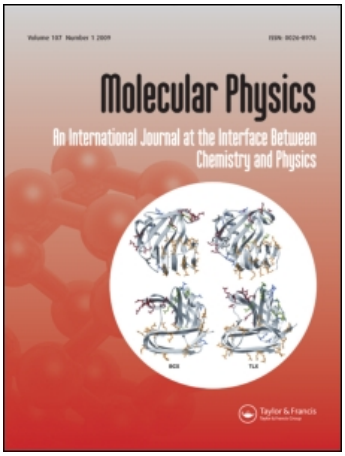

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INVITED ARTICLE

Barrier-free proton transfer induced by electron attachment to the complexes between 1-methylcytosine and formic acid

Yeon Jae Ko[a], Haopeng Wang[a], Dunja Radisic[a], Sarah T. Stokes[a], Soren N. Eustis[a], Kit H. Bowen[a]*, Kamil Mazurkiewicz[b], Piotr Storoniak[b], Arkadiusz Kowalczyk[b], Maciej Haranczyk[c], Maciej Gutowski[d] and Janusz Rak[b]

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We report the photoelectron spectra of anionic complexes between 1-methylcytosine (mC) and formic acid (FA) in 1 : 1 and 1:2 stoichiometries that have been measured with 2.54 eV photons. Each spectrum consists of a broad peak with maxima at 1.85 and 2.1 eV, respectively, confirming the generation of stable valence anions in the gas phase. The neutral and anionic complexes of mC(FA) and $mC(FA)_2$ were also studied computationally at the B3LYP, second-order Møller–Plesset, and coupled-cluster levels of theory with the 6–31++G** and aug-cc-pVDZ basis sets. Based on the calculations, we conclude that the photoelectron spectra of $mC(FA)^-$ and $mC(FA)_2^-$ are due to anions that originate from a barrier-free proton transfer (BFPT) triggered by excess electron attachment. They can be viewed as neutral radicals of hydrogenated 1-methylcytosine solvated by a deprotonated formic acid.

Keywords: anion photoelectron spectroscopy; barrier-free proton transfer

1. Introduction

A decade has passed since Sanche's group discovered that interactions between low-energy electrons (LEEs) and DNA lead to strand breakage in the biopolymer [1]. LEEs, secondary products formed in the course of water radiolysis [2], when attached to nucleic acid bases (NABs), initially induce resonance anions that play a crucial role in the strand cleavage process [3–5]. However, many theoretical [6–18] and experimental works [19–28] suggest that, with the relaxation of these metastable anions, a chance arises to inhibit the cleavage of the C−O sugar-phosphate bond.

On the one hand, anion photoelectron spectroscopy (PES) shows that so-called rare tautomers of NAB anions exist and have a relatively high vertical detachment energy (VDE) of about 2.5 eV for pyrimidine bases [25–28]. These valence anions are products of electron-induced intramolecular proton transfer, i.e. tautomerization. On the other hand, the canonical anions of NABs have been measured and calculated to have negative electron affinities [9,29–37]. From these facts, one can infer that proton transfer may be a key to the stabilization of NAB valence anions and, in consequence, the prevention of possible DNA lesions following electron attachment to the biomolecule.

Indeed, experimental and theoretical research has shown that electron-induced proton transfer leads to the strong stabilization of NABs and other NAB derivatives [25–28,38–53]. Besides the above-mentioned investigations on rare tautomers, our experimental study on the anionic adenosine-5′-monophosphate (5′-AMPH) and 2′-deoxyadenosine-5′-monophosphate (5′-dAMPH) [38] shows that the parent (intact) anions of these species do not undergo a fragmentation in the gas phase, equivalent to the strand breakage in DNA. A computational study conducted at the B3LYP/6–31++G(d,p) level of theory [39] by one of the present authors indicates that the stabilization of the 5′-dAMPH anions occurs as a result of the electron-induced intramolecular barrier-free proton transfer (BFPT). It has been proposed that the excess electron localizes on the π^* orbital of adenine, and triggers proton transfer from

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the phosphate group to the nearest N3 site of the base which leads to the formation of a distonic anion.

A number of studies concerning intermolecular PT induced by electron attachment have been reported, in addition to the above research on intramolecular proton transfer. As a matter of fact, calculations on the adenine–thymine (AT) [54–57] and guanine–cytosine (GC) [57–60] base pairs predicted the existence of stable anions in the gas phase and several experimental studies [40–42] did register the PES signals for $(AT)^-$ and $(GC)^-$ and for other anions of binary complexes involving NABs [43].

In order to mimic the Watson–Crick/Hoogsteen base pairing in a DNA context, the sugar-binding sites of the studied bases are usually methylated. A comparison of the anionic base pair of (9-methyladenine)...(1-methylthymine) (mAmT) [40] with that of (9-methylguanine)...(1-methylcytosine) (mGmC) [41,42] indicates that only in the latter system does the attachment of an electron lead to a strong stabilization of the resulting anion due to a low-barrier PT. Thus, this finding suggests that, in the DNA molecule, electron attachment to the AT base pair rather than to the GC base pair is responsible for the strand breakage.

