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Mercuration of analog of the uracil: Attachments sites of to nucleic acid bases and isotropic NMR shielding tensor in gas phase & SCRF method

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ABSTRACT

The behavior of (1,3-dimeU-C5) Hg with replacement by other model nucleobases (1-methylcytosine, 9-ethylguanine) have been studied. The molecular complexes were optimized using Becke3LYP density functional theory (DFT) approach and LANL2DZ basis set. The C-5 site of the uracil and NH(4'), N(3') sites of cytosine and N(1') site of guanine of the trans[PtNH₂CH₂Cl-G] complexes are preferred mercuration reactions. The gauge invariant atomic orbital (GIAO) method was employed to calculate isotropic atomic shielding using B3LYP/LANL2DZ at the Gas Phase. The effect of solvent on stabilization of complexes shows interesting results.

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KEYWORDS

Ab initio calculation;
NMR shielding tensor;
(1,3-dimethyl uracil-5-yl)
mercury (II);
Mercuration reactions.

INTRODUCTION

Reactions mercury(II) with nucleobases^[1] and mechanisms of detoxification^[2] have received particular attention. The chemistry of mercury(II) has been intensively studied, with regard both to its properties as a soft acid^[3] and to its toxicity^[4] and related to it this, to its reactivity toward biomolecules^[5].

The main NMR spectroscopic parameters are dependent on the second-order molecular property tensors^[4]. The NMR shielding tensor σ , nuclear spin-spin coupling J can be all written as second derivatives of the energy.

(NMR shielding) $\sigma = (\partial^2 E / \partial B \partial m)_{B=0, m=0}$

(NMR coupling) $J = (\partial^2 E / \partial n \partial m)_{n=0, m=0}$

where E is the energy of the molecule, B external mag-

netic field, E electric intensity, and n, m nuclear magnetic moments. Scalar parameters χ_{nm} and σ observable for an isotropic medium are defined as a 1/3 of the traces of the tensors χ and σ , respectively^[13].

The solvent effect is taken into account via the Self-Consistent Reaction field (SCRF) method. This method is based on Onsager reaction field theory of electrostatic salvation. In this model, the solvent is considered as a uniform dielectric with a given dielectric constant. The solute is placed into a cavity within the solvent. SCRF approaches differ in how they define the cavity and the reaction field. Tomasi's Polarized Continuum Model (PCM)^[16] defines the cavity as a union of a series of interlocking atomic spheres.

In this context, we report ab initio optimized structure of the Hg complexes using LANL2DZ basis set

