magnetometer, which was purchased with the aid of a grant from the National Science Foundation.

Registry No. $[Cu(O_2CCF_3)_2(tempo)]_2$, 100021-75-8; $[Cu(O_2CCCl_3)_2(tempo)]_2$, 100021-76-9; $[Cu(O_2CCBr_3)_2(tempo)]_2$, 100045-26-9; $[Cu(O_2CCl_3)_2(proxyl)]_2$, 100021-77-0.

Supplementary Material Available: Tables of observed and calculated structure factors, anisotropic thermal parameters, distances and angles within the CCl_3 groups, and hydrogen atom coordinates (53 pages). Ordering information is given on any current masthead page.

Contribution from the Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland 20899, and Department of Chemistry, Bar Ilan University, Ramat Gan, Israel

Binding of $Pt(NH_3)_3^{2+}$ to Nucleic Acid Bases

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The ab initio SCF energies for $Pt(NH_3)_3^{2+}$ binding to guanine, adenine, cytosine, and thymine are calculated. A relativistic effective potential is used to represent the core electrons of Pt, and compact effective potentials are also used to replace the core electrons in carbon, nitrogen, and oxygen to simplify the calculation of these large molecules. In order to analyze the bonding, SCF calculations were also done for H_2O, NH_3, imidazole, pyrimidine, 2- and 4-pyrimidone, and several deprotonated anions. The binding is calculated to have a large electrostatic component, but there is a significant contribution from polarization of the base. The valence-all-electron binding energies can be reproduced by an SCF energy for a system where the $Pt(NH_3)_3^{2+}$ complex is replaced by an effective point charge, Z_{eff}. The binding order for all the sites on the nucleic acid bases was calculated by this means after checking the accuracy with all-valence-electron calculations on binding to the N7 and O6 sites on guanine. Force constants were calculated for one-dimensional energy curves between $Pt(NH_3)_3^{2+}$ and selected bases. Valence-all-electron SCF calculations were used to show that chelate bonding of the N7 and O6 sites of guanine to either $Pt(NH_3)_2^{2+}$ or $Pt(NH_3)_3^{2+}$ is unlikely to compete with intrastrand binding of the N7 sites on neighboring guanines.

Introduction

The interest in platinum amines binding to the purine and pyrimidine bases has been inspired by the antitumor properties of these complexes.[1] One of the main goals of such studies is to determine the binding site preferences of the *cis*-$Pt(NH_3)_2^{2+}$ (PDA) moiety. At this time neither the PDA–base bond energies nor even a stability order of binding to different base sites is experimentally available,[2] although a number of monofunctional binding sites have been identified in model systems. Binding is observed to the neutral bases guanine (G), adenine (A), cytosine (C),[3] and thymine (T),[4] as well as to the deprotonated anions.[3,5] The N7 site on guanine, G(N7), has been identified as a preferred site.[6] An intramolecular chelate of the N7 and O6 sites of guanine with PDA has also been proposed,[7,8] although the binding to G(O6) may be through a hydrogen bond.[9]

Quantum-mechanical calculations of the bond energies for Pt–base binding permit an analysis of the type of bonding and competition among the available sites. Binding of PDA to two heterocyclic bases would result in a large and expensive calculation. Since at least three nitrogen sites are bound to Pt in all cases considered, the binding of a single base to $Pt(NH_3)_3^{2+}$ (PTA) was considered a suitable model. This paper will report the details of the electronic structure and interaction energies of the PTA complex interacting with a number of model bases and the nucleic acid bases G, C, A, and T. In addition, the possibility of PDA chelate binding to guanine is examined. An ab initio calculation of the binding of metal cations such as Zn^{2+} to nucleic acid bases has shown that the preferred binding sites can be correctly identified in the free bases.[10]

Relativistic effective potentials (REP)[11] are used to simplify the calculations by eliminating the core electrons. The REP also allow the incorporation of relativistic effects on the valence electrons,[12] which are important in a heavy element like Pt. In addition, the valence-electron basis set for carbon and nitrogen can be compact but still reasonably accurate since they are nodeless.[13] Interaction energy curves for the binding of H_2O, NH_3, imidazole, pyrimidine, 1,2- and 1,4-pyrimidone, guanine, cytosine, adenine, thymine, and several deprotonated species like OH^- to the PTA square-planar complex are obtained in self-consistent-field (SCF) molecular orbital calculations with the