The role of the interactions between a single NAB molecule and various solvent models such as water [20,61], rare gases [20], inorganic and organic acids [44–48], alcohols [49], and amino acids [50–52] for stabilization of the valence anions of nucleobases has been studied. These works demonstrate that solvation plays a crucial role in the stabilization of an excess electron on the base. It is well known that isolated canonical NABs do not support valence bound anions. However, when they are complexed even by a single molecule (atom), stable valence anions are formed in the gas phase and, as the number of ligand molecules increases, the degree of stabilization also increases. Very recently, we extended our studies on binary complexes comprising a single molecule of NAB to trimers involving a base pair of nucleobases. In fact, we have demonstrated [53] that electron binding to the complex of mAmT with formic acid (FA) induces an intermolecular proton transfer from the carboxylic group of FA to the oxygen atom of mT that leads to a strong stabilization of the resulting radical anion.

The present work is a continuation of our studies on the role of solvation effects on the stability of the valence anions supported by NABs. Here we study, using photoelectron spectroscopy and molecular modelling at the quantum chemistry level, the vulnerability of complexes between 1-methylcytosine (mC) and formic acid when binding an excess electron. In order to mimic the cytosine present in DNA, the C1 sugar-binding site of the base has been methylated. Formic acid, on the other hand, is considered to be a general model of organic acids abundant in living cells. The complexes of mC with FA are studied in 1:1 and 1:2 stoichiometries in order to show how the stability of the mC^- anion increases with the number of solvent molecules. The photoelectron spectra of $mC(FA)^-$ and $mC(FA)_2^-$ were recorded in the gas phase. In parallel, molecular modelling at the B3LYP level was carried out. Since the analysis of anionic species requires a basic knowledge of the corresponding neutrals, the QM description of the anions was preceded by respective calculations for the neutral complexes. Comparison of the experimental peaks' maxima with the calculated VDEs and the stabilities characteristic of the particular anionic complexes allowed our PES experiment to be deciphered.

2. Methods

2.1. *Experimental*

Anion PES is conducted by crossing beams of mass-selected negative ions and fixed-frequency photons and energy analysing the resultant photodetached electrons. This technique is governed by the energy conserving relationship $h\nu = \mathrm{EBE} + \mathrm{EKE}$, where $h\nu$ is the photon energy, EBE is the electron-binding energy, and EKE is the measured electron kinetic energy.

The apparatus has been described previously [62]. The anions of interest were generated in a supersonic expansion, nozzle-ion source, where a mixture of 1-methylcytosine and formic acid was heated to approximately 180°C. Argon gas at a pressure of 1–2 atm was used as the expansion gas, and the nozzle diameter was 25 μm. Electrons were injected into the emerging gas from a negatively biased hot filament in the presence of an axial magnetic field. The resulting anions were then extracted and mass selected with a 90° magnetic sector mass spectrometer. Electrons were photodetached from the mass-selected anions by crossing the ion beam with an intracavity laser beam at ~200 circulating Watts, and energy analysed with a hemispherical electron energy analyser. The typical resolution of the electron analyser is 25 meV, and the photodetachment of electrons was accomplished with 2.54 eV photons.

2.2. *Computational*

Two types of neutral structures were characterized within the current study, i.e. the complexes of 1-methylcytosine (mC) with one or two molecules of formic acid. These geometries will be labelled as

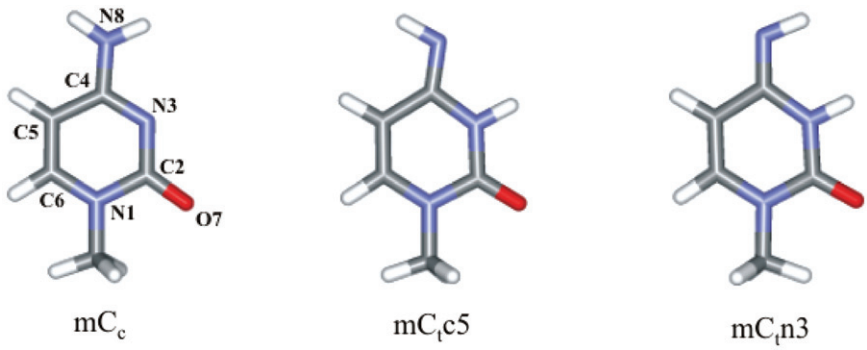

Figure 1. Low-energy tautomers of 1-methylcytosine.

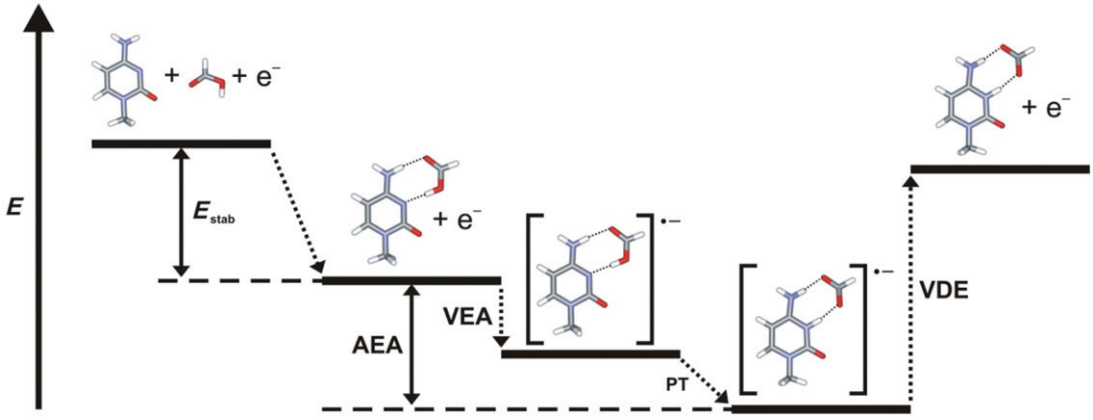

Figure 2. Definition of the stabilization energy (E_{stab}), adiabatic electron affinity (AEA) and vertical detachment energy.