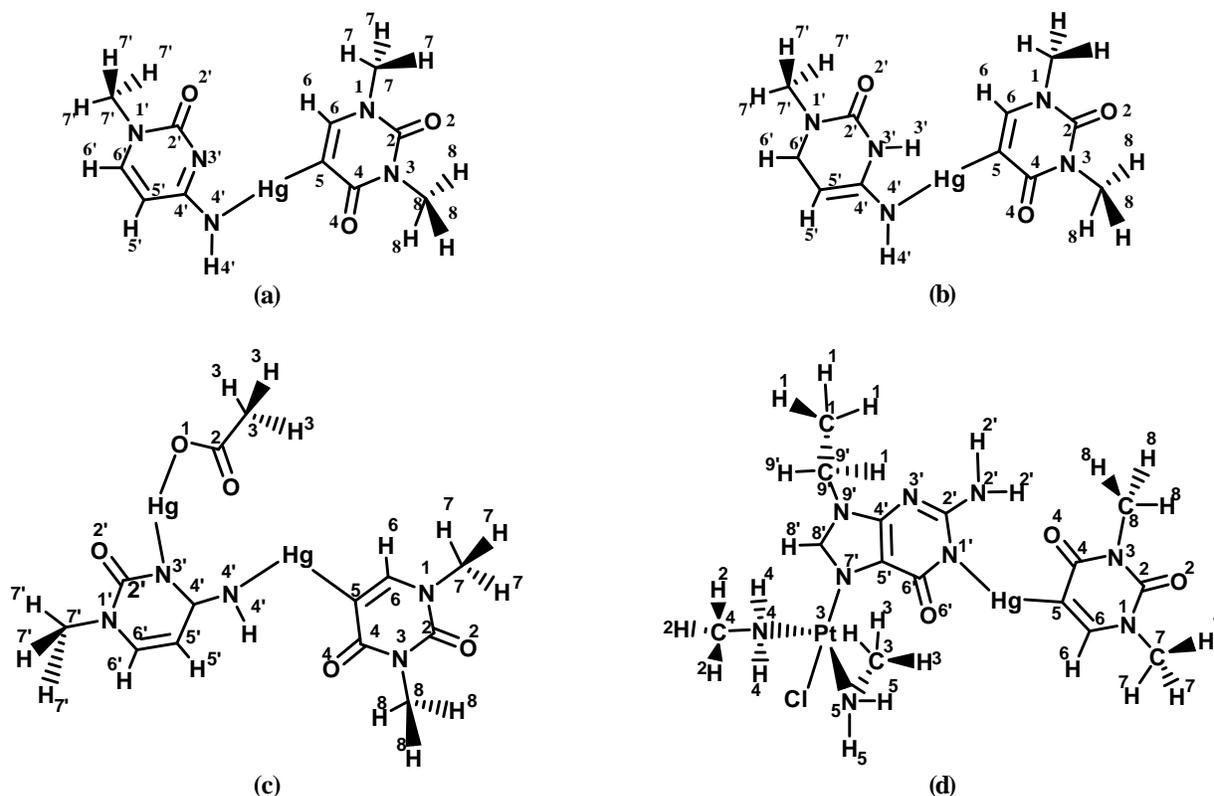


Figure 1 : Optimized structures of Hg complexes in the B3LYP/LANL2DZ

TABLE 1 : Optimized bond length (Å) of Hg complexes in the B3LYP/LANL2DZ

Bond Length	A	B	C	D
Hg-C5	2.180	2.164	2.199	2.183
Hg-N4'	2.241	2.228	2.314	
Hg-N1'				2.342
Hg-N3'				2.299
Pt-N7'				2.062
Pt-N5				2.074
Pt-N4				2.105
Pt-Cl				2.404

and the B3LYP hybrid density function method and the structures was supported by comparing the measured $^1\text{H-NMR}$ spectra to the results of ab initio gauge-invariant atomic orbital (GIAO)^[15] computations of chemical shifts using density functional theory at the B3LYP/LANL2DZ level. PCM calculations in this report have been performed at the B3LYP/LANL2DZ level in GAUSSIAN 98.

Computational details

Quantum chemical calculations have been performed by using GAUSSIAN-98 computer pro-

TABLE 2 : Optimized bond angle (Å) of Hg complexes in the B3LYP/LANL2DZ

Bond angles	A	B	C	D
Hg-C5-C6	126.440	138.792	135.582	134.860
Hg-C5-C4	114.5015	101.292	105.295	106.222
Hg-N4'-H4'	138.825	111.239	98.968	
Hg-N4'-C4'	102.052	135.313	145.575	
Hg-N1'-C6				96.557
Hg-N1'-C2'				139.792
N7'-Pt-N5				93.007
N7'-Pt-N4				93.513
Cl-Pt-N5				87.222
Cl-Pt-N4				86.2005
C5'-N7'-Pt				128.392
C8'-N7'-Pt				125.415
Pt-N7'-C5'				128.392
Pt-N7'-C8'				125.415
Hg-N3'-C4'			141.836	
Hg-N3'-C2'			94.299	
N4'-C4'-N3'	113.509	120.043	120.704	
N4'-C4'-C3'			123.988	
H4'-N4'-C4'	119.123	113.449	115.457	
N4'-C4'-C5'	126.549	124.707		

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TABLE 3 : Stability energies(Hartree) for Hg complexes in gas phase with B3LYP/LANL2DZ level

Complexes	B3LYP/LANL2DZ
A	-969.070
B	-969.466
C	-1240.101
D	-1481.761

gram^[12]. The structures of all the systems were optimized using the DFT level of theory and LANL2DZ basis set for atoms.

