

Theoretical investigation of the interaction of uracil and mono hydrated uracil – water complexes with alkali metals

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Quantum chemistry calculations have been applied in order to explore the interaction of alkali metals with oxo groups of uracil. The optimised geometries, harmonic vibrational frequencies and the energies of uracil, metalated uracil, monohydrated uracil and monohydrated metalated uracil have been calculated. The calculations show that interaction of metals with uracil through O3 (UO3) is stronger than the interaction of metals with O1 (UO1). The presence of water stabilises the UO1, UO3 structures. In mono-hydrated uracil the stability of UO3W rather than UO1W is more than for non hydrated species. Calculations show that after monohydration, the frequency shift of the stretching vibrations of N6-H is related to the atomic number of the metal.

Keywords: uracil, metalated uracil, mono hydrated uracil, hydrogen bonding, vibrational frequencies

The structure and properties of DNA depend on metals. Metal ions can interact with many sites in DNA¹⁻³; and the interactions of mono and bivalent metals have been studied.⁴⁻¹¹ The relative stability of tautomers of the pyrimidine base cytosine is very important in the structure of DNA. The occurrence of rare tautomers has been put forward as a possible mechanism of spontaneous mutation.¹² Metalation can change the probability of the formation of rare (minor) tautomers of bases and could affect the ability of a nucleobase to be protonated or deprotonated.¹³ Formation of rare nucleobase tautomers can occur under the influence of a metal entity. When a hydrogen atom of the N4 amino group of cytosine is replaced by a metal entity,¹⁴⁻¹⁸ the N3 position is protonated to produce a metalated form of the rare iminooxo-tautomers of this base. Alkali cations, at high concentration, interact with the nucleic acid bases, destroying the base pair hydrogen bonding and, consequently, compromise the structure integrity of the nucleic acid polymer.¹⁹⁻²¹ Furthermore, the presence of these ions in the cell nucleus has an inhibitory effect on the chain initiation process by RNA polymerase.^{19,20} So the alkali ions affect syntheses, replication, structure integrity, and cleavage of nucleic acids. For these reasons, knowledge of the thermochemical and structural features that govern the interaction between alkali cations and nucleic acid bases can indicate how they might interact with more complex nucleic acids polymers.

Not only monovalent alkaline cations interact exclusively with the phosphate group of the backbone, but also the divalent alkaline cations (Mg²⁺, Ca²⁺, Ba²⁺) interact mostly with the phosphate group.¹⁻³ This does not mean that interaction with bases is excluded. For example, a high resolution X-ray study of Z-DNA hexamer shows a barium cation bridging two side-by-side Z-DNA helices in the crystal by simultaneously coordinating to the O and N of two guanines. This cation is, at the same time, coordinated to four water molecules.²²

Specific solvation effects are known to be vital in DNA bases pair interactions. The water molecules in the first coordination sphere represent an inherent part of the DNA structures, and they are known to be very flexible. Since the stabilisation of the two DNA strands proceeds through the formation of a number of hydrogen bonds, the study of this phenomenon augmented by investigation of the specific solvation effects has greatly attracted the attention of both theoreticians and experimentalists in order to understand base pairing mechanisms.¹⁰ The main objective of this work is to investigate the interaction between metalated uracil and one water molecule, to compare the results with nonmetalated uracil,

and to draw some conclusions on the diversity of metalated and nonmetalated uracil. Fig. 1 indicates the molecular structure and the atom numbering of the studied molecules.

Computational details

The calculations of systems containing C, H, N, O are described by the standard 6-31+G* basis set.^{23,24} For alkali metals (Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺) a standard LANL2DZ basis set is used²⁵⁻²⁸ and Na, K, Rb and Cs are described by effective core potential (ECP) of Wadt and Hay pseudopotential^{23,26} with a doublet- ξ valance using the LANL2DZ. All systems have been optimized at the Hartree–Fock level. In the all cases, the steady-state nature (minimum on the potential energy surface) of the optimized complexes has been confirmed by calculating the corresponding frequencies at the same computational level. For the optimised geometries the correlation energies were calculated by Becke3LYP density functional theory (DFT). The calculations have been performed by using the GAUSSIAN 98 suite of programs.²³ We limit the optimisation to the planar C_s structures of the base...Mⁿ⁺ complexes, where metal cations Mⁿ⁺ interact with the O1 and O3 atom of uracil.