$[mC_c]^y_x$FA/$[mC_ts]^y_x$FA and $[mC_c]^{yw}_{xz}$2FA/$[mC_ts]^{yw}_{xz}$2FA, respectively, where mC_c, mC_t and FA indicate the canonical tautomer of 1-methylocytosine, its imino tautomer (see Figure 1), and formic acid, respectively. 's' indicates one of the two rotamers of mC_t, c5 or n3 (see Figure 1), while *y*,*w* and *x*,*z* represent the proton donor (superscript) and proton acceptor (subscript) sites of methylcytosine, respectively, involved in hydrogen bonding with FA. For example, $[mC_tc5]^{N3}_{N8}$FA denotes a hydrogen-bonded dimer of the mC_tc5 imino tautomer (see Figure 1) stabilized by two hydrogen bonds, in which the N3 atom of the mC tautomer plays the role of proton donor while its N8 atom is a proton acceptor. The symbols for the anions are preceded with 'a', i.e. $a[mC_c]^y_x$FA indicates the *parent* neutral structure $[mC_c]^y_x$FA which the anionic structure is related to. More precisely, the anionic structure $a[mC_c]^y_x$FA is determined in the course of geometry optimization initialized from the optimal geometry for the neutral structure $[mC_c]^y_x$FA. For several anionic structures, the attachment of an electron leads to a proton transfer from formic acid to the mC anion. The names of such anions are augmented with the suffix _pt. For instance, $a[mC_c]^{N8}_{N3}$FA_pt developing from $[mC_c]^{N8}_{N3}$FA due to electron attachment is a result of proton transfer from the acidic hydroxyl group of FA to the N3 site of the canonical mC.

The stabilization energies, E_{stab}, of the neutral complexes are calculated as the difference between the energy of the complex and the sum of the energies of the fully optimized isolated monomers (see Figure 2). Therefore, E_{stab} obtained in this way includes the deformation energies of the monomers. The values of E_{stab} were not corrected for basis set superposition errors because our earlier results demonstrated that the values of this error in B3LYP/6–31++G** calculations for similar adenine(9-methyladenine)–formic acid complexes were smaller than 1 kcal mol^{-1} [47]. In addition to the stabilization energies we calculated the stabilization free energies, G_{stab}. The latter result from correcting the values of E_{stab} for zero-point vibration terms, thermal contributions to the energy,

pV terms, and entropy terms. These terms were calculated in the rigid rotor-harmonic oscillator approximation for $T = 298$ K and $p = 1$ atm.

Electron VDEs—direct observables in our photoelectron spectroscopy experiments—were evaluated as the difference between the energy of the neutral and anionic complex at the geometry of the fully relaxed anion (see Figure 2). The difference in Gibbs free energies of the neutral and the anion at their corresponding fully relaxed structures, i.e. the adiabatic electron affinity, is denoted AEA_G (see Figure 2).

As our primary research method we applied density functional theory (DFT) with Becke's three parameter hybrid functional (B3LYP) [63–65] and the 6–31++G** basis set [66,67]. The usefulness of the B3LYP/6–31++G** method to describe intra- and intermolecular hydrogen bonds has been demonstrated by comparison with the second-order Møller–Plesset (MP2) predictions [68]. The ability of the B3LYP method to predict excess electron binding energies has been reviewed and the results were found to be satisfactory for the valence-type molecular anions [69].

It is known that the B3LYP method underestimates barriers for proton transfer (PT) reactions [70], and thus the lack of a barrier for a PT reaction may be an artifact of the B3LYP method. For this reason, we performed additional geometry optimizations using the MP2 method and the MPW1K exchange-correlation functional, which was parameterized to reproduce barrier heights for chemical reactions [70]. In the MP2 calculations we used aug-cc-pVDZ basis sets [71] while we settled for the 6–31++G** basis set in the MPW1K approach. Finally, to strengthen our conclusion, single-point calculations were performed for the most stable structures of anions and neutrals at the coupled-cluster level of theory with single, double, and non-iterative triple excitations [72] (CCSD(T)/aug-cc-pVDZ) at the optimal MP2 geometries. The open-shell CCSD(T) calculations were carried out at the R/UCCSD(T) level. In this approach, a restricted open shell Hartree–Fock calculation was initially performed to generate the set of molecular orbitals and the spin constraint was relaxed in the coupled-cluster calculation [73–75]. The 1s orbitals of carbon, nitrogen, and oxygen were excluded from the MP2 and coupled-cluster treatments.

All MP2 and DFT calculations were carried out with the GAUSSIAN 03 [76] code and the CCSD(T) calculations with the MOLPRO [77] package on dual Intel Itanium 2 nodes. The pictures of molecules and orbitals were plotted with the MOLDEN program [78].