NMR analysis have been performed using LANL2DZ basis set and the B3LYP level. The GIAO^[11] methods were used to calculate the isotropic NMR shielding at the B3LYP/LANL2DZ of theory.

SCRF calculations has proved useful in describing the effects of the solvent on some characteristics of the nucleotides and Magnesium Hydrate complexes in solution and have been performed at B3LYP/LANL2DZ of theory.

RESULTS AND DISCUSSION

Experimental findings confirmed previous reports on C(5) mercuration reactions of uracil and cytosine nucleobases^[6,7]. N(3'), N(4) at 1-methyl cytosine (1-MeC) and N(1'), N(7') at the 9-EtG are metal binding site. The structures of several (1,3-dimethyl uracil)Hg complexes with the 1-MeC nucleobase were optimized using the B3LYP/LANL2DZ (Figure 1).

The structures of Hg complexes have been determined experimentally^[17] and then are compared with those predicted from at the B3LYP/LANL2DZ level in TABLE 1.

Bond lengths and angles are then estimated to have converged to within 0.001 Å and 0.1 Å°, respectively.

The Hg-C5 and Hg-N4' and Hg-N3' and Hg-N1' Pt-N7' bond length is in the expected range for organomercurials^[18] and agrees with Abinitio calculation at B3LYP/LANL2DZ level at Hg-complexes.

The bond angles of N7'-Pt-N5 and N7'-Pt-N4 are 93.007 and 93.515 and the angles of Cl-Pt-N5 and Cl-Pt-N4 in the D complex are 86.2005 and 87.222, respectively. These results show the D complexes of Platinum is square planner and owing to the loss of symmetry in platinum complexes, X-Pt-Y (X,

TABLE 4 : Relative (to TMS) shifts in ppm for ¹³C-NMR of Hg-complexes using GIAO method at B3LYP/LANL2DZ. The ¹³C-NMR chemical shift ($\delta = \sigma_{\text{iso}}^{\text{TMS}} - \sigma_{\text{iso}}^{\text{Sample}}$), TMS: Isotropic carbon shielding tensor= 193.803 at B3LYP/LANL2DZ and GIAO method

Atom	A	B	C	D
C6'	147.236	151.139	145.539	171.558
C5'	93.079	97.595	111.546	118.704
C4'	174.263	162.740	167.539	158.6138
C2'	163.722	155.280	175.176	164.5582
C7'(CH3)	46.173	48.345	44.147	
C8(CH3)	35.640	38.989	38.273	38.0533
C6	150.230	150.371	150.639	151.7882
C5	128.342	132.879	131.136	127.541
C4	175.889	180.824	180.280	181.3414
C2	161.905	159.041	159.918	160.0928
C7(CH3)	45.797	48.426	47.432	
C3				175.7661
C1				19.7221
C9'(CH3)				50.6490
C8'				144.4936
C4(CH3)				37.8528
C7(CH3)				47.9870

Y=N7'(G), N(NH3), Cl) angles differ from the ideal value of 90°.

Protonation and mercuration of N3' atom at the B, C complexes have been increase of the Hg-N4'-C4' angle comparison with the A complex (TABLE 2).

The computed stabilization energies (Hartree) of C complexes in gas phase with two Hg atoms is more stable of the A and B complexes at the B3LYP/LANL2DZ level and D complex with Hg and Pt atoms is very stable.

We calculate nuclear magnetic isotropic spectroscopic shielding for all atoms in Hg complexes using density functional theory at the B3LYP/6-31g** level. In this letter, we use both the GIAO method procedure, which is implemented in the GAUSSIAN 98 program.

In high-resolution NMR, the isotropic part σ_{iso} of σ is measured by taking the average of σ with respect to the orientation to the magnetic field, i.e., $\sigma_{\text{iso}} = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$, where σ_{11} , σ_{22} and σ_{33} are the principal axis values of σ . The results calculated are summarized in TABLE 4 and 5.