The natural bond orbital (NBO)²⁹⁻³³ analysis has been performed by using NBO as implemented in the GAUSSIAN98 systems. NBO calculations have been performed at the Hartree–Fock level.

The interaction energies (E_I) were determined as the difference between the optimised energy of the base...metals cation [$E(B...M^{n+})$] systems and the sum of the energies of the base [$E(B)$] and the metal cation [$E(M^{n+})$]:

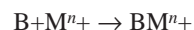
$$E_I = E(B...M^{n+}) - [E(B) + E(M^{n+})] \quad (n = 1)$$

The final interaction energies (E_I) have been calculated as the difference between the energy of the complex and the sum of the energies of the monomers, and have been corrected from the inherent basis set superposition error (BSSE) which is calculated, by using the Boys–Bernardi counterpoise technique:

$$E_{I+BSSE}(B...M^+) = E(B...M^+)_{BM} - [E(B)_B + E(M^+)_M] + [E(B')_B - E(B')_{BM} + E(M')_M - E(M')_{BM}]$$

Where $E(B...M^+)_{BM}$ represents the energy of the complex, $E(B)_B$ the energy of the isolated monomer B with its basis set, $E(B^+)_B$ the energy of B in its geometry within the complex calculated with its basis set, and $E(B')_{BM}$ the energy of B in its geometry within the complex with the complete basis set of the complex (B...M⁺).³⁴

Metal ion affinity (MIA) was assumed as the negative of the enthalpy variations (ΔH) for the process:



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In other words the MIA corresponds to the dissociation energy of the B-M₊ bond.

The variations in zero point energies were considered together with thermochemical analysis at 298 K in order to obtain the entropic (ΔS) and free energy (ΔG) variation for the considered process.

Results and discussion

Relative energies

The calculations find that the preferred binding site for the alkali cations to uracil is at O3 (see Table 1). The C=O-M⁺ bond angle is very nearly linear but shifted slightly away from the adjacent NH group. It is interesting to note that this shift is away from the global dipole moment of uracil (Fig. 1). Changes to the structure of the uracil molecule upon metal ion complexation are minor. We find that the alternate binding site at O1 is higher in energy by 4.11 kcal/mol for Li⁺, 3.55 kcal/mol for Na⁺, 3.10 kcal/mol for K⁺, 2.92 kcal/mol for Rb⁺, 2.74 kcal/mol for Cs⁺ (in HF level) (see Table 1).

We also obtained results for hydrated uracil. See Table 1. Here the preferred binding sites are the same as uracil, O3 and O1, but there are larger perturbations on the structure. In all of the MB⁺ systems, the measured binding energy varies with the metal ion such that strength of binding varies: Li⁺ > Na⁺ > K⁺ > Rb⁺ > Cs⁺, because these complexes are largely electrostatic in nature, this is easily understood on the basis of the size or, equivalently, the charge density on the metal. The smaller the ion, the greater the charge density of the metal, and therefore, the greater the strength of the ion-dipole and ion-induced dipole interactions in these systems. In this simplistic point of view, the strength of the interaction of the metal ions with the nucleic acid bases appears to be driven principally by the ion-induced dipole interaction. The relative bond strengths vary inversely as the dipole moments. To some extent, this is because the metal ions are not able to bind at sites that allow alignment with the dipole moment.

