Reaction Mechanism and Dynamics for C8-hydroxylation of 9-Methylguanine Radical Cation by Water Molecules

Wenjing Zhou[a,b] and Jianbo Liu*[a,b]

[a] Department of Chemistry and Biochemistry, Queens College of the City University of New York, 65-30 Kissena Blvd., Queens, NY 11367, USA; [b] Ph.D. Program in Chemistry, The Graduate Center of the City University of New York, 365 5th Ave., New York, NY 10016, USA

Table of Contents

Instrumentation and Experimental Methods

Collision-induced reactions of $9MG^{\bullet+}\cdot H_2O$ were measured on a home-built guided-ion beam scattering tandem mass spectrometer. The apparatus consists of an electrospray ionization (ESI) ion source, a radio frequency (rf) hexapole ion guide, a quadrupole mass filter, an rf octopole ion guide running through a scattering cell, a second quadrupole mass filter and a pulse-counting electron multiplier ion detector. Details of the instrument can be found in previous reports.[1, 2]

$9MG^{\bullet+}\cdot H_2O$ was generated by ESI of Cu(II)-9MG complexes, following the methods reported by the O′Hair group[3-6] and the Bohme group.[7] A 2:1 (v : v) methanol/water solution of 0.25 mM $Cu(NO_3)_2$ (Alfa Aesar, 99.999%) and 0.5 mM 9MG (Chemodex, > 98%) was freshly prepared and sprayed into the air through an ESI needle at a flow rate of 0.06 mL/hr. The ESI needle was maintained at 2.7 kV with respect to the ground. The Cu(II) complexes of 9MG formed in the electrospray entered the source chamber of the mass spectrometer through a desolvation capillary which is located 7 mm away from the tip of the ESI needle. The capillary was biased at 145 V with respect to the ground and heated up to 175 ºC. Charged droplets underwent desolvation as they passed through the heated capillary. The source chamber was evacuated to a pressure of 1.7 τ. A skimmer with a 1.0 mm-diameter orifice was located 3 mm away from the end of the desolvation capillary, separating the source chamber and the hexapole ion guide. The skimmer was biased at 20 V with respect to the ground. The electrical field between the capillary and the skimmer prompted dissociation of Cu^{II}-9MG complexes with the background gas in the source chamber, of which the $9MG^{\bullet+}$ radical cations were formed by the redox separation of $[Cu^{II}(9MG)_3]^{\bullet 2+} \rightarrow [Cu^{I}(9MG)_2]^{+} + 9MG^{\bullet+}$.[3-5, 7] Under mild heating and collision conditions, both dry and hydrated $9MG^{\bullet+}$ ions were produced in the ion beam. The ion beam intensities of $9MG^{\bullet+}$ and $9MG^{\bullet+}\cdot H_2O$ were 1.5×10^6 and 5×10^3 count/s, respectively.

The radical cations were transported into the hexapole ion guide for collisional focusing and thermalization to 310 K, followed by mass selection of $9MG^{\bullet+}\cdot H_2O$ (m/z = 183) in the first quadrupole mass filter. By the combination of collisional damping in the hexapole and reducing the radius of the ion beam at the exit of the first quadrupole, initial kinetic energy of the ion beam was reduced to 0.8 eV with an energy spread of < 0.7 eV (FWHM of a Lorentzian line shape). The mass-selected $9MG^{\bullet+}\cdot H_2O$ reactant radical ions were injected into the octopole ion guide that passes the 10-cm scattering cell containing the Xe gas (Spectral Gases, 99.995%). In addition to generating an rf potential for trapping ions in the radial direction, the octopole was biased at a DC potential of variable amplitude. The DC offset was utilized to adjust the kinetic energy of reactant ions in the laboratory frame (E_{lab}) and thereby control the collision energy (E_{col}) between radical cations and Xe in the center-of-mass frame, *i.e.*, $E_{col} = E_{lab} \times m_{neutral}/(m_{ion} + m_{neutral})$ where $m_{neutral}$ and m_{ion} are the masses of Xe and radical cations, respectively.

The product ions resulting from the collision-induced dissociation and reactions as well as the remaining reactant ions were collected by the octopole, passed into the second quadrupole mass filter for mass analysis, and pulse-counted by the ion detector.

Product ion cross sections were calculated from the ratio of reactant/product ion intensities at each E_{col}, the pressure of Xe in the scattering cell, and the effective cell length. The scattering cell gas pressure was maintained at 0.015 mτ using a leak valve and continuously measured using a MKS Baratron capacitance manometer. At this pressure, $9MG^{\bullet+}\cdot H_2O$ had at most single collisions with Xe, so a thin-target limit (analogous to the Beer-Lambert Law)[8] could be assumed in the calculations of absolute product ion cross sections and reaction energy dependence. The entire measurement was repeated five times to reduce experimental uncertainty.