Table I. Binding of $Pt(NH_3)_3^{2+}$ to Bases

base	R_e, Å	D_e, kcal/mol SCF VAL[a]	SCF EFF[b]	ΔE(pol)	ω_e, cm^{-1}
NH_3	2.07_5	72			
H_2O	2.06_0	56.5			560
OH^-	1.90_9	297			870
imidazole (ImH)	1.98_7	100.5	101.5	33.1	387
Im^-	1.94_0	262			430
pyrimidine	2.00_9	83	85.0	32.8	351
2-pyrimidone (O)	2.00	84		22.6	
2-pyrimidone (N)	2.00	99.5			
4-pyrimidone (O) (4-PyH)	2.01_5	77	77.3	23.5	303
$4\text{-}Py^-$	1.91_2	237			372
guanine (N7)	2.00	114	117	37.1	
guanine (O6)	2.00	93	95	25.1	
guanine (N3)	2.00		74		
adenine (N1)	2.00		87		
adenine (N3)	2.00		88		
adenine (N7)	2.00		81		
cytosine (N3)	2.00		104		
cytosine (O2)	2.00		101		
thymine (O2)	2.00		70		
thymine (O4)	2.00		73		

[a] Obtained by using all valence electrons. [b] Obtained by using an effective point charge (q = 1.25) to replace $Pt(NH_3)_3^{2+}$.

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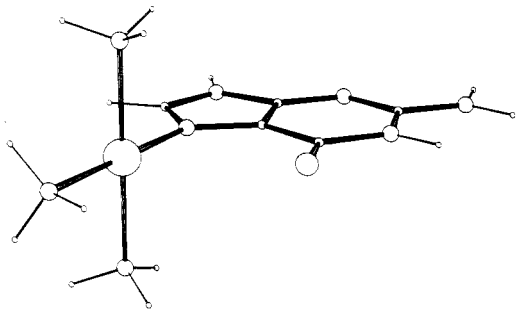

Figure 1. Ligated base sites arranged in a square-planar complex. The base is perpendicular to the plane of the Pt–ligand bonds.

effective potentials. A number of calculations are also designed to examine the likelihood of the guanine N7–O6 chelate. Bidentate binding to these sites is considered for both PDA and PTA.

Details of the Calculation

The REP and the corresponding atomic valence basis set for Pt were taken from Basch et al.[12] For the description of H_2O and NH_3, the effective core potentials (ECP) reported by Topiol[14] were considered adequate. For the heterocyclic bases, a set of more accurate but compact effective potentials (CEP) were generated in this laboratory.[13] These potentials are represented by compact analytic expansions (a single Gaussian for the p potential and two Gaussians for the s potential), but comparative tests between CEP and all-electron calculations for molecules containing first- and second-row atoms have shown that they reproduce all-electron binding energies and optimized conformations for the comparable basis set.[13] The minimum-energy geometries of H_2O, NH_3, imidazole, pyrimidine, and the pyrimidones were separately gradient-optimized. All gradient-optimized geometries are given in the supplementary material. The nucleic acid bases were fixed at experimental geometries.[15] The $Pt(NH_3)_n^{2+}$ (for $n = 2$ or 3) moiety geometry was fixed with 90° N–Pt–N bond angles, tetrahedral conformations about each nitrogen atom, a Pt–N bond length of 2.052 Å, and N–H bond lengths of 1.014 Å. Valence-electron self-consistent-field (SCF) molecular orbital calculations were performed by using the HONDO and GAMESS[17] codes, which have been modified to use effective potentials. Analytic energy gradient optimization of the geometries is a feature of these codes. The valence-electron SCF base binding energies, $D_e(Pt(NH_3)_3^{2+}–X)$, shown in Table I, were obtained from calculations of one-dimensional potential energy curves with frozen fragment (PTA and X) geometries. As seen in Table I, in almost all cases an optimum Pt–base atom distance close to 2 Å was found. The general geometric conformation is shown in Figure 1 for PTA–guanine. All heterocycles were oriented perpendicular to the square-planar complex of PTA, and the bond to the base was oriented along the axis of the nitrogen or bifurcated the oxygen lone pair. For the binding of H_2O, this molecule was kept in the plane of the complex, and the bond between Pt and O bisected the oxygen lone pair. The $Pt(NH_3)_4^{2+}$ complex was oriented to always retain C_s symmetry. All the fragment coordinates necessary to reproduce the calculation are given in the supplementary material. The base sites are given in Figure 2 together with the calculated bond energies and optimized geometries for pyrimidine and 2- and 4-pyrimidone.