Indeed in uracil complexes bound at the O3 position the metal ions prefer to tilt away from the adjacent NH group even though this moves the ion into a position almost perpendicular to the dipole moment of the molecule. This motion is because the steric interactions with the NH group are substantially greater than those with the CH group. In contrast, when the metal ions bind to the O1 position, when there is an adjacent NH group on both sides, the metal ion tilts toward the direction leading to a strong interaction with the

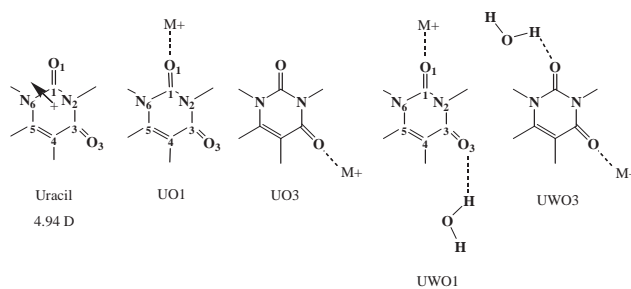


Fig. 1 Structures of uracil systems: (U) Uracil major form. Properly scaled dipole moments in Debye are shown as arrows (+ indicates the positive end of the dipole); (UO1) Metalated form through O1; (UO3) Metalated form through O3; (UO1W) Metalated form through O1 and interaction of water with O3; (UO3W) Metalated form through O3 and interaction of water with O1.

dipole moment of the molecule. Theoretical examination of the charge retained on the metals in these complexes shows that for uracil complexes the charge of the metal has the following order: Li⁺ < Na⁺ < K⁺ < Cs⁺. See Table 2. These results confirm the electrostatic nature of the binding, but also demonstrates that there is some covalence in the metal-ligand interaction, especially in the Li⁺ system.

The relative energies of all the structures are listed in Table 1. In both hydrated and nonhydrated systems the calculations predicts interaction with O3 is stronger than O1. The interaction between water and uracil causes more stabilization the UO3 form.

Interaction between metalated uracil UO1, UO3 and one water molecule: We will now discuss the properties of the 1:1 adducts of metalated uracil and water. The structure of complexes of one water molecule with uracil are shown schematically in Fig. 1. By analogy with uracil-water 1:1 adducts, the most stable complexes UO1, UO3 are the ones in which one water accepts the acidic NH proton and donates its H_w proton to the carbonyl oxygen. The binding energies of the metalated species with one water molecule are given in Table 3 for purposes of comparison, with the interaction energies of the corresponding metalated-water 1:1 adducts.³⁴

The interaction energies of metalated uracil: Table 3 shows the interaction energies of metalated uracil which systematically increase with atomic number of M. This increase is due to larger dipole

Table 1 Relative energy of metalated uracil UO1, UO3 and metalated uracil-water complexes UO1W, UO3W in HF and B3LYP levels

M ⁿ⁺	ΔE^{HF} (kcal/mol)				ΔE^{B3LYP} (kcal/mol)			
	UO1	UO3	UO1W	UO3W	UO1	UO3	UO1W	UO3W
-	0.00	0.00	3.13	0.00	0.00	0.00	3.38	0.00
Li	4.11	0.00	9.76	0.00	4.83	0.00	11.01	0.00
Na	3.55	0.00	8.84	0.00	4.10	0.00	9.79	0.00
K	3.10	0.00	8.11	0.00	3.58	0.00	8.98	0.00
Rb	2.92	0.00	7.84	0.00	3.33	0.00	8.75	0.00
Cs	2.74	0.00	7.57	0.00	3.18	0.00	8.34	0.00

Table 2 Charge of M, O1 and O3 atoms in metalated uracil UO1, UO3 and metalated uracil-water complexes UO1W, UO3W