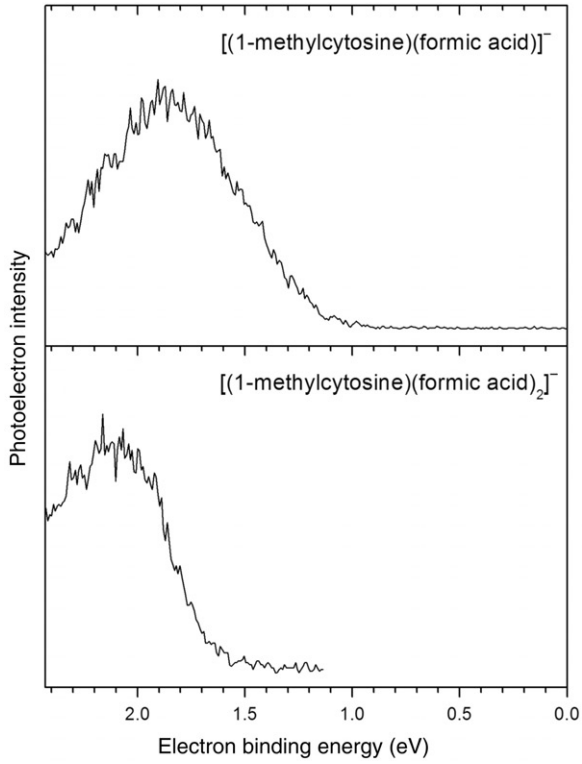

Figure 3. Photoelectron spectra of [(1-methylcytosine)...(formic acid)]$^-$ and [(1-methylcytosine)...(formic acid)$_2$]$^-$ recorded with 2.54 eV photons.

3. Results and discussion

3.1. *PES spectra of anionic complexes between 1-methylcytosine and formic acid*

PES spectra of mC(FA)$^-$ and mC(FA)$_2^-$ are shown in Figure 3. Both consist of a broad band that has an onset at EBEs of about 1.1 eV and 1.6 eV, respectively. The maxima of the PES signals, which correspond to the experimental VDEs, are at about 1.85 eV and 2.1 eV, respectively. These relatively large EBEs prove that stable valence anions are produced under the experimental conditions. Indeed, dipole bound states, the other type of anions characterized within the PES experiments, feature narrow and sharp peaks at substantially lower EBEs, usually under 0.5 eV [19].

Our studies on the anionic complexes of NABs carried out so far [40,44–53] indicate that, in most studied systems, EBEs are measured over 1 eV, with the maximum intensity larger than 1.5 eV. We have demonstrated that such large EBEs are the result of an electron-induced proton transfer process, which leads to the valence-type anionic complex where the excess electron resides in the π^* orbital of the neutral hydrogenated base radical which interacts with the closed-shell anion originating from the deprotonated

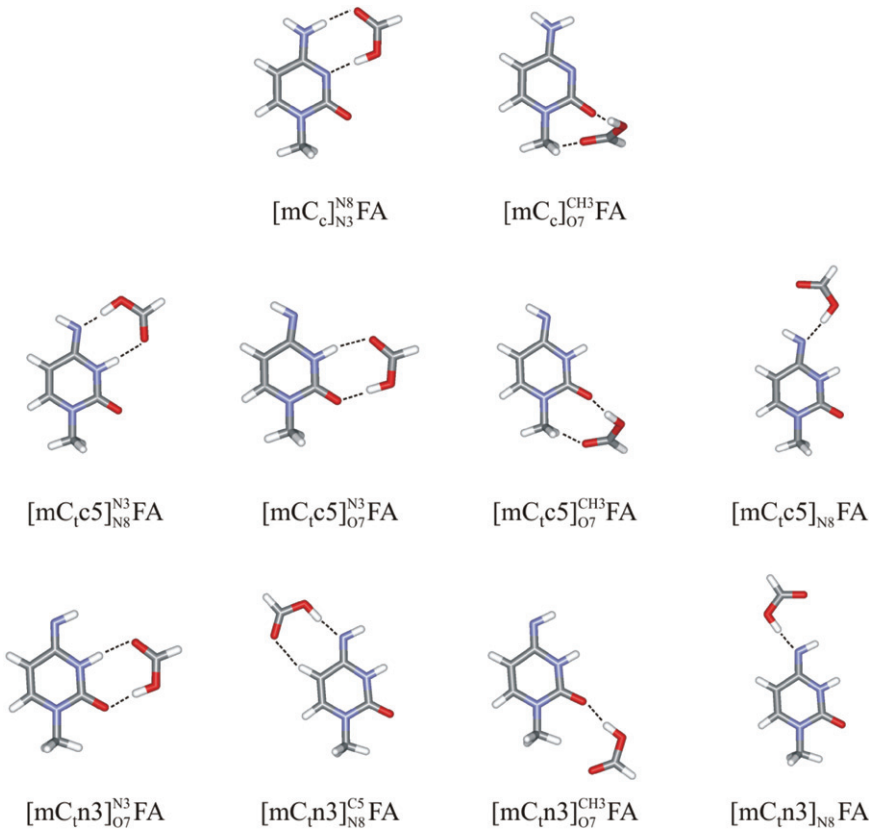

Figure 4. Optimized structures of neutral [(1-methylcytosine)...(formic acid)] complexes.

proton donor [40,44–53]. Hence, the PES spectra depicted in Figure 3 suggest that proton transfer from FA to mC takes place under our experimental conditions.

Moreover, the shift towards higher EBE values of the onset and maximum of the PES signal registered for $mC(FA)_2^-$ (see the spectra presented in Figure 3) reveals that the trimeric complexes are better electron scavengers than the respective dimers.