The interaction energy was found to be dominated by electrostatic interactions. The extent of the electrostatic contribution to the binding was determined by the following calculations. A point charge was placed symmetrically at 2 Å from the N or O atom of each base, and the interaction energy was calculated with and without SCF relaxation of the base in the field of the charge. The interaction energy without SCF relaxation is simply a measure of the electrostatic potential of the base at the position of the point charge. The optimized SCF energy, which includes polarization of the base, was then fit to a quadratic function of the point charge, Z, and the value of Z that reproduces the valence-all-electron interaction energy of the Pt complex with the base was determined. An essentially constant value of $Z_{eff} = 1.25$ was found for all of the aromatic systems. This value of Z_{eff} for a point charge can be used in SCF calculations in place of the all-valence-electron PTA to probe the energy dependence of small angle variations on arcs of fixed Pt–base atom separation or to calculate monodentate binding at base sites in comparable systems. This was done, for example, to predict the energy

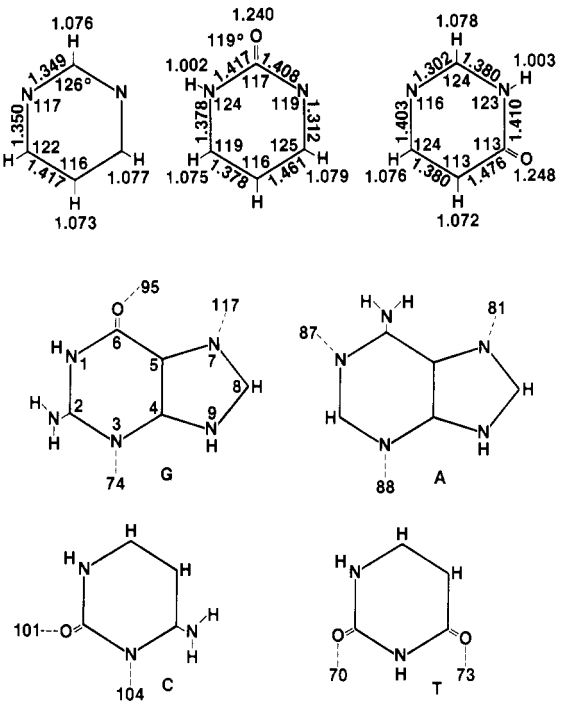

Figure 2. Binding sites on the bases identified together with the binding energy to PTA. The dashed lines indicate the maximum binding is in the vicinity of the maximum density for the lone-pair electrons. In the cases of pyrimidine and 2- and 4-pyrimidone, the gradient-optimized geometries of the base are also given.

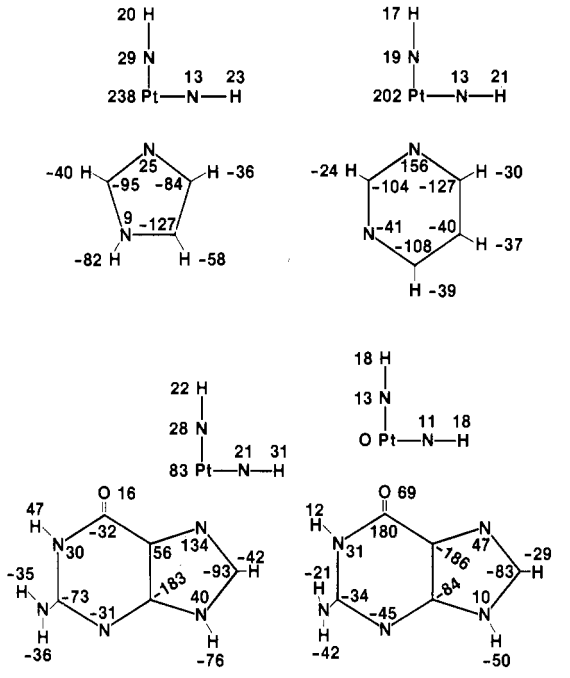

Figure 3. Mulliken population shifts upon binding of PTA complexes with imidazole, pyrimidine, and guanine (at both N7 and O6 sites). The populations are given in millielectrons.