Atom	Structure	M ⁿ⁺					
		-	Li	Na	K	Rb	Cs
M	UO1	-	0.99086	0.99551	0.99943	0.99973	1.00027
	UO3	-	0.99075	0.99521	0.99937	0.99967	1.00029
	UO1W	-	0.99073	0.99548	0.99945	0.99975	1.00030
	UO3W	-	0.99036	0.99501	0.99936	0.99968	1.00035
O1	UO1	-0.72104	-0.96758	-0.91279	-0.88005	-0.86559	-0.85342
	UO3	-0.72104	-0.66401	-0.67511	-0.68389	-0.68719	-0.69013
	UO1W	-0.75955	-0.97085	-0.91536	-0.88247	-0.86779	-0.85546
	UO3W	-0.71829	-0.69245	-0.70558	-0.71597	-0.71980	-0.72324
O3	UO1	-0.68468	-0.62596	-0.63732	-0.64636	-0.64973	-0.65283
	UO3	-0.68468	-0.95096	-0.89177	-0.85634	-0.84087	-0.82795
	UO1W	-0.68793	-0.65684	-0.67023	-0.68058	-0.68446	-0.68796
	UO3W	-0.72279	-0.95996	-0.90029	-0.86497	-0.84937	-0.83645

Table 3 Interaction energy (E_i) (kcal/mol), Binding Energy^a (kcal/mol) and basis set superimposition energy (BSSE) (kcal/mol) of metalated uracil UO1, UO3 and metalated uracil–water complexes UO1W, UO3W in HF level

M^{n+}	E_i (kcal/mol)				Binding energy (kcal/mol)		E_i +BSSE(kcal/mol)			
	UO1	UO3	UO1W	UO3W	UO1W	UO3W	UO1	UO3	UO1W	UO3W
Li	-46.16	-50.28	-45.82	-52.45	-6.14	-11.79	-46.87	-50.96	-47.07	-56.12
Na	-32.07	-35.62	-31.54	-37.24	-5.95	-11.23	-32.84	-36.38	-32.84	-38.55
K	-20.73	-23.83	-20.08	-25.06	-5.82	-10.84	-22.27	-25.36	-22.14	-27.13
Rb	-20.29	-21.33	-17.71	-22.42	-5.78	-10.70	-19.14	-22.06	-18.97	-23.69
Cs	-15.60	-18.35	-14.87	-19.31	-5.75	-10.58	-16.36	-19.10	-16.15	-20.60

^aThe total energy of free water molecule is -76.0177431 hartree

moments for metalated uracil with heavy atoms. Also, the interaction energy values show that the interaction energy of UO1W is more than UO1, and UO3W is less than UO3. Table 3 shows E_i and E_i +BSSE for the metalated uracil. Clearly for the all complexes, values of BSSE are rather small.

Geometry parameters

Intermolecular parameters: All the intermolecular distances M–O3, M–O1 for UO1, UO1W, UO3, and UO3W structures are shown

in Table 4. The intermolecular M–O distances monotonically increase with atomic number for the alkaline metals (Table 4). The increase is more pronounced where this difference is about 1.26 Å in UO1 and UO1W and 1.25 Å in UO3, UO3W.

The intermolecular $H'_w \dots O$ distances lie between 2.640 and 2.366 Å; that is, they are longer than the corresponding $H'_w \dots O$ distances in nonmetalated species, which are between 2.019 and 2.100 Å. The $O_w H'_w \dots O$ angles do not differ substantially and lie in the interval between 126.9° to 137.6° for UO1W and 119.6° to 10.0° for UO3W.

Table 4 Results of geometry optimization of uracil UO1, UO3 and metalated uracil–water complexes UO1W,UO3W (lengths in Å, angles in degrees).