Ab initio calculation yield show that the values for

TABLE 5 : Relative (to TMS) shifts in ppm for ¹H-NMR of Hg complexes using GIAO method at B3LYP/LANL2DZ. The ¹H-NMR chemical shift ($\delta = \sigma_{\text{iso}}^{\text{TMS}} - \sigma_{\text{iso}}^{\text{Sample}}$). TMS: Isotropic hydrogen shielding tensor = 23.762 at B3LYP/LANL2DZ and GIAO method

Atom	A	B	C	D
H6'	6.815	7.487	7.563	
H7'(CH3)	3.548	3.958	3.506	
H7'(CH3)	3.543	2.952	3.506	
H7'(CH3)	2.215	4.717	4.969	
H8(CH3)	4.67	3.680	3.799	3.6906
H8(CH3)	3.249	3.6780	3.799	3.6654
H8(CH3)	3.246	3.677	3.799	5.0033
H6	7.735	7.526	7.437	7.5708
H7(CH3)	3.825	4.122	4.091	4.1088
H7(CH3)	2.862	2.905	2.782	2.9098
H7(CH3)	3.826	4.120	4.092	4.1301
H5'	5.382	5.868	6.738	
H4'(N4')	3.670	4.312	7.812	
H3'(N3')		6.230		
H9'(CH2)				4.6049
H9'(CH2)				3.5567
H4(NH2)				0.6618, 2.4399
H3(CH3)				2.0946
H3(CH3)				2.5627
H3(CH3)				1.4329
H1(CH3)				1.2311
H1(CH3)				2.0942
H1(CH3)				1.5835
H2'(NH2)				8.711
H2'(NH2)				5.0682
H5(NH2)				2.0827
H5(NH2)				5.7014
H2(CH3)				3.5828
H2(CH3)				2.438
H2(CH3)				2.586
H8'				7.269

the chemical shifts to TMS of C5 atom of the uracil and C5', H4' atoms of the cytosine in the A, B complexes and C5 atom of the uracil and C5' of the cytosine in the C complex have been decreased for the reason that the anisotropic effect Hg that the leading to deshielding of the C, H atoms.

The chemical shifts to TMS of C5 atom of the uracil and C5' atom of the guanine have been decreased and imply that the anisotropic effect Hg and Platinum

TABLE 6 : Dipole moment (debye) for structures Hg complexes in gas phase and various solvent in B3LYP/LANL2DZ level

Solvent	A	B	C
Gas Phase	6.347	10.714	4.857
Cyclohexane	6.992	11.558	5.541
Dichloroethane	7.712	12.424	6.194
Methanol	9.189	13.573	6.795
H ₂ O	9.328	13.639	6.815

TABLE 7 : Free energy (KCal mol⁻¹) for structures Hg complexes in various solvent in B3LYP/LANL2DZ

Solvent	A	B	C
Cyclohexane	-3.73	-23.02	-16.91
Dichloroethane	-10.86	-46.62	-36.30
Methanol	-23.26	-69.44	-53.36
H ₂ O	-19.16	-65.37	-47.58

TABLE 8 : Polar solute-solvent(P) and solute polarization (S) for structures Hg complexes in various solvent in B3LYP

Complexes	Cyclohexane	Dichloroethane	Acetone	H ₂ O	
A	P	-5.26	-11.97	-13.48	-33.59
	S	0.24	1.14	1.42	6.16
B	P	-24.20	-49.06	-54.29	-82.76
	S	0.63	3.31	4.23	9.81
C	P	-21.42	-40.75	-44.75	-65.33
	S	0.34	1.62	2.08	4.57

metal. Chemical shifts to TMS H4' atom in the B, C complexes did not change importantly because bond angle of Hg-N4'-C4' have been increased in the B, C complexes (135°, 145°) to the A complex (102°).

The effect of solvent on the complexes of show that with the increase of dielectric constants of solvent the Dipole moment and Free energy and Polar solute-solvent and Solute Polarization at the Hg-complexes have been increased (TABLE 6-8).

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