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Table II. Orbital Energies for Pyrimidine (eV)

σ orbitals	calcd[a]	calcd[b]	σ orbitals	calcd[a]	calcd[b]
12	36.57	36.79	6	19.15	19.17
11	33.25	33.40	5	18.18	17.80
10	29.82	29.72	4	16.41	16.22
9	24.76	24.60	3	16.33	16.03
8	24.62	24.43	2	12.73	12.57
7	20.43	20.23	1	11.07	10.99

π orbitals	calcd[a]	calcd[b]	exptl[b]
3	15.81	15.90	
2	11.56	11.58	
1	10.50	10.39	10.5

[a] Present work. [b] Reference 19.

of binding at O2 in 2-pyrimidone after the model was checked at O4 in 4-pyrimidone.

The constant-point-charge model can be justified only if the Pt complex interaction with the bases involves either no charge transfer, the same amount of charge transfer regardless of the binding site, or charge-transfer differences exactly cancelled by exchange repulsion differences. A Mulliken population analysis can give some measure of charge movement, but it can be very misleading if used to quantify charge-transfer effects. Examination of the Mulliken populations in Figure 3 reveals small but significant increases in population on the metal. However, this increase is entirely in the 6s and 6p diffuse orbitals located on the metal, which renders the interpretation ambiguous. When the population increase at Pt is calculated for the linear approach along the carbonyl bond (in guanine or pyrimidone, for example), the population change on the metal is found to be essentially zero. Since this geometry minimizes the overlap of the metal orbitals with the oxygen lone-pair orbitals, the superposition error is avoided. This suggests that any actual charge transfer in these systems is small. The Pt d orbitals are predominantly localized and weak bond/antibond orbital pairs are formed with the ligands. Polarization, on the other hand, is significant and may be calculated within the point-charge model as the difference between the point-charge interaction energy before and after SCF relaxation of the base. The polarization contribution to the interaction energy for the model bases ranged from 30% for binding at O2 in 2-pyrimidone to over 50% for binding and N1 in pyrimidine, as seen in Table I. Because of the aromatic character of the molecules, the population shifts due to polarization are not localized to the binding site, suggesting possible synergistic effects on hydrogen bonding[18] or even induced deprotonation at nearby sites.

The accuracy of the orbital energies calculated with the CEP is shown to be good by comparing the pyrimidine values in Table II with those reported in an accurate all-electron calculation[19] where the molecular orbitals and ionization potentials are described in detail. With Koopmans' Theorem for these closed-shell systems, the orbital energies of the nucleic acid bases can be related to the observed ionization potentials.[20-24] However, definitive assignment of the photoelectron spectra would require evaluation of both the cation relaxation energy and the differential correlation energy between neutral and ionized species. Only the highest orbital energies compare well with experimental energies. The CEP highest orbital energies, from the $\pi 1$ orbital, for the bases G, C, A, and T are 7.84, 9.21, 8.76, and 9.59 eV, respectively, which are to be compared to the experimental vertical ionization potentials of 8.30,[23] 8.82,[22,23] 8.48,[24] and 9.20 eV,[20] respectively. Since the molecules are heated to obtain an adequate vapor pressure, the Franck–Condon envelopes are quite broad. The experimental assignments all agree that the ground state of all the bases arises from ionizing a delocalized $\pi 1$ orbital with substantial contributions from the exocyclic heteroatoms where present. In fact, in the case of cytosine, the dominant atomic contribution to the orbital is on O2.