Intramolecular parameters							
Bond	Structure	M^{n+}					
		–	Li	Na	K	Rb	Cs
C1–O1	UO1	1.195	1.236	1.228	1.222	1.220	1.217
	UO3	1.195	1.183	1.185	1.187	1.187	1.188
	UO1W	1.194	1.237	1.229	1.222	1.220	1.218
	UO3W	1.203	1.189	1.191	1.193	1.193	1.194
C3–O3	UO1	1.195	1.184	1.186	1.187	1.188	1.188
	UO3	1.195	1.235	1.227	1.220	1.218	1.216
	UO1W	1.202	1.188	1.190	1.192	1.193	1.194
	UO3W	1.195	1.238	1.228	1.222	1.220	1.218
C1–N2	UO1	1.369	1.337	1.344	1.349	1.351	1.353
	UO3	1.369	1.388	1.384	1.382	1.381	1.380
	UO1W	1.371	1.339	1.345	1.351	1.352	1.354
	UO3W	1.365	1.386	1.383	1.380	1.380	1.379
N2–C3	UO1	1.390	1.415	1.410	1.407	1.406	1.404
	UO3	1.390	1.354	1.361	1.367	1.369	1.371
	UO1W	1.383	1.412	1.407	1.402	1.401	1.400
	UO3W	1.391	1.355	1.362	1.368	1.369	1.371
C3–C4	UO1	1.462	1.461	1.462	1.462	1.461	1.462
	UO3	1.462	1.433	1.441	1.446	1.447	1.449
	UO1W	1.460	1.461	1.460	1.461	1.461	1.460
	UO3W	1.461	1.429	1.437	1.442	1.444	1.445
M–O1	UO1	–	1.746	2.122	2.567	2.783	3.015
	UO1W	–	1.742	2.119	2.564	2.778	3.010
M–O3	UO3	–	1.740	2.114	2.554	2.767	2.995
	UO3W	–	1.732	2.107	2.544	2.755	2.980

Intermolecular parameters							
	Structure	M^{n+}					
		–	Li	Na	K	Rb	Cs
(N)H...O _w	UOW3	2.034	1.890	1.908	1.923	1.928	1.934
H' _w ...O	UOW1	2.019	2.366	2.291	2.237	2.219	2.202
	UOW3	2.100	2.640	2.532	2.444	2.415	2.390
<NH...O _w	UOW3	145.0	155.9	153.6	151.7	151.2	150.7
<O _w H' _w ...O	UOW1	157.3	126.9	131.4	134.9	136.3	137.6
	UOW3	136.0	110.0	113.9	117.3	118.6	119.6
<C=O...H' _w	UOW1	115.3	113.1	113.3	113.5	113.5	113.5
	UOW3	111.9	108.5	109.4	110.1	110.3	110.5

		Vibrational frequencies*					
Assignment	Structure	M ⁿ⁺					
		-	Li	Na	K	Rb	Cs
ν ₃ (H ₂ O)	UO1W	4172	4162	4163	4163	4162	4162
	UO3W	4165	4151	4155	4156	4157	4158
ν ₁ (H ₂ O)	UO1W	4004	4041	4039	4035	4034	4033
	UO3W	4004	4032	4032	4030	4029	4028
ν(N6H)	UO1	3881	3863	3870	3874	3875	3876
	UO3	3881	3837	3844	3850	3852	3854
	UO1W	3789	3864	3870	3875	3876	3877
	UO3W	3841	3661	3686	3702	3709	3714
ν(N2H)	UO1	3842	3825	3833	3838	3840	3841
	UO3	3842	3819	3828	3833	3835	3836
	UO1W	3843	3826	3834	3839	3840	3841
	UO3W	3879	3823	3831	3836	3837	3839
ν(C=O)	UO1	1982	2030	2020	2012	2010	2007
	UO3	1982	1841	1861	1873	1879	1884
	UO1W	1972	1882	1892	1897	1901	1905
	UO3W	1981	1835	1854	1866	1872	1877
ν(N2H)	UO1	725	745	737	732	730	729
	UO3	725	752	744	739	736	735
	UO1W	721	747	741	736	734	733
	UO3W	731	755	747	741	739	737
ν(N6H)	UO1	594	631	618	611	608	606
	UO3	594	692	676	633	659	655
	UO1W	617	635	623	616	613	611
	UO3W	810	897	891	883	881	878

*The OH distance in free water calculated at the same level is 0.9475 Å. ν=stretching; γ=out-of-plane deformation vibration. The ν(OH) frequencies in the free water molecule calculated at the same level of theory are equal to 4191 and 4072 cm⁻¹.

