O, pD 7.0) of **5c**, with ^{199}Hg satellites indicated (∗).

$$\mathbf{5b} \rightleftharpoons (1,3\text{-DimeU-}C5)Hg^{II} + 9\text{-EtGH}$$

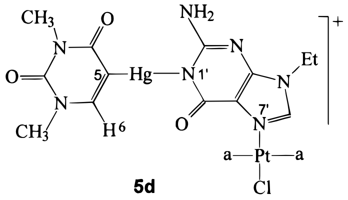
The ^{199}Hg resonance is shifted very little only. If the pH of an aqueous solution of **5b** is brought to 6−7 by addition of base, precipitation of **5a** takes place. ^1H NMR spectroscopy (in DMSO-d_6) proves that the precipitate is identical with **5a** isolated on a preparative scale. Therefore, the following metal migration can be postulated:

$$\underset{\mathbf{5b}}{[(1,3\text{-DimeU-}C5)Hg(9\text{-EtGH-}N7)]^+} \xrightarrow[-H_2O]{+OH^-} \underset{\mathbf{5a}}{(1,3\text{-DimeU-}C5)Hg(9\text{-EtG-}N1)}$$

5a is insoluble in water, but dissolves in DMSO-d_6. Although guanine resonances of **5a** and of free base have very similar shifts, addition of free 9-EtGH does not lead to signal averaging. Therefore **5a** is nonlabile in DMSO-d_6 on the ^1H NMR scale.

When (1,3-DimeU-*C5*)Hg^{II} is added to **5a**, however, only a single set of 1,3-DimeU resonances is observed with resonances being broader than in the case of **5a**. We attribute this behavior to formation of the dinuclear complex **5c** with rapidly interchanging Hg entities (Figure 4). A similar observation has been made for the bis(methylmercury) complex of guanosine.[5e]

A Heteronuclear Derivative of 5a. 5a, when treated with *trans*-$(CH_3NH_2)_2PtCl_2$ in water, pH 5.2, becomes soluble. Relative to free 9-EtGH, the guanine H(8′) resonance of the new species **5d** is shifted downfield by 0.67 ppm, and the ^{195}Pt signal appears in the range (−2398 ppm) characteristic for a PtN_3Cl coordination sphere. The ^{199}Hg−H(6) coupling constant of 183 Hz is in the range for a C−Hg−N enviroment (Table 6), thereby suggesting the following composition of **5d**:



5d

With time the spectrum undergoes changes with multiple new guanine H(8′) signals appearing. At times, this spectral region is closely similar to that of an aged aqueous solution of *trans*-

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(35) (a) Schöllhorn, H.; Thewalt, U.; Lippert, B. *J. Chem. Soc., Chem. Commun.* **1984**, 769. (b) Dieter, I.; Lippert, B.; Schöllhorn, H.; Thewalt, U. *Z. Naturforsch.* **1990**, 45b, 731.

(36) The compound was prepared in analogy to the 1-MeT compound[34] from HgO and 1-MeUH and characterized by elemental analysis and IR spectroscopy.

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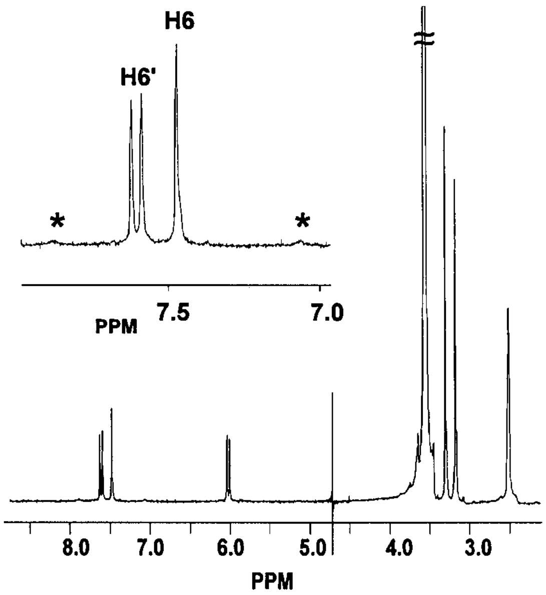
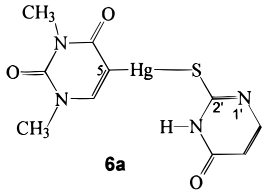


Figure 5. ^{1}H NMR spectrum (200 MHz, DMSO-d_6) of **6a**, with ^{199}Hg satellites indicated (*).