3.2. *Structures and energetics of the neutral complexes*

In contrast to the neutral uracil [79–83] or thymine [84–86], which do not posses low-energy tautomers, three such low-energy isomers exist for cytosine and two for 1-methylcytosine (see Figure 1). In the latter case these tautomers constitute the amino and imino form of mC (see Figure 1). Furthermore, the imino tautomer of mC may appear as two rotamers, mC_tc5 and mC_tn3, which are depicted in Figure 1. Limiting the considered binary complexes to those that are stabilized by two hydrogen bonds (such structures should be more stable than the complexes stabilized by just one hydrogen bond (HB) and geometries with three or more HBs are not possible for the binary complexes between mC and FA), one can design the 10 complexes depicted in Figure 4. Their energetic characteristics are gathered in Table 1. The stabilization energies of the studied complexes span a range of –17.4 to –9.5 kcal mol^{-1} and –5.1 to 2.8 kcal mol^{-1} in terms of the electronic and free energy, respectively (see Table 1). Furthermore, their relative stabilities differ by about 12 kcal mol^{-1} at most, both on the electronic and free energy scale (see Table 1). The formation of almost all structures is accompanied by a negative change in the free energy, indicating that the development of most complexes is spontaneous in the gas phase at 298 K. The most stable structure, $[mC_c]^{N8}_{N3}FA$, is about 3 kcal mol^{-1} more stable than the second most stable complex, $[mC_tc5]^{N3}_{N8}FA$. Therefore, the equilibrated gas-phase mixture of mC and FA should be dominated by the $[mC_c]^{N8}_{N3}FA$ complex.

The relative stabilities of the binary complexes should correlate with the proton affinities (PAs) and deprotonation energies (DPEs) of the proton donor/proton acceptor centres involved in the stabilizing hydrogen bonds [87]. The largest PA (~237 kcal mol^{-1};

Table 1. Values of the stabilization energy (E_{stab}) and the stabilization free energy (G_{stab}) as well as their relative values (ΔE and ΔG) for the neutral (1-methylcytosine)...(formic acid) complexes calculated at the B3LYP/6–31++G** level. All values given in kcal mol^{-1}.

Complex	E^*_{stab}	ΔE	G_{stab}	ΔG
(1-Methylcytosine)...(formic acid)				
$[mC_c]^{N8}_{N3}FA$	−17.39	0.00	−5.11	0.00
$[mC_tc5]^{N3}_{N8}FA$	−17.13	2.72	−4.49	2.82
$[mC_c]^{CH3}_{O7}FA$	−12.29	5.09	−1.27	3.85
$[mC_tn3]^{N3}_{O7}FA$	−15.50	6.19	−3.75	5.70
$[mC_tc5]^{N3}_{O7}FA$	−12.84	7.01	−0.78	6.53
$[mC_tn3]^{C5}_{N8}FA$	−14.30	7.39	−3.03	6.43
$[mC_tc5]_{N8}FA$	−11.86	7.99	−1.22	6.09
$[mC_tn3]_{N8}FA$	−12.32	9.37	−2.57	6.89
$[mC_tc5]^{CH3}_{O7}FA$	−9.99	9.86	1.76	9.07
$[mC_tn3]^{CH3}_{O7}FA$	−9.52	12.17	2.81	12.27
(1-Methylcytosine)...(formic acid)$_2$				
$[mC_c]^{N8CH3}_{N3O7}2FA$	−28.80	0.00	−5.31	0.00
$[mC_tn3]^{C5N3}_{N8O7}2FA$	−30.17	2.94	−5.20	4.46
$[mC_tc5]^{N3CH3}_{N8O7}2FA$	−27.23	4.04	−3.40	4.11
$[mC_tn3]^{N3}_{O7N8}2FA$	−27.40	5.71	−5.32	4.34
$[mC_tc5]^{N3}_{O7N8}2FA$	−24.96	6.32	−1.75	5.76
$[mC_tn3]^{C5CH3}_{N8O7}2FA$	−23.58	9.53	−0.97	8.69
$[mC_tc5]^{CH3}_{O7N8}2FA$	−21.22	10.05	0.54	8.05
$[mC_tn3]^{CH3}_{O7N8}2FA$	−21.58	11.53	0.02	9.68

Table 2. Proton affinities (PA) of the N atoms and deprotonation energies (DPE) of the NH bonds for selected sites of 1-methylcytosine calculated at the B3LYP/6–31++G** level. All values given in kcal mol^{-1}.

PA		DPE	
Site	Value	Site	Value
mC_c			
N3	232.2	N8 (N3 side)	356.0
mC_tc5			
O7 (N3 side)	205.6	N3	353.2
N8 (N3 side)	235.0	C5	378.1
mC_tn3			
O7 (N3 side)	203.5	N3	345.7
N8 (C5 side)	236.8	C5	385.1

see Table 2) and smallest DPE (~346 kcal mol^{-1}; see Table 2) were predicted for the N8 and N3 atoms of the mC_tn3 tautomer, respectively. Consequently, $[mC_tc5]^{N3}_{N8}FA$ should be the most stable binary structure. In reality, however, $[mC_tc5]^{N3}_{N8}FA$ is the second most stable geometry (see Table 1). The greater stability of the $[mC_c]^{N8}_{N3}FA$ dimer (see Table 1) may be attributed to the relative stabilities of the mC tautomers, which, on the energy scale, change in the order mC_c (0.0 kcal mol^{-1}) > mC_tc5 (2.5 kcal mol^{-1}) > mC_tn3 (4.3 kcal mol^{-1}).