Analysis of the Binding Energy

Binding energies have been calculated for interactions of the Pt-fragment complex or effective point charge with all the lone-pair sites in guanine, adenine, cytosine, and thymine. In order to assess the effect on binding at a given site of a nearby substituent in the bases G, A, C, and T, calculations were also carried out on the bases imidazole, pyrimidine, 2-pyrimidone, and 4-pyrimidone as models for the purine/pyrimidine bases. The N7 site on guanine and adenine is modeled by N3 in imidazole, for example. The interaction sites are described in Figure 2. All the binding energies reported in the figure were calculated by the point-charge approximation. The binding energies for G(N7) and G(O6), determined by valence-all-electron calculations including the Pt complex, agree with the point-charge calculations to within 3 kcal (Table I).

It is clear from the electrostatic potential maps of Pullman et al.[25,26] that the carbonyl group in guanine enhances the basicity at G(N7) while the amino group in adenine reduces the basicity at A(N7). As seen from Table I, the calculations support the conclusions drawn from a study of the electrostatic potential and show the G(N7) binding increasing by 17 kcal and A(N7) decreasing by 19 kcal, relative to binding at imidazole (N3) (100 kcal). In fact, the ordering of the binding energies predicted by the electrostatic potential energy well depths generally agrees with the SCF-calculated order in Table I. Polarization contributions are large (Table I), nonetheless, and change the order of binding in some of the model bases. For example, the energy of binding at N in pyrimidine at the electrostatic level is incorrectly predicted to be smaller than that at O in 4-pyrimidone. In addition, the positions of the wells predicted by electrostatic potential maps do not reflect the repulsive interaction between the base lone pair and the charge distribution of the complex.

Large binding energies are calculated for N3 and O2 sites in cytosine, which are reflected by the electrostatic potential map. These binding energies are comparable to the N and O binding energies in 2-pyrimidone, which can serve as a model for cytosine. Surprisingly, even for the N site, which is closest to the amino group in cytosine, the 2-pyrimidone and cytosine values are similar. Apparently, replacing an H atom by an amino group has only a small effect on the lone-pair binding site at N3.

Binding of the Pt complex to H_2O allows an estimate to be made of the exothermicity of the replacement of this ligand by one of the bases. Since the PTA–OH_2 binding is only 56.5 kcal, the exothermicity is large and suggests that excess energy is available to make bonds conformationally less than optimal or to distort the DNA framework.[27] Since water is a smaller ligand, solvation is likely to increase the effective binding of the water to the complex relative to the binding of the nucleic acid bases. This may explain the paucity of observation of single-site binding to neutral thymine,[4,5] where the calculated excess binding energy relative to water is small.

Binding of Pt complexes to monoanions of thymine has been reported,[5] and deprotonation for guanine has been discussed in terms of its implications in base mispairing.[28] The hydroxo anion is found to bind very strongly to metal cations because of its small size.[29] Binding of the Pt complex to the deprotonated bases imidazole (Im^-) and 4-pyrimidone ($4\text{-}Py^-$) was investigated to show the effects of the size of the base relative to OH^- on bond distances and energies. The largest decrease in R_e is found for OH^- relative to H_2O, but the R_e for oxygen in $4\text{-}Py^-$ is only 0.003 Å larger. Nonetheless, the binding to the $4\text{-}Py^-$ anion is 60 kcal less than binding to OH^- while the binding to the neutral base, 4-Py, is 21 kcal larger. The binding energy of Pt complexes to the aromatic

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Table III. Energy Dependence on the Angle (θ) about Ligated Atom X in $Pt(NH_3)_3^{2+}$–L[a]

θ, deg	energy, kcal	
	pyrimidine	4-pyrimidone
−30		−2.9
0	0.0	0.0
10	0.9	
20	3.5	
30	7.9	−3.4
60		0.6

[a] θ is defined with the following constraints: The pyrimidine ring is perpendicular to and bisects the ligated atoms. The 4-pyrimidone ring lies in the plane of the ligated atoms.

anions is reduced by the delocalized nature of the anion charge, which leads to a smaller Coulombic attraction. The Mulliken atomic population on oxygen in OH^- is about 0.7 greater than that for 4-Py^- in the bound complex. An analogous reversal of binding energies for the neutrals relative to those of the anions occurs for imidazole when compared to water.