References

1 Y. Fang and J. Liu, *J. Phys. Chem. A*, 2009, **113**, 11250-11261.
2 Y. Sun, W. Zhou, M. M. Moe and J. Liu, *Phys. Chem. Chem. Phys.*, 2018, **20**, 27510-27522.
3 S. Wee, R. A. J. O'Hair and W. D. McFadyen, *Rapid Commun. Mass Spectrom.*, 2005, **19**, 1797-1805.
4 A. K. Y. Lam, B. F. Abrahams, M. J. Grannas, W. D. McFadyen and R. A. J. O'Hair, *Dalton Trans.*, 2006, 5051-5061.
5 L. Feketeová, E. Yuriev, J. D. Orbell, G. N. Khairallah and R. A. J. O′Hair, *Int. J. Mass Spectrom.*, 2011, **304**, 74-82.
6 L. Feketeová, B. Chan, G. N. Khairallah, V. Steinmetz, P. Maitre, L. Radom and R. A. J. O′Hair, *J. Phys. Chem. Lett.*, 2017, **8**, 3159-3165.
7 P. Cheng and D. K. Bohme, *J. Phys. Chem. B*, 2007, **111**, 11075-11082.
8 P. B. Armentrout, *J. Am. Soc. Mass Spectrom.*, 2002, **13**, 419-434.

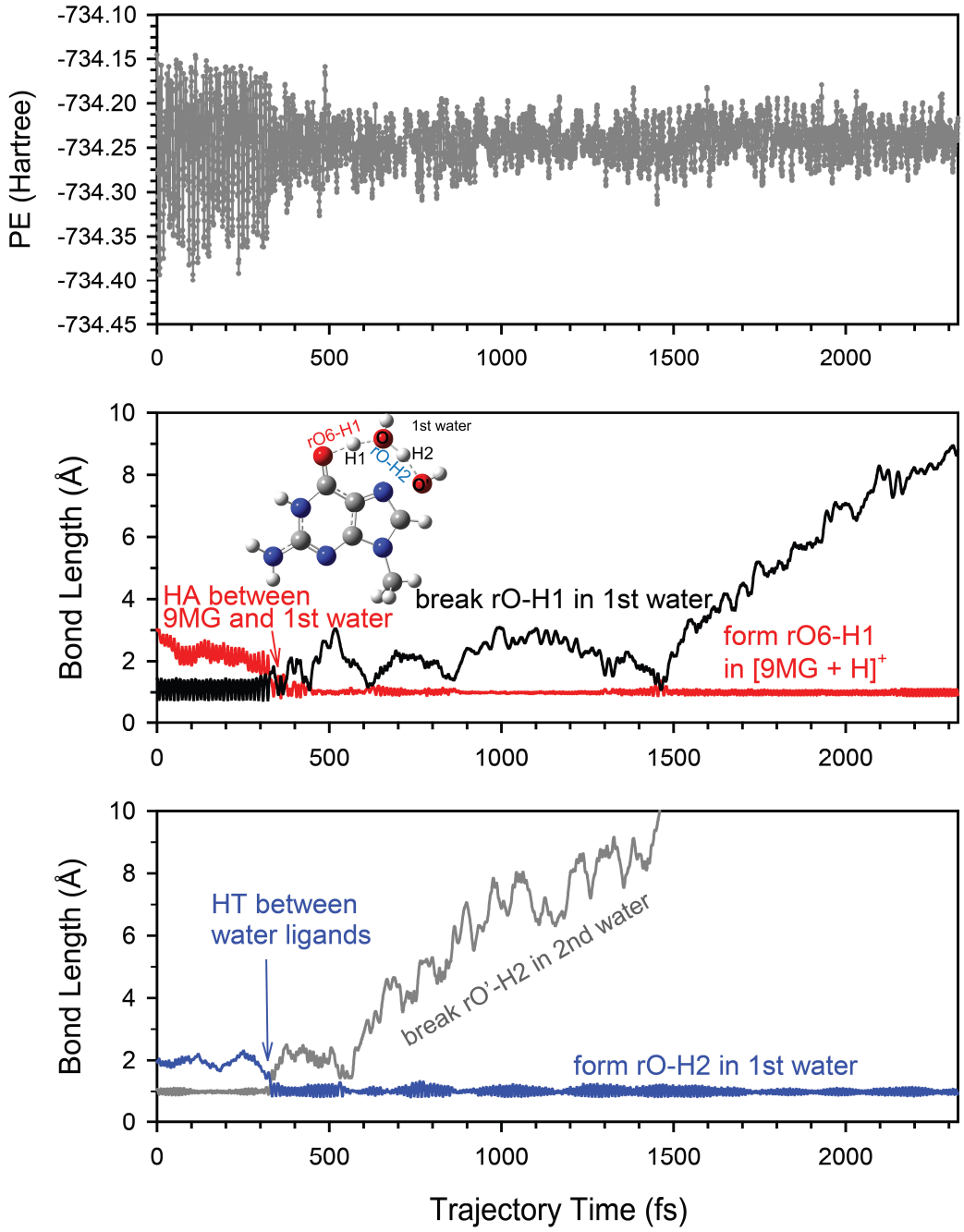

Fig. S1 A trajectory for water-assisted HA_{O6} in $9MG^{\bullet+}\cdot(H_2O)_2$ simulated at 1200 K using the B3LYP/6-31G(d) method. The top frame shows the change of PE, and the middle and bottom frames show the variations of bond lengths that are participating in the reaction. A trajectory video is provided in the Supporting Information.