Table 5 Enthalpy (ΔH=MIA), entropy (TS) and free energy (ΔG) variations for the formation process (UO1), (UO3), (UO1W) and (UO3W) metalated complexes, at T(298 K), computed at HF level of theory

	Structure	HF				
		Li	Na	K	Rb	Cs
ΔH(kcal/mol)	UO1	-45.28	-31.50	-21.11	-17.97	-15.18
	UO3	-49.35	-35.01	-24.17	-20.85	-17.89
	UO1W	-42.08	-28.07	-17.54	-14.34	-11.52
	UO3W	-54.78	-39.86	-28.61	-25.14	-19.00
TΔS(kcal/mol)	UO1	-7.21	-6.99	-6.55	-6.36	-6.14
	UO3	-7.29	-7.05	-6.61	-6.41	-6.21
	UO1W	-6.67	-6.54	-6.17	-5.98	-5.79
	UO3W	-7.97	-7.84	-7.55	-7.4	-4.18
ΔG(kcal/mol)	UO1	-38.07	-24.51	-14.56	-11.61	-9.04
	UO3	-42.06	-27.96	-17.56	-14.44	-11.68
	UO1W	-35.41	-21.53	-11.37	-8.36	-5.73
	UO3W	-46.81	-32.02	-21.06	-17.74	-14.82
T(298K)	UO1	1.0154	1.009	1.005	1.004	1.003
	UO3	1.017	1.011	1.007	1.005	1.004
	UO1W	1.014	1.008	1.004	1.003	1.002
	UO3W	1.019	1.013	1.008	1.007	1.006

Very small difference are predicted for the C=O...H_w angles, which vary from 113.1° to 113.5° for UO1W and from 108.5° to 110.5° for UO3W. In the 1:1 adducts of uracil and water UO1W and UO3W, the (N) H...O_w distances range between 1.890 and 1.934 Å and the corresponding angles between 155.9° and 150.7°.

The CH...O hydrogen bonds are weaker than the NH...O bonds, mainly because of a large reduction in the electrostatic contribution. Marked differences reflecting the weaker nature of the CH...O hydrogen bond occur in the structures.

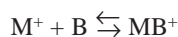
Intramolecular parameters: The geometries of isolated bases and bases in the complexes differ considerably (See Table 4). We analysed

only bond lengths and bond angles among complexes because only these geometric parameters could be determined from X-ray measurement. Because the complexes were held planar, the dihedral angles were not allowed to change. The two largest bond length deviations of uracil...M complexes are summarized in Table 4 (distances of C1-N2 and N2-C3). The C1-N2 distance in UO1 and UO1W increases with increasing of atomic number of the alkali metals. But, the C1-N2 distance in UO3 and UO3W decreases with increasing of atomic number of alkali metals. The N2-C3 distance in UO1 and UO1W decreases with increasing of atomic number of alkali metals. But, the N2-C3 distance in UO3 and

UO3W increases with increasing of atomic number of alkali metals. The bond strength of C1–N2, N2–C3 is the following order: (UO3)>(UO1).

For the UO1W, UO3W complexes, the largest variations in the ring distances are predicted for the N2–C3 in UO1W and C3–C4 in UO3W. Hydrogen bond formation results in an elongation by 0.04–0.06 Å of the C=O bond.

Thermochemical analysis: Thermochemical analysis is studied for metalated and nonmetalated thymine and its tautomers. The values of ΔH , ΔS and ΔG are reported at 298 K in Table 5. ΔS values are almost the same for all complexes. The equilibrium constants of all complexes are given in Table 5. Which is less for more electropositive metals (compatible with symbiosis effect³⁵). The absolute value of ΔG decreases with increasing metal ion radius which shows that the stability of the complexes decline correspondingly. See Table 5. This is expected since, with metal ion radius increment the bond length increases, as a result the bonding strength decreases. The reaction can be considered as:



The free energy for the formation of UO1.H₂O is more than UO1, but ΔG of UO3.H₂O is less than UO3 without water assistance.