The most stable $[mC_c]^{N8}_{N3}FA$ structure utilizes the proton-accepting N3 atom and proton-donating N8H site (PA = 232.2 and DPE = 356.0 kcal mol^{-1}, respectively—see Table 2). How DPE determines the relative stability of a particular dimer can, for instance, be illustrated by the $[mC_tn3]^{C5}_{N8}FA$ complex, in which formic acid interacts with the proton-accepting imine N8 and the proton-donating C5 site. While the PA of the imine N8 atom is equal to 237 kcal mol^{-1}, which is close to the PA of N3 of $[mC_c]^{N8}_{N3}FA$ (see Table 2), the DPE of C5 is as much as 30 kcal mol^{-1} larger than that of N8 in the most stable geometry (see Table 2), which justifies the predicted stability order (see Table 1). On the other hand, the effect of PA can be illustrated by $[mC_tc5]^{N3}_{N8}FA$ and $[mC_tc5]^{N3}_{O7}FA$. In both structures, FA is bonded to the N3H proton-donor site and they differ by mC's proton-accepting centre. Namely, in $[mC_tc5]^{N3}_{N8}FA$ the imine N8 atom plays the role of proton acceptor, while O7 is a proton-accepting site in $[mC_tc5]^{N3}_{O7}FA$. The PA values of N8 and O7 differ substantially and amount to 235.0 and 205.6 kcal mol^{-1}, respectively (see Table 2). Hence, such a large difference in PA may justify the observed order of stability (see Table 1).

The eight neutral geometries of the complexes between mC and two molecules of formic acid (see Figure 5) were generated in a similar way as that used to design the studied dimers. The formation of these complexes is again in most cases coupled to the negative change in the free energy (see Table 1). As a consequence, they should form spontaneously in the gas phase at 298 K. The most stable is the complex involving the canonical tautomer of cytosine, $[mC_c]^{N8CH3}_{N3O7}2FA$ (see Figure 5 and Table 1). Thus, taking into account the free energy difference between this structure and the second most stable structure (see Table 1), one can suggest that the equilibrated gas-phase mixture of mC and FA is completely dominated by the complex based on mC_c.

The studied neutral trimers can be divided into three groups employing as a criterion the tautomer of 1-methylcytosine. Thus, only one structure belongs to the group of the mC_c tautomer, four structures are present in the group of tautomer mC_tn3 and the group of mC_tc5 consists of three structures (see Figure 5). For dimeric complexes, the relative stability of the trimers within a particular group of conformers is governed by the DPA/PA values of the cytosine sites interacting

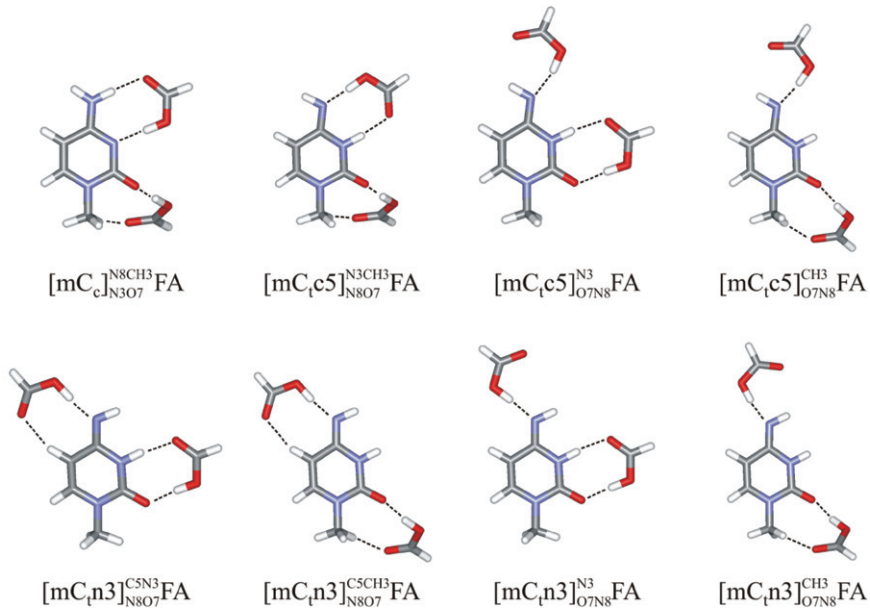

Figure 5. Optimized structures of neutral [(1-methylcytosine)...(formic acid)$_2$] complexes.

with the two molecules of formic acid. Indeed, the [mC$_t$n3]$^{N3}_{O7N8}$2FA structure is more stable than the [mC$_t$n3]$^{CH3}_{O7N8}$2FA structure since, in the former, the carbonyl oxygen of one of the FA molecules interacts with the mC tautomer via its N3–H site while, in the latter, the methyl group of mC, having a much higher DPE than N3–H, is involved in the interaction. For the same reason, [mC$_t$c5]$^{N3}_{O7N8}$2FA is more stable than [mC$_t$c5]$^{CH3}_{O7N8}$2FA.

3.3. *Thermodynamic properties, vertical detachment energies and proton transfer within the anionic complexes*

The present study clearly demonstrates that 1-methylcytosine is capable of forming stable valence-bound anions when it interacts with a relatively strong proton donor. The PES spectra corresponding to those anions may be explained by the theoretically derived characteristics only if a thermodynamic equilibrium attains in the ion source. This assumption allows one to link the characteristics calculated for low-energy anions to the PES spectra.

The attachment of an electron to the binary complexes leads to the formation of adiabatically stable valence anions (see Table 3 and Figure 6). In all cases the excess electron attaches to the π^* orbital localized on the cytosine moiety. Moreover, when formic acid interacts with the N3 atom of the canonical mC or the N8 atom of the imino tautomer, the excess

Table 3. Values of the relative electronic energy and the free energy (ΔE and ΔG) with respect to the most stable anion. The adiabatic electron affinity (AEA_G) and electron vertical detachment energies (VDE) for the anionic (1-methylcytosine)...(formic acid) complexes calculated at the B3LYP/6–31++G** level. ΔE and ΔG values given in kcal mol^{-1}, AEA_G and VDE in eV.