Cartesian coordinates for structures in Fig. 6, optimized at B3LYP/6-31+G(d,p)

9MG$^{\bullet+}$

C1 1.204426 1.379573 -0.000003
C2 -0.215551 1.038288 0.000001
H3 3.007038 0.367513 -0.000007
C4 1.538965 -1.093398 -0.000005
C5 -2.328112 0.955876 0.000007
N6 2.006751 0.184393 -0.000005
N7 -1.296430 1.818769 0.000004
N8 0.215554 -1.402887 -0.000001
C9 -0.580658 -0.355482 0.000001
N10 2.391552 -2.116381 -0.000007
H11 2.010377 -3.054571 -0.000007
H12 3.396417 -2.003995 -0.000011
O13 1.729698 2.466296 -0.000003
H14 -3.368120 1.257131 0.000009
C15 -2.829089 -1.540815 0.000007
H16 -3.865606 -1.204458 0.000003
H17 -2.636558 -2.137740 0.893112
H18 -2.636553 -2.137747 -0.893091
N19 -1.958066 -0.358287 0.000005

H_2O

O1 0.000000 0.000000 0.116499
H2 0.000000 0.769461 -0.465997
H3 0.000000 -0.769461 -0.465997

9MG$^{\bullet+}$·H_2O

C1 -1.656296 -1.464058 -0.000038
C2 -0.275045 -0.992283 0.000175
H3 -3.545130 -0.625357 -0.000350
C4 -2.219814 0.967060 -0.000198
C5 1.824935 -0.711059 0.000534
N6 -2.566659 -0.349409 -0.000206
N7 0.873187 -1.667608 0.000400
N8 -0.933821 1.399086 -0.000010
C9 -0.041428 0.430639 0.000163
N10 -3.167792 1.904372 -0.000374
H11 -2.877480 2.874178 -0.000358
H12 -4.156813 1.696059 -0.000523
O13 -2.080269 -2.595039 -0.000083
H14 2.895890 -0.891741 0.000697
C15 2.093949 1.815043 0.000559
H16 3.153733 1.559062 0.000081
H17 1.846110 2.392768 0.892975
H18 1.845464 2.393365 -0.891285
N19 1.327717 0.560946 0.000389
O20 4.924466 -0.159735 -0.000828
H21 5.499860 -0.281606 0.767047
H22 5.498560 -0.282291 -0.769566

TS_HA$_{N7}$

C1 -0.125893 -1.643589 0.000050
C2 0.473454 -0.333924 0.000054
H3 -2.035790 -2.412363 -0.000036
C4 -2.253624 -0.343546 -0.000089
C5 1.788486 1.392136 0.000078
N6 -1.547519 -1.521362 -0.000028
N7 1.782202 0.055714 0.000112
N8 -1.667653 0.860228 -0.000085
C9 -0.336482 0.804567 -0.000015
N10 -3.593322 -0.395211 -0.000157
H11 -4.102641 0.477960 -0.000203
H12 -4.116006 -1.258495 -0.000166
O13 0.420938 -2.730397 0.000098
H14 2.680660 2.002473 0.000106
H15 2.737311 -0.636513 0.000164
O16 3.868931 -1.289745 0.000054
H17 3.770401 -2.262279 0.000043
C18 0.135269 3.304152 -0.000052
H19 -0.457207 3.514141 0.891843
H20 -0.457122 3.514095 -0.892014
H21 1.034984 3.918838 -0.000025
N22 0.531891 1.889847 0.000003

[9MG + H$_{N7}$]$^{+}$··· $^{\bullet}$OH

C1 0.477276 -1.477549 -0.000002
C2 0.586272 -0.047924 -0.000001
H3 -1.036678 -2.855149 -0.000005
C4 -1.963064 -0.984154 0.000001
C5 1.238236 2.049231 -0.000002
N6 -0.884874 -1.850685 -0.000001
N7 1.680685 0.794955 -0.000002
N8 -1.828677 0.336800 0.000002
C9 -0.552560 0.741551 0.000000
N10 -3.195840 -1.518721 -0.000002
H11 -3.986099 -0.889710 0.000011
H12 -3.370724 -2.511688 0.000021
O13 1.370771 -2.318825 -0.000005
H14 1.861231 2.931329 -0.000002
H15 2.658685 0.443416 -0.000002
O16 3.854746 -0.922987 0.000007
H17 3.229410 -1.695449 -0.000002
C18 -0.983637 3.244470 0.000000
H19 -1.612413 3.228598 0.891467
H20 -1.612422 3.228592 -0.891459
H21 -0.360775 4.138468 -0.000006
N22 -0.112649 2.060842 0.000000

[9MG + H$_{N7}$]$^{+}$

C1 1.157916 1.401804 -0.000002
C2 -0.214672 0.968391 -0.000002
H3 2.994683 0.483731 0.000002

C4 1.592596 -1.059168 0.000004
C5 -2.414104 0.793718 -0.000004
N6 2.004343 0.258101 0.000001
N7 -1.405474 1.668369 -0.000005
N8 0.312662 -1.418981 0.000003
C9 -0.530179 -0.379129 0.000000
N10 2.537722 -2.014425 0.000007
H11 2.238810 -2.979101 0.000008
H12 3.526229 -1.816073 0.000005
O13 1.595656 2.536135 -0.000004
H14 -3.463343 1.048008 -0.000006
H15 -1.496496 2.678915 -0.000007
C16 -2.694622 -1.709269 0.000001
H17 -2.443351 -2.285990 0.891330
H18 -2.443350 -2.285993 -0.891326
H19 -3.756677 -1.465894 0.000000
N20 -1.921163 -0.459459 -0.000001