Analysis of vibrational frequencies

The vibrational frequencies have been calculated there at HF level and with the same basis sets that were used for optimization. (See Table 4). In complexes UO1, UO3, UO1W and UO3W $\nu(\text{CH})$ and ring vibrations are rather insensitive to hydrogen bond formation with one water molecule. As we expected, the ν_1 and ν_3 vibrations of water, the $\nu(\text{N6H})$ vibrations of UO3W, and the $\nu(\text{C=O})$ vibrations of the bonds involved in the interaction with one water molecule are red shifted, and the $\gamma(\text{N2H})$, $\gamma(\text{N6H})$ vibrations that are generally strongly sensitive to hydrogen bond formation are blue-shifted. The in-plane deformation vibrations, $\delta(\text{NH})$, are coupled with ring modes. In uracil, the mode calculated at 1647 cm⁻¹ contains $\delta(\text{N6H})$ contributions, and the mode at 1565 cm⁻¹ shows predominate $\delta(\text{N2H})$ character. In UO1W the predominate $\delta(\text{N6H})$ mode appears at 1675(29) cm⁻¹ and one mode at 1561(27) cm⁻¹ involves mainly $\delta(\text{N1H})$ vibrations. The same remarks also hold for the other molecules, and these modes will not be discussed further in this article.

After monohydration, the frequency shift, $\Delta\nu(\text{N6H})$, of the ν stretching vibrations of N6–H is related to the atomic number of the metal:

$$\Delta\nu(\text{N6H}) = \nu_{\text{Hydrated}}(\text{N6H}) - \nu(\text{N6H}) = 107.02 Z^{-1} + 141.83 \quad R^2 = 0.9278$$

Fig. 2 compares the frequency shifts with atomic number of metal.

Conclusions

Therefore in this paper we have shown:

- (1) *Ab initio* calculations indicate that metalation of the oxo group of uracil by the elements of group IA (Li, Na, K, Rb and Cs) stabilise it relative to the nonmetalate form.
- (2) Interaction of alkali metals with O3 is stronger than interaction with O1.
- (3) The stability of metalated uracil increases with increasing of atomic number of metals.
- (4) Theoretical examination of the charge on the metals demonstrates that there is some covalency in the metal-ligand interaction, especially in the Li⁺ system.
- (5) The strongest bonding interactions have been found for metalated uracil with heavy alkali metals.

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References

- 1 G.L. Eichhon, *Adv. Inorg. Biochem.*, 1981, **3**, 1.
- 2 R.B. Martin, *Acc. Chem. Res.*, 1985, **18**, 32.
- 3 H. Sigel *Chem. Soc. Rev.*, 1993, **22**, 255.
- 4 M. Monajjemi, *et al. Main Group Metal Chemistry*. 2002, **25**, 733.
- 5 (a) M. Monajjemi and R. Ghiasi, *Appl. Orgmetal. Chem.*, 2003, **17**, 635; (b) M. Monajjemi and R. Ghiasi, *J. Chem. Res.*, 2003 in press; (c) M. Monajjemi and R. Ghiasi, *Internet Electron. J. Mol. Des.* 2003, **2**, 741.
- 6 I.E. Del Bene, *J. Phys. Chem.*, 1983, **87**, 367.

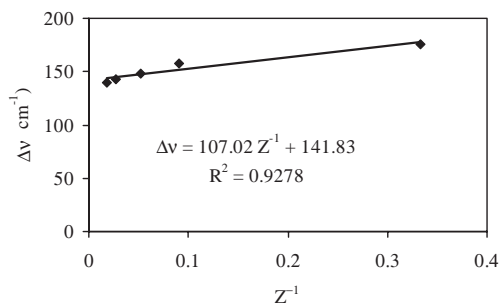


Fig. 2 $\Delta\nu(\text{cm}^{-1})$ as a function of Z^{-1} for NH...O hydrogen bonds in metalated uracil, complexed with one water molecule (UO3W).