Anion	ΔE	ΔG	AEA_G	VDE (VDE$_{ccsd(t)}$)
(1-Methylcytosine)...(formic acid)				
a [mC$_c$]$^{N8}_{N3}$FA_pt	0.00	0.00	0.93	1.61 (1.53)[a]
a [mC$_t$c5]$_{N8}$FA_pt	1.95	1.31	1.14	1.91 (1.76)[a]
a [mC$_t$n3]$^{C5}_{N8}$FA_pt	4.77	4.81	1.00	2.03
a [mC$_c$]$^{CH3}_{O7}$FA	14.44	12.35	0.56	1.03
a [mC$_t$c5]$^{N3}_{O7}$FA	22.56	22.40	0.24	0.71
a [mC$_t$c5]$^{CH3}_{O7}$FA	22.74	22.05	0.37	0.85
a [mC$_t$n3]$^{N3}_{O7}$FA	23.71	23.71	0.15	0.62
a [mC$_t$n3]$^{CH3}_{O7}$FA	26.50	25.60	0.35	0.78
(1-Methylcytosine)...(formic acid)$_2$				
a [mC$_c$]$^{N8CH3}_{N3O7}$2FA_pt	0.00	0.00	1.11	1.98
a [mC$_t$c5]$^{CH3}_{O7N8}$2FA_pt	2.86	1.18	1.41	2.20
a [mC$_t$n3]$^{C5N3}_{N8O7}$2FA_pt	2.88	3.32	1.16	2.06
a [mC$_t$c5]$^{N3}_{O7N8}$2FA_pt	3.85	3.45	1.21	2.21
a [mC$_t$n3]$^{C5CH3}_{N8O7}$2FA_pt	6.22	5.65	1.25	2.36

Note: [a]CCSD(T) estimates of VDE are given in parentheses.

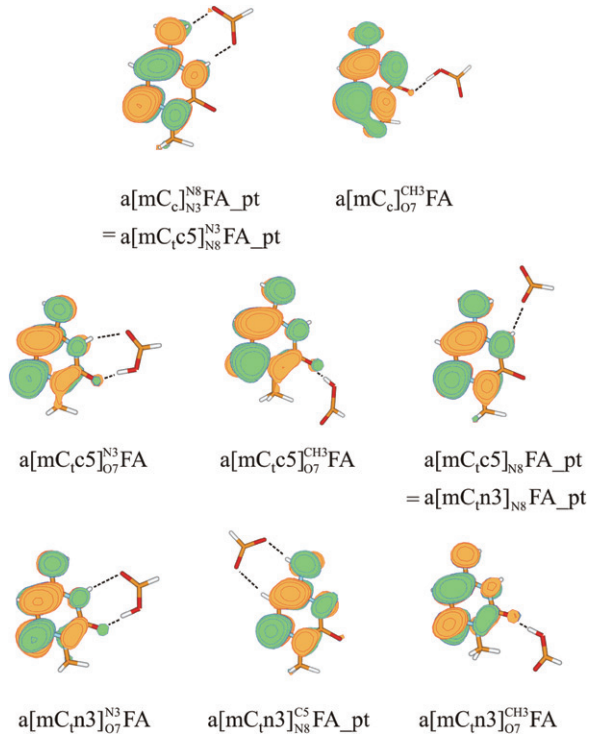

Figure 6. Optimized structures of [(1-methylcytosine)...(formic acid)]$^-$ anionic complexes and their singly occupied molecular orbitals plotted with a contour value of 0.03 bohr$^{-3/2}$.

electron induces a barrier-free proton transfer that leads to additional stabilization. This is why the PT complexes are more stable than their non-PT counterparts (see Table 3). Since the B3LYP method has a tendency to underestimate the kinetic barriers of chemical reactions, we carried out additional MP2 and MPW1K optimizations. The results confirm the BFPT predicted at the B3LYP level.

The anionic stabilities estimated at the B3LYP level suggest that the experimental spectra of mC(FA)$^-$ should feature a broad band with the maximum around 1.8 eV. Indeed, the two most stable anionic structures, a[mC$_c$]$^{N8}_{N3}$FA_pt and a[mC$_t$c5]$_{N8}$FA_pt, should contribute to the shape and position of the experimental spectrum, as indicated by their relative free energies (see Table 3). For the first anion, a[mC$_c$]$^{N8}_{N3}$FA_pt, HCOO$^-$ lies in the plane of the mC radical, while, in the second, a[mC$_t$c5]$_{N8}$FA_pt, it is located out of the mC plane and interacts via its delocalized π-bond system.

The B3LYP VDEs of the two low-energy anions amount to 1.61 and 1.91 eV (see Table 3), respectively. For better accuracy, additional calculations for these geometries were conducted at the CCSD(T) level and the respective values diminished to 1.53 and 1.76 eV, respectively. Note that the latter value reproduces the experimental maximum excellently. In addition, it is worth mentioning that the usage of the correlation equation [47] leads to VDEs that are equal to 1.55 and 1.82 eV, respectively, which also fits well to the spectrum.