•OH
O1 0.000000 0.000000 0.108863
H2 0.000000 0.000000 -0.870904

TS_8OH_H_{N7}
C1 -1.281977 1.474961 -0.083000
C2 0.013775 0.879085 -0.291604
H3 -3.182839 0.793705 0.289988
C4 -1.983348 -0.906258 0.149204
C5 2.152716 0.438456 -0.590457
N6 -2.240405 0.448835 0.132853
N7 1.244574 1.428347 -0.524558
N8 -0.770691 -1.421533 -0.043277
C9 0.176983 -0.506118 -0.254010
N10 -3.010862 -1.740315 0.369684
H11 -2.821354 -2.732583 0.389362
H12 -3.955839 -1.426566 0.530578
O13 -1.576243 2.654539 -0.081574
H14 3.187851 0.561408 -0.866601
O15 2.839204 0.441833 1.602200
H16 1.445339 2.420678 -0.587366
H17 3.526716 1.077365 1.885414
C18 2.175712 -2.061621 -0.400904
H19 1.427074 -2.825198 -0.606648
H20 2.584938 -2.191073 0.603479
H21 2.971916 -2.112595 -1.144167
N22 1.518719 -0.750641 -0.482477

[8OH-9MG + H_{N7}]$^{•+}$
C1 -1.280562 1.489353 -0.036587
C2 0.021666 0.887901 -0.147286
H3 -3.230983 0.854437 0.149978
C4 -2.052863 -0.861902 0.082396
C5 2.283675 0.407455 -0.269314
N6 -2.286502 0.488951 0.074437
N7 1.238670 1.440913 -0.284630
N8 -0.831284 -1.402569 -0.012096
C9 0.167702 -0.534754 -0.122844
N10 -3.097656 -1.690656 0.191261
H11 -2.915787 -2.685117 0.199624
H12 -4.052119 -1.373271 0.274826
O13 -1.549503 2.678429 -0.033585
H14 2.880644 0.448389 -1.189919
O15 3.087537 0.508040 0.861012
H16 1.440527 2.430473 -0.199488
H17 4.008645 0.690275 0.626098
C18 2.088151 -2.144972 -0.189466
H19 1.289791 -2.885416 -0.154485
H20 2.714735 -2.236651 0.701353
H21 2.693509 -2.306597 -1.086219
N22 1.476793 -0.820463 -0.232197

TS_S_N2_H_{N7}
C1 -2.312751 -0.561514 0.000047
C2 -0.955158 -1.034791 -0.000004
H3 -3.244333 1.271427 0.000059
C4 -1.198858 1.666179 -0.000022
C5 0.931219 -2.163494 -0.000050
N6 -2.314787 0.862178 0.000027
N7 -0.419866 -2.296879 -0.000003
N8 0.046770 1.190998 -0.000059
C9 0.127195 -0.149816 -0.000050
N10 -1.373863 2.998890 -0.000033
H11 -0.550904 3.585154 -0.000067
H12 -2.281244 3.439724 -0.000012
O13 -3.345174 -1.206604 0.000094
H14 1.604398 -3.009178 -0.000067
H15 -0.942343 -3.165817 0.000020
O16 4.792598 0.953772 0.000149
H17 5.584791 0.378269 -0.000033
C18 3.117002 -0.009768 -0.000040
H19 3.363260 -0.488544 0.936087
H20 2.623355 0.948181 -0.000187
H21 3.363431 -0.488761 -0.936006
N22 1.297217 -0.887842 -0.000080

7HG$^{•+}$
C1 -0.218521 1.464201 -0.000056
C2 0.825557 0.461100 -0.000013
H3 -2.279216 1.485825 -0.000068
C4 -1.702814 -0.514804 0.000010
C5 2.642363 -0.776230 0.000043
N6 -1.495623 0.837495 -0.000040
N7 2.165001 0.544453 -0.000009
N8 -0.704531 -1.432109 0.000050
C9 0.523574 -0.943917 0.000039
N10 -2.943917 -0.993252 0.000021
H11 -3.057800 -2.001063 0.000058

H12 -3.771931 -0.411992 -0.000005
O13 -0.093055 2.671431 -0.000101
H14 3.705041 -0.982984 0.000056
H15 2.719373 1.395648 -0.000038
N16 1.694503 -1.670727 0.000072

CH_3OH
O1 0.749416 0.122407 0.000002
H2 1.154832 -0.753206 0.000118
C3 -0.667836 -0.020690 -0.000013
H4 -1.030235 -0.545561 0.894472
H5 -1.082708 0.989401 -0.000127
H6 -1.030197 -0.545747 -0.894404