$[(CH_3NH_2)_2Pt(9\text{-EtGH-}N7)(D_2O)]^{2+}$, for which we had postulated oligomer formation via N(1′),N(7′)Pt binding.[39]

Reaction of 1a with 2-ThioUH. The nucleobase 2-ThioUH offers at least three potential binding sites for (1,3-DimeU-C5)-Hg^{II}: N(1′), N(3′), and S(2′) and combinations thereof. Reaction of **1a** with 2-ThioUH takes place with deprotonation of the 2-ThioUH, even at moderately acidic pH, and formation of water-insoluble neutral complex (1,3-DimeU-*C5*)Hg(2-ThioU) (**6a**). In view of the ^3J coupling constant of ^{199}Hg with H(6) of the 1,3-DimeU (163 Hz, DMSO-d_6) (Figure 5), and the shift of the ^{199}Hg resonance (−2247 ppm, DMSO-d_6) we propose the 2-ThioU ligand to be coordinated via S (cf. also data of **1e**). The site of deprotonation, N(1′) or N(3′), is unclear, however. In DMSO-d_6, **6a** undergoes disproportionation according to



6a

$$2\ \mathbf{6a} \rightarrow \mathbf{7a} + \mathbf{6b}$$

with formation of **7a** and $Hg(2\text{-ThioU})_2$ (**6b**). The identity of **6b** is confirmed by alternative synthesis from $Hg(OAc)_2$ and 2-ThioUH (cf. Experimental).

Neither **6a** nor **6b** dissolves in water upon addition of excess metal species such as $Hg(OAc)_2$, *trans*-$(NH_3)_2PdCl_2$, and *trans*-$(NH_2CH_3)_2PtCl_2$.

Summary

^{1}H and ^{199}Hg NMR spectroscopy has been applied to study acetate exchange reactions of (1,3-DimeU-*C5*)Hg(CH_3COO) (**1a**). The observation of ^3J coupling of the ^{199}Hg isotope with H(6) of 1,3-DimeU ligand has been shown to be helpful with regard to identification of the donor atom *trans* to C(5) of the uracil ring. The disproportionation reaction of (1,3-DimeU-*C5*)HgX complexes, previously reported for X = I^-,[9] has been confirmed for other X ligands and was used to prepare the bis(nucleobase) complex **7a**, which is the first example of its kind so far studied by X-ray crystallography. In addition, a series of mixed nucleobase complexes (1,3-DimeU-*C5*)HgL (L = second nucleobase) has been prepared and studied in solution. Formation and solution behavior of these compounds in many respects is similar to that of CH_3Hg^{II}. For example, strong binding to N(3) of uracil and thymine, to N(4) of cytosine, and N(1) of guanine is observed, as compared to weak binding to guanine-N(7). Selectivity appears to be essentially thermodynamically controlled, as in the case of CH_3Hg^{II}.[4a,40] A major difference exists in the ability of 1,3-DimeU ligand to use its exocyclic oxygens, notably O(4), for H bonding interactions or as a donor atom for a second nucleobase. This latter aspect appears to be relevant to suggestions that pairwise binding of metal ions to DNA and other ordered duplex oligonucleotides may occur.[5f,42] In the present case, such a pattern could apply to single-stranded RNA or duplex RNA with uracil in *syn* rather than the usual *anti* arrangement of the sugar moiety. If Hg^{II} binding to cytosine-C(5)[8] is also considered, many more potential binding patterns of Hg^{II} with DNA emerge, which are different from those of the major adenine/thymine adducts.[43]

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Supporting Information Available: Tables of intermolecular distances and thermal displacement parameters, a figure of the crystal packing of **7a**, and figures of ^{1}H NMR spectra and pH* dependence of **4a** and **4b** (8 pages). Ordering information is given on any current masthead page.

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