The R_e values obtained from the one-dimensional interaction energy curves are given in Table I. The R_e are in a range normally found in Pt compounds,[30-33] but no experimental values have been reported for the $Pt(NH_3)_3^{2+}$ complexes reported here. No attempt has been made to determine the complete multidimensional potential surface in the vicinity of the nucleophilic sites, so it is not known whether the energy minimum along the calculated line is a true minimum in the hypersurface.

In addition to the R_e values, force constants have also been calculated for the one-dimensional curves. Approximate frequencies calculated in the point-mass approximation are also given in Table I for the Pt–X (X = O or N) stretch. There are no completely analogous experimental results. A Pt–guanine (N7) stretching band in the region 340–360 cm^{-1} has been identified in the Raman spectra of Pt–nucleoside complexes.[34] The Pt–imidazole bond-stretching vibration of 387 cm^{-1} is most comparable to that in guanine. The calculated bond energy of PTA to imidazole is large (100 kcal) but still smaller than the value for G(N7) binding (117 kcal). The proportionately larger force constant for guanine is offset by the larger mass. Considering the simplicity of the point-mass approximation, the estimated frequency of 322 cm^{-1} compares reasonably with the experimental band frequency.

The accuracy of the calculation is limited by both the use of an SCF calculation to determine the energy curve and the use of a one-dimensional curve to approximate the interaction. The calculated value should be considered as indicative of the frequency range only. Pt–O stretching frequencies are not reported in the only example of Pt(II) complexes containing terminal H_2O and OH ligands.[35]

Because of the many geometric constraints, binding of *cis*-$Pt(NH_3)_2^{2+}$ to the bases in DNA may not occur in an optimal conformation. The bond should be along the axis of the lone-pair electrons or should bifurcate a pair of lone pairs for maximum binding. However, these calculations suggest that the energy surface in the vicinity of this optimal conformation is not very steep. The deviation of the Pt–Py(N) bond from the optimum line along the N3 lone pair in the $Pt(NH_3)_3^{2+}$–Py complex was varied up to 30° in the plane of the pyrimidine. The bond energy variation is shown in Table III, and it is seen to decrease by only 8 kcal at 30°.

The energy variation as a function of bending in and perpendicular to the molecule plane in binding to the carbonyl oxygen in the 4-pyrimidone was also explored with an effective-charge calculation. The energy minimum in the plane for this system corresponds to a 30° bond away from the line of the carbonyl bond in the direction of the adjacent carbon. This conformation is about 3 kcal more stable than an approach along the carbonyl bond. Bending toward the adjacent nitrogen yields a slightly flatter surface because of the larger positive charge on the H6 atom. In either direction, though, the energy variation is small compared to the total bond energy. These results suggest that strained bonds with DNA could be formed without much loss of energy.[27]

Significant variation in the structure of the base to accommodate binding of the complex does not occur very readily. The possibility of binding to the exocyclic amino group in cytosine is often suggested, but our calculations do not support such binding. In order to maximize binding to the lone pair on N, the amino hydrogens were rotated out of the plane into a tetrahedral binding orientation. However, this distortion requires 40 kcal. Although the binding to the prepared (tetrahedral) site is high, about 100 kcal, the net binding energy including the energy required to distort the amino group does not yield a bond as strong as any given in Table I for an aromatic base.

Bidentate bonding of the platinum complex to N7–O6 in guanine has been suggested,[7,8] but Raman spectra have not yielded evidence for such bonding.[36] Calculation of the binding of PTA at a point approximately 2.0 Å equidistant from N7 and O6 yields values of 78 and 64 kcal, respectively, for square-pyramidal and trigonal-bipyrimidal conformations. In these conformations the system is five-coordinate, and an additional antibonding contribution is found relative to the four-coordinate square-planar arrangement.

Bidentate binding of the PDA complex in the plane of N7 and O6 with a 2.0-Å Pt–N7 bond that is bent 30° from the C6=O6 bond in the direction of N7 yields a bond energy of about 160 kcal. Although this energy is large, it is substantially smaller than the value that would be obtained for simultaneous binding to two guanines at the N7 sites. It is this binding to adjacent guanines in DNA with which the intramolecular bidentate arrangement must compete. These calculations were done with all the valence electrons. The effective-charge method is inappropriate in this case since the charge interacts with both binding sites and the model no longer incorporates the appropriate repulsive interactions.