TS_HA_{O6}
C1 0.054639 -1.510573 0.048036
C2 0.571838 -0.208962 0.069456
H3 -1.742464 -2.475694 -0.006381
C4 -2.128996 -0.411546 -0.009396
C5 1.810538 1.540472 0.039424
N6 -1.324501 -1.550178 0.018480
N7 1.868115 0.227713 0.100817
N8 -1.640376 0.818495 -0.016393
C9 -0.300265 0.877423 0.013937
N10 -3.460255 -0.602060 -0.032809
H11 -4.053728 0.214975 -0.056545
H12 -3.894973 -1.511575 -0.022814
O13 0.740761 -2.578453 0.042149
H14 2.657752 2.211364 0.027057
H15 1.908208 -2.236998 -0.042947
O16 2.976978 -1.681468 -0.230850
H17 3.493106 -1.566636 0.589906
C18 0.057668 3.387963 -0.041301
H19 -0.454961 3.639335 0.889344
H20 -0.621679 3.527659 -0.883697
H21 0.928938 4.030751 -0.165896
N22 0.506355 1.991392 -0.004290

$[9MG + H_{O6}]^+\cdots{}^\bullet OH$
C1 0.187629 -1.469464 0.053029
C2 0.603815 -0.143730 0.064963
H3 -1.493355 -2.616444 0.004624
C4 -2.084723 -0.602154 -0.013548
C5 1.645846 1.711846 0.054297
N6 -1.171888 -1.652758 0.020828
N7 1.857927 0.418789 0.099668
N8 -1.711451 0.666894 -0.023467
C9 -0.385479 0.853485 0.011958
N10 -3.391138 -0.919251 -0.039357
H11 -4.058944 -0.161775 -0.069122
H12 -3.738830 -1.865608 -0.032569
O13 0.934792 -2.526447 0.064889
H14 2.413844 2.473272 0.056523
H15 1.926315 -2.227261 0.007964
O16 3.215619 -1.452388 -0.249123
H17 3.758946 -1.163718 0.509912
C18 -0.285836 3.381421 -0.047273
H19 -0.942397 3.531800 0.811620
H20 -0.856185 3.500990 -0.970382
H21 0.522274 4.112194 -0.020903
N22 0.299055 2.037584 0.004563

$[9MG + H_{O6}]^+$
C1 -1.127108 1.243594 0.000517
C2 0.223982 0.974004 0.000117
H3 -2.963849 0.361518 0.001094
C4 -1.509240 -1.150291 -0.000334
C5 2.333151 0.961054 -0.001313
N6 -1.967573 0.162501 0.000467
N7 1.329170 1.798643 -0.000335
N8 -0.220455 -1.450933 -0.000714
C9 0.597469 -0.393020 -0.000742
N10 -2.429825 -2.129999 -0.000532
H11 -2.099775 -3.084964 -0.000746
H12 -3.424771 -1.966499 -0.000364
O13 -1.730398 2.416408 0.001140
H14 3.377939 1.243362 -0.002298
H15 -1.080442 3.142036 0.001064
C16 2.841438 -1.551770 0.003014
H17 2.611714 -2.191745 -0.850759
H18 2.709857 -2.114987 0.929154
H19 3.872303 -1.205461 -0.069504
N20 1.957547 -0.382490 -0.002358

TS_8OH_H_{O6}
C1 -1.190593 1.338350 -0.119772
C2 0.084945 0.842892 -0.298934
H3 -3.120568 0.781876 0.223977
C4 -1.938139 -0.951047 0.141396
C5 2.153853 0.464400 -0.544712
N6 -2.181076 0.418216 0.092721
N7 1.281260 1.468610 -0.519915
N8 -0.729596 -1.466278 -0.018648
C9 0.237862 -0.571440 -0.233550
N10 -2.988555 -1.758661 0.357966
H11 -2.814984 -2.753423 0.401475
H12 -3.931262 -1.429767 0.500409
O13 -1.589326 2.594840 -0.123588
H14 3.187484 0.561362 -0.843274
O15 2.707327 0.631521 1.517713
H16 2.982838 1.559814 1.649915
C17 2.269203 -2.068036 -0.321328
H18 1.537409 -2.874238 -0.358709
H19 2.809085 -2.094790 0.628339
H20 2.968264 -2.170058 -1.153066
N21 1.557350 -0.793423 -0.435245

H22 -0.840740 3.198381 -0.278815

[8OH-9MG + H_{O6}]$^{\bullet+}$
C1 -1.241009 1.356308 -0.039992
C2 0.062616 0.878261 -0.140476
H3 -3.197613 0.779255 0.126409
C4 -1.993947 -0.935782 0.080030
C5 2.240813 0.492858 -0.287920
N6 -2.248611 0.424425 0.062028
N7 1.211724 1.535213 -0.248385
N8 -0.770651 -1.449777 -0.004058
C9 0.222580 -0.565840 -0.111050
N10 -3.042153 -1.763036 0.186204
H11 -2.856194 -2.756750 0.202242
H12 -3.998504 -1.451254 0.265631
O13 -1.640464 2.616624 -0.033381
H14 2.785959 0.559765 -1.241355
O15 3.104018 0.537327 0.807374
H16 3.697903 1.298904 0.729027
C17 2.198840 -2.097203 -0.185901
H18 1.448542 -2.878210 -0.064871
H19 2.901537 -2.117887 0.649794
H20 2.741245 -2.252088 -1.122935
N21 1.522144 -0.804497 -0.213247
H22 -0.877837 3.218761 -0.101822