- 7 I.E. Del Bene, *J. Phys. Chem.*, 1984, **88**, 5927.
- 8 J.V. Burda, J. Spomer and P. Hobza, *J. Phys. Chem.*, 1996, **100**, 7250.
- 9 M.T. Rodgers and P.B. Armentrout, *J. Am. Chem. Soc.*, 2000, **122**, 8548.
- 10 N.U. Zhanpeisov and J. Leszczynski, *J. Phy., Chem A*. 1998, **102**, 6167.
- 11 J. Spomer and P. Hobza, *J. Phy. Chem.*, 1994, **98**, 3161.
- 12 M. Monajjemi, *et al. J. Mol. Struct (THEOCHEM)*. 2002, **581**, 51.
- 13 J. Spomer, J.E. Spomer, L. Gorb, J. Leszczynski and B. Lippert, *J. Phys. Chem A*. 1999, **103**, 11406.
- 14 M.J. Clarke, *J. Am. Chem. Soc.*, 1978, **100**, 5068 and references there in.
- 15 B. Lippert and H. Schollhorn, *J. Am. Chem., Soc.*, 1986, **108**, 6616.
- 16 (a) F. Pichierri, F. Hoithenrich, E. Zangrando, B. Lippert and L. Randaccio, *J. Biol. Inorg. Chem.*, 1996, **1**, 439.
- 17 J. Muller, E. Zangrdo, N. Pahlke, E. Freisinger, L. Randaccio and B. Lippert, *Eur. J. Chem.*, 1998, **4**, 397.
- 18 J. Muller, F. Glahe, E. Freisinger and B. Lippert, *Inorg. Chem.*, 1999, **38**, 3160.
- 19 S.J. Lippard and J.M. Berg, *Principle of Bioinorganic Chemistry*, University Science Books, Mill Valley, CA, 1994.
- 20 W. Kaim and B. Schwedersky, *Bioinorganic Chemistry: Inorganic elements in the Chemistry of Life*; John Wiley & Sons: Chichester, 1994.
- 21 L.A. Lobew and A.R. Zakour, *In Nucleic Acid-Metal Ion Interactions*; John Wiley & Sons, New York, 1980, pp. 115-144.
- 22 Y.C. Jean, Y.G. Gao and A.H. Wang, *J. Biochem.*, 1993, **32**, 381.
- 23 Gaussian 98, Revision A.6, M.J. Frisch, G.W. Trucks, B.H. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, and J.A. Pople, Gaussian, Inc., Pittsburgh PA, 1998.
- 24 T. Clark, J. Chandrasekhar, G.W. Spitznagel and P.V.R. Schlegler, *J. Comp. Chem.*, 1983, **4**, 294.
- 25 A. Schaefer, H. Horn and R. Ahlrichs, *J. Chem. Phys.*, 1992, **93**, 2571.
- 26 P.J. Hay and W.R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270.
- 27 P.J. Hay and W.R. Wadt, *J. Chem. Phys.*, 1985, **82**, 284.
- 28 P.J. Hay and W.R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299.
- 29 J.E. Carpenter and F. Weinhold, *J. Mol. Struct (THEOCHEM)*. 1988, **169**, 41.
- 30 J.P. Foster and F. Weinhold, *J. Am. Chem. Soc.*, 1980, **102**, 7211.
- 31 A.E. Reed and F. Weinhold, *J. Chem. Phys.*, 1983, **78**, 4066.
- 32 A.E. Reed, L.A. Curtiss and F. Weinhold *Chem. Rev.*, 1988, **88**, 899.
- 33 A.E. Redd, R.B. Weinstock and F. Weinhold, *J. Chem. Phys.*, 1985, **83**, 735.
- 34 I. Alkorta, I. Rozas, J. Eleguero, *J. Mol. Struct (THEOCHEM)*. 2001, **537**, 139.
- 35 J.E. Huheey, E.A. Keiter and R.L. Keiter, *Inorganic Chemistry, Principles of structure and Reactivity*, 4th edn, Harpar and Row, New York, 1994 pp 348-350, 518-519.