The B3LYP calculations carried out for the anionic complexes of 1:2 stoichiometry enabled us to localize five valence-type anions originating from eight neutral trimers (see Table 3 and Figure 7). Similarly to the 1:1 complexes, all trimeric anions are adiabatically stable (see Table 3) and the excess electron is localized on the π^* orbital of 1-methylcytosine (see Figure 7). The attachment of an excess electron induces BFPT in all studied trimers and their stabilities, displayed in Table 3, suggest that only two structures, a[mC$_c$]$^{N8CH3}_{N3O7}$2FA_pt and a[mC$_t$c5]$^{CH3}_{O7N8}$2FA_pt, are present under the experimental conditions. The relative instability of the less-stable structure, with a VDE of 2.20 eV, amounts to 1.18 kcal mol^{-1} on the free energy scale (see Table 3) and indicates that, at 298 K, only 14% of the equilibrated mixture is represented by these anions. Note, however, that the PES maximum was registered at 2.1 eV (see Figure 3), which suggests that the mixture of anions is dominated by the a[mC$_t$c5]$^{CH3}_{O7N8}$2FA_pt rather than the a[mC$_c$]$^{N8CH3}_{N3O7}$2FA_pt anion for the calculated VDE of 1.98 eV (see Table 3). One should nevertheless realize that the relative instability of the mC$_t$c5 tautomer with respect to the canonical form of mC is significantly overestimated in our computational model. Indeed, the energy difference between the mC$_t$c5 and mC$_c$ isomers amounts to 0.2 and 2.5 kcal mol^{-1} at the QCISD(T)/TZV(2df,2pd) [86] and B3LY/6–31++G** level, respectively. Therefore, the free energy difference between the two discussed anionic trimers should be corrected by an increment resulting from the stability difference between the two mC tautomers predicted at the above levels of theory, i.e. by 2.3 kcal mol^{-1}. Accordingly, the ultimate ΔG for the a[mC$_t$c5]$^{CH3}_{O7N8}$2FA_pt anion amounts to –1.12 kcal mol^{-1}. The latter value corresponds to the equilibrated mixture in which a[mC$_t$c5]$^{CH3}_{O7N8}$2FA_pt accounts, at 298 K, for as much as 86% of the total number of anions. Moreover, taking into account the fact that, at the B3LYP level, the predicted VDEs are typically overestimated by 0.1–0.15 eV, the VDE of 2.20 eV calculated for a[mC$_t$c5]$^{CH3}_{O7N8}$2FA_pt (see Table 3) matches well the experimental maximum (see Figure 2).

In contrast to the complexes of adenine with two molecules of FA where the attachment of an electron leads to double BFPT [48] (both formic acid molecules

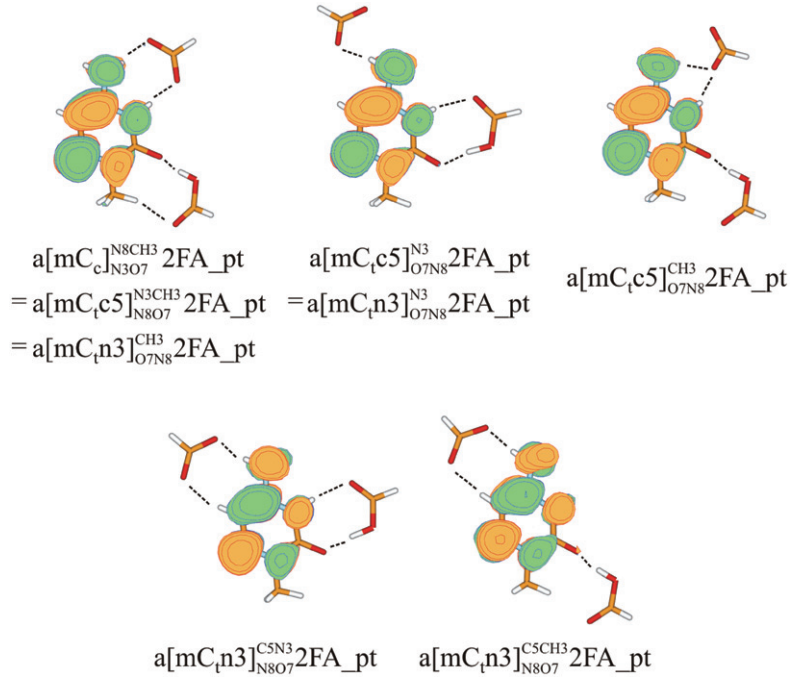

Figure 7. Optimized structures of $[(1\text{-methylcytosine})\ldots(\text{formic acid})_2]^-$ anionic complexes and their singly occupied molecular orbitals plotted with a contour value of 0.03 $\text{bohr}^{-3/2}$.

transfer their proton to adenine spontaneously), an excess electron triggers only single BFPT in $mC(FA)_2$ anions. One of our previous studies on uracil–formic acid ($U(FA)^-$) [46] and thymine–formic acid ($T(FA)^-$) [46] suggests that the asymmetric distribution of the unpaired electron in pyrimidines could be one of several factors responsible for the above difference. Moreover, due to the differences in size between the two types of nucleobases, the excess protons are better separated in purines than in pyrimidines.

4. Summary

The propensity of the neutral complexes of mC(FA) and $mC(FA)_2$ to bind an excess electron was studied using anion photoelectron spectroscopy and computational chemistry. The PES spectra of these complex anions reveal broad bands centred at 1.85 eV and 2.1 eV, respectively, and are well reproduced by the VDE calculated for the low-energy anionic structures. All anionic complexes characterized within this study are the valence-bound anions in which the excess electron is delocalized over the π^* orbital of the NAB moiety. The electron attachment process leads to barrier-free proton transfer from formic acid to one of the proton-accepting sites of 1-methylcytosine. BFPT provides additional stabilization which explains the relatively high VDEs calculated for these anions. Lastly, the hydrogenated neutral radicals of mC, resulting from the BFPT process, may play a critical role in DNA strand breaking.

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