TS_S_N2_H_{O6}
C1 -2.103352 -0.633669 -0.096536
C2 -0.802429 -1.068647 -0.002823
H3 -3.259554 1.045530 -0.146904
C4 -1.255011 1.631275 0.042353
C5 1.043699 -2.091149 0.112384
N6 -2.299321 0.723031 -0.073995
N7 -0.246274 -2.332153 -0.005251
N8 0.008881 1.253378 0.143626
C9 0.204351 -0.072897 0.125187
N10 -1.567458 2.940683 0.045346
H11 -0.810839 3.603221 0.140000
H12 -2.511173 3.292778 0.002825
O13 -3.208673 -1.349796 -0.204558
H14 1.797966 -2.866378 0.148276
H15 -3.002726 -2.301483 -0.214406
O16 4.586298 0.921376 -0.369564
H17 5.206708 0.255350 -0.728228
C18 3.141995 0.115229 0.203757
H19 2.739213 0.987540 0.693532
H20 2.984056 -0.021351 -0.875040
H21 3.575295 -0.664283 0.812130
N22 1.373391 -0.754141 0.240968

6-*enol*-G$^{\bullet+}$
C1 0.179571 1.343149 0.000005
C2 -0.871958 0.428857 0.000072
H3 2.216687 1.466748 -0.000030
C4 1.662503 -0.562937 -0.000007
C5 -2.644758 -0.737235 0.000017
N6 1.438541 0.811670 -0.000005
N7 -2.192111 0.599614 0.000118
N8 0.680243 -1.474371 -0.000037
C9 -0.547505 -0.990478 -0.000044
N10 2.922770 -0.992720 0.000117
H11 3.070020 -1.996438 -0.000003
H12 3.732817 -0.387322 -0.000222
O13 0.122325 2.651136 -0.000077
H14 -3.707913 -0.944215 0.000027
H15 -0.801198 2.967871 -0.000032
N16 -1.728892 -1.687603 -0.000105

TS_HE
C1 -1.300270 1.511540 -0.048178
C2 0.044609 0.903391 -0.167650
H3 -3.243309 0.865381 0.132345
C4 -2.069806 -0.853151 0.088383
C5 2.172127 0.431497 -0.337245
N6 -2.296587 0.502632 0.060979
N7 1.191495 1.485456 -0.280404
N8 -0.852964 -1.413939 0.013697
C9 0.150423 -0.561958 -0.112963
N10 -3.119636 -1.666511 0.200324
H11 -2.947844 -2.663548 0.222099
H12 -4.073407 -1.340224 0.266005
O13 -1.583746 2.683039 -0.045262
H14 2.741662 0.451813 -1.279137
O15 3.083653 0.585267 0.757551
H16 4.592534 0.286718 0.336851
H17 3.089504 1.524690 1.028839
C18 2.087636 -2.152893 -0.172173
H19 2.708451 -2.276301 -1.063734
H20 1.305373 -2.911286 -0.160312
H21 2.708447 -2.245917 0.722082
N22 1.450695 -0.837400 -0.195224

8OH-9MG^{+} + H
C1 -1.257235 1.556281 -0.039570
C2 0.076222 0.894871 -0.135420
H3 -3.223820 0.986055 0.129255
C4 -2.116204 -0.777346 0.082110
C5 2.194918 0.324400 -0.306689
N6 -2.290280 0.588837 0.065752
N7 1.229587 1.433386 -0.226107
N8 -0.926878 -1.392007 -0.004021
C9 0.118930 -0.588604 -0.106025
N10 -3.198772 -1.544023 0.190345
H11 -3.070015 -2.548018 0.202109
H12 -4.137204 -1.177730 0.268474
O13 -1.490799 2.735994 -0.047912

H14	2.657696	0.373054	-1.304894
O15	3.113430	0.326528	0.723899
H16	5.206798	2.463171	0.326122
H17	3.762114	1.041355	0.600024
C18	1.981644	-2.255427	-0.159907
H19	2.448749	-2.482283	-1.122293
H20	1.188083	-2.974140	0.042000
H21	2.734876	-2.288103	0.630002
N22	1.395205	-0.917419	-0.195352

Cartesian coordinates for structures in Fig. 8, optimized at B3LYP/6-31+G(d,p)

$9MG^{\bullet+}\cdot(H_2O)_2$

C1 -1.173135 -1.677627 0.022499
C2 -0.205547 -0.586331 0.015843
H3 -3.228653 -1.882909 0.009846
C4 -2.860845 0.156847 -0.009736
C5 1.489834 0.699693 0.012944
N6 -2.513148 -1.160614 0.006840
N7 1.126839 -0.604898 0.023486
N8 -1.954931 1.166558 -0.013762
C9 -0.701210 0.765276 -0.001161
N10 -4.147352 0.503759 -0.022888
H11 -4.373858 1.490561 -0.035132
H12 -4.904997 -0.165447 -0.021931
O13 -0.976279 -2.870315 0.039254
H14 2.531193 1.034076 0.015508
O15 4.426282 0.822068 0.084222
H16 2.937025 -1.938714 -0.029455
H17 5.291569 1.206521 -0.098554
O18 3.900216 -1.886822 -0.131742
H19 4.516091 -0.151621 0.025162
H20 4.269807 -2.726942 0.166112
C21 0.471347 3.021294 -0.015710
H22 -0.043795 3.410967 0.863906
H23 -0.009460 3.393954 -0.921828
H24 1.516164 3.329444 0.001939
N25 0.427807 1.553160 -0.001894

$TS(H_2O)\_HA_{N7}$

C1 -0.892980 -1.652809 0.048495
C2 -0.067781 -0.467541 0.075144
H3 -2.904575 -2.077290 -0.064331
C4 -2.758847 -0.003149 -0.082349
C5 1.515032 1.002449 0.168330
N6 -2.270317 -1.284197 -0.040072
N7 1.282412 -0.315308 0.159422
N8 -1.975044 1.081231 -0.044474
C9 -0.674869 0.800251 0.032253
N10 -4.085001 0.179513 -0.164981
H11 -4.432116 1.128374 -0.195359
H12 -4.748689 -0.579582 -0.204743
O13 -0.555599 -2.819522 0.095070
H14 2.506654 1.435278 0.218463
O15 4.391817 0.428678 -0.243069
H16 2.256059 -1.197601 0.097611
H17 5.233114 0.620496 -0.693740
O18 3.268341 -1.770751 -0.076083
H19 3.942021 -0.972967 -0.151699
H20 3.520501 -2.409263 0.606316
C21 0.219514 3.174509 0.080655
H22 -0.373470 3.491619 0.940220
H23 -0.275363 3.486423 -0.840582
H24 1.213169 3.618458 0.133936
N25 0.360209 1.713983 0.091734

$[9MG + H_{N7}]^{+}\cdot H_2O\cdots{}^{\bullet}OH$

C1 -0.027407 -1.441473 -0.083671
C2 -0.020213 -0.006677 -0.077866
H3 -1.445896 -2.919085 0.011932
C4 -2.493371 -1.116911 0.097082
C5 0.488784 2.121699 -0.109594
N6 -1.362582 -1.907147 0.011656
N7 1.013713 0.903880 -0.151122
N8 -2.452563 0.208593 0.100143
C9 -1.207914 0.701305 0.011469
N10 -3.685185 -1.737276 0.181243
H11 -4.514328 -1.164405 0.241728
H12 -3.789896 -2.739620 0.179759
O13 0.916859 -2.217573 -0.155884
H14 1.046639 3.045189 -0.149557
O15 5.941628 -0.078616 0.478827
H16 2.026227 0.596408 -0.227590
H17 6.736128 -0.652883 0.446888
O18 3.241733 -0.437229 -0.402418
H19 4.166284 -0.433736 -0.093711
H20 2.877506 -1.335898 -0.327873
C21 -1.803022 3.167537 0.061425
H22 -2.366223 3.108799 0.994122
H23 -2.491433 3.116683 -0.783638
H24 -1.241335 4.100686 0.025972
N25 -0.860038 2.045139 -0.009821

$TS(H_2O)\_8OH\_HA_{N7}$

C1 -0.605435 1.619756 0.022860
C2 0.205097 0.456983 -0.214876
H3 -2.591230 2.013389 0.338606
C4 -2.442455 -0.055530 0.104722
C5 1.817506 -0.998372 -0.517220
N6 -1.958676 1.237791 0.165937
N7 1.552543 0.309873 -0.398146
N8 -1.667336 -1.113248 -0.107477
C9 -0.373737 -0.813226 -0.257929
N10 -3.762833 -0.238709 0.267822
H11 -4.117609 -1.183997 0.233267
H12 -4.410919 0.513459 0.443971
O13 -0.258417 2.791673 0.102621
H14 2.775017 -1.416944 -0.783116
O15 2.388479 -1.520523 1.616941
H16 2.213006 1.121377 -0.412111
H17 3.120122 -0.980495 1.976912
O18 2.596281 2.748938 -0.204670
H19 3.251445 3.378604 -0.530220
H20 1.749089 3.215562 -0.082718
C21 0.549681 -3.165296 -0.470717

H22 -0.487190 -3.428200 -0.674789
H23 0.847890 -3.534784 0.513034
H24 1.196642 -3.583033 -1.242914
N25 0.656167 -1.701641 -0.485292

[8OH-9MG + H_{N7}]$^{\bullet+}$ ·H_2O
C1 -0.692720 1.595539 0.020594
C2 0.184161 0.462179 -0.089243
H3 -2.713013 1.946458 0.163460
C4 -2.475317 -0.121313 0.063286
C5 1.950735 -1.010179 -0.237462
N6 -2.047705 1.182921 0.090735
N7 1.518199 0.390469 -0.189615
N8 -1.649238 -1.166596 -0.037782
C9 -0.356858 -0.862927 -0.113127
N10 -3.790791 -0.361293 0.140422
H11 -4.098185 -1.324035 0.121391
H12 -4.484685 0.366099 0.227119
O13 -0.391801 2.784049 0.052885
H14 2.499879 -1.207695 -1.168378
O15 2.699826 -1.377492 0.877676
H16 2.141298 1.220034 -0.158845
H17 3.634164 -1.488286 0.650996
O18 2.495814 2.927311 -0.181291
H19 3.189391 3.527562 0.118967
H20 1.638212 3.369880 -0.062261
C21 0.588761 -3.181076 -0.239621
H22 -0.462273 -3.464312 -0.194738
H23 1.118722 -3.585186 0.626209
H24 1.031802 -3.574248 -1.159451
N25 0.666879 -1.724151 -0.230217

TS(H_2O)_HA_{O6}
C1 0.163253 -1.380303 0.087447
C2 0.244297 0.023008 0.080797
H3 -1.219660 -2.870012 0.070782
C4 -2.271585 -1.062417 0.016752
C5 0.775373 2.099101 0.015704
N6 -1.138526 -1.857726 0.073259
N7 1.308511 0.904944 0.099285
N8 -2.208951 0.256210 -0.033596
C9 -0.960987 0.745067 -0.003784
N10 -3.468078 -1.680138 0.009346
H11 -4.295920 -1.103830 -0.038112
H12 -3.579880 -2.680923 0.049908
O13 1.089030 -2.252731 0.100277
H14 1.330668 3.026634 -0.005572
O15 3.571720 0.921762 0.180960
H16 2.199925 -1.898306 -0.122971
H17 3.510468 1.088019 1.141261
O18 3.319474 -1.539813 -0.428952
H19 3.516825 -0.565584 -0.172417
H20 4.050196 -2.127223 -0.193176
C21 -1.514284 3.207991 -0.150654
H22 -2.205565 3.205005 0.694023
H23 -2.078281 3.149489 -1.083519
H24 -0.924882 4.124716 -0.137392
N25 -0.601825 2.065794 -0.048102

[9MG + H_{O6}]$^{+}$·H_2O···$^{\bullet}$OH
C1 -0.125586 -1.383204 -0.088411
C2 -0.243473 0.012212 -0.079554
H3 1.279490 -2.850141 -0.073131
C4 2.296929 -1.022252 -0.018723
C5 -0.816261 2.071844 -0.014063
N6 1.179291 -1.839431 -0.075273
N7 -1.328168 0.869536 -0.098919
N8 2.206502 0.294815 0.034745
C9 0.950147 0.758983 0.006380
N10 3.505024 -1.615848 -0.013965
H11 4.321198 -1.022926 0.033171
H12 3.637517 -2.613993 -0.059491
O13 -1.030943 -2.290054 -0.104954
H14 -1.389270 2.988768 0.006753
O15 -3.629746 0.912925 -0.199300
H16 -2.068829 -1.964822 0.096152
H17 -3.553647 1.057130 -1.162657
O18 -3.290205 -1.596457 0.437355
H19 -3.534124 -0.649488 0.196529
H20 -4.035472 -2.191388 0.284036
C21 1.450072 3.231954 0.157401
H22 2.153682 3.236021 -0.676975
H23 2.001071 3.194598 1.099160
H24 0.841487 4.135596 0.126317
N25 0.563507 2.069801 0.051578

TS(H_2O)_8OH_HA_{O6}
C1 -0.575054 1.483512 -0.010127
C2 0.280993 0.398440 -0.221755
H3 -2.531967 1.937377 0.295759
C4 -2.387283 -0.144876 0.102641
C5 1.874721 -0.993441 -0.487489
N6 -1.902456 1.155592 0.139492
N7 1.638241 0.315521 -0.401984
N8 -1.602500 -1.191008 -0.090664
C9 -0.308832 -0.892772 -0.246968
N10 -3.709332 -0.318948 0.267629
H11 -4.063954 -1.265038 0.255256
H12 -4.355975 0.434024 0.445492
O13 -0.302323 2.745125 0.064275
H14 2.820994 -1.424477 -0.778772
O15 2.390352 -1.322028 1.572976
H16 0.715161 2.950960 -0.043657
H17 3.038899 -0.633917 1.818294
O18 2.176053 3.036845 -0.155801
H19 2.473161 2.131261 -0.384896

H20 2.641169 3.685642 -0.700655
C21 0.657810 -3.218865 -0.419667
H22 -0.383187 -3.522686 -0.522926
H23 1.058266 -3.567939 0.535197
H24 1.242609 -3.629996 -1.244176
N25 0.715768 -1.756407 -0.461091

[8OH-9MG + H_{O6}]$^{\bullet+}$ ·H_2O
C1 -0.914772 1.343988 -0.013688
C2 0.181374 0.469753 -0.123738
H3 -2.947729 1.375060 0.149047
C4 -2.340510 -0.624615 0.069925
C5 2.133887 -0.606408 -0.270862
N6 -2.157560 0.742392 0.071288
N7 1.490235 0.709515 -0.231173
N8 -1.336089 -1.489853 -0.021564
C9 -0.120719 -0.949530 -0.114144
N10 -3.594579 -1.089299 0.162923
H11 -3.725300 -2.091562 0.168928
H12 -4.406355 -0.496841 0.250618
O13 -0.930224 2.640799 0.014781
H14 2.691131 -0.711908 -1.213636
O15 2.953499 -0.847747 0.835889
H16 0.021325 3.065597 -0.013167
H17 3.813893 -0.420060 0.716890
O18 1.434617 3.470729 0.010239
H19 1.914670 2.630252 -0.155068
H20 1.802774 4.176055 -0.538142
C21 1.256686 -3.035646 -0.207649
H22 0.289916 -3.530988 -0.121743
H23 1.889534 -3.298798 0.642722
H24 1.744965 -3.346289 -1.135904
N25 1.036902 -1.593614 -0.221028