Concluding Remarks

The calculated binding order (Table I) for PTA is found to be G(N7) (117) > C(N3) (104) > C(O2) (101) > G(O6) (98) > A(N3) (88) ≃ A(N1) (87) > A(N7) (81) > G(N3) (74) > T(O4) (73) > T(O2) (70), with the binding energy (kcal/mol) given in parentheses. These values were used to determine that binding to a tetramer of double-stranded DNA is calculated to be intrastrand with PDA preferentially binding to G(N7) on neighboring guanines.[27] The strong binding sites calculated for cytosine are not normally accessible in double-stranded DNA. The calculated binding energies indicate the reaction of PDA with DNA is significantly exothermic, possibly disrupting the DNA or, once the DNA is bound, making it difficult to repair the lesion.

Bifunctional binding to the G(N7) and G(O6) sites was calculated to be unfavorable. This calculation does not rule out monofunctional binding of Pt to G(N7) and hydrogen bonding of a ligand to G(O6).[7,36] Since the Pt bonds are calculated not to be rigid with respect to angle variation, it is likely that hydrogen bonds are formed readily. If the ligand is OH^-, calculations find that the H-bond energy of adjacent ligands is large (~13 kcal) and the bond angles are significantly distorted.[37]

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Registry No. PTA, 99924-19-3; PTA-NH_3, 16455-68-8; PTA-OH_2, 17524-19-5; PTA-OH, 97732-33-7; PTA-ImH, 99924-20-6; PTA-Im, 99924-21-7; PTA-4-PyH, 99924-25-1; PTA-4-Py, 99924-26-2; PTA-pyrimidine, 99924-22-8; PTA-2-pyrimidone (O), 99924-23-9; PTA-2-pyrimidone (N), 99924-24-0; PTA-guanine (N7), 99924-27-3; PTA-guanine (O6), 99924-28-4; PTA-guanine (N3), 99924-29-5; PTA-adenine (N1), 99924-30-8; PTA-adenine (N3), 99924-31-9; PTA-adenine (N7), 99924-32-0; PTA-cytosine (N3), 99924-33-1; PTA-cytosine (O2), 99924-34-2; PTA-thymine (O2), 99924-35-3; PTA-thymine (O4), 99924-36-4.

Supplementary Material Available: Tables showing atomic charges and coordinates (8 pages). Ordering information is given on any current masthead page.

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Azolate Complexes of Nitrosyl(protoporphyrin IX dimethyl esterato)iron(II)

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Nitrosyl(protoporphyrin IX dimethyl esterato)iron(II) (Fe(PPIXDME)(NO)) complexes with various azolates as a trans axial ligand have been prepared in solution, and their EPR and electronic spectra have been measured at room temperature and at 77 K. The apparent EPR line shape of Fe(PPIXDME)(NO) complexes with azolates resembled that of the complexes with neutral azoles, while significant differences were found in EPR parameters. The basicity of the coordinated azolates is estimated from the EPR g values of the azolate complexes on the basis of the approximately linear relationship between g values and the basicity ($pK_a(BH^+)$) of azoles. The Soret band in the electronic spectra of Fe(PPIXDME)(NO) complexes with azolates was red-shifted compared to those of the azole complexes. These results are discussed in relation to the dissociation of the $N_\delta H$ proton in proximal histidyl imidazole in hemoproteins.

Introduction

The imidazole group of histidine residues is coordinated axially to heme iron in the majority of hemoproteins. The hydrogen bonding of the axial imidazole $N_\delta H$ proton to amino acid residues of the polypeptide chain leads either to fractional deprotonation or to complete deprotonation or imidazolate formation.[1] It has been suggested that such histidyl imidazolate is present in several hemoproteins.[2-5] Both the ferrous and ferric porphyrin complexes as model systems for hemoproteins have been investigated in order to clarify the differences between axial imidazole (ImH) and imidazolate (Im^-) in bonding ability to heme iron.[6-15] These studies have demonstrated that the imidazolate has greater σ-donor ability than the imidazole. However, the magnitude of change in basicity from imidazole to imidazolate has not yet been shown.

In preceding papers, we have reported EPR, IR, and electronic spectral studies on nitrosyl(protoporphyrin IX dimethyl esterato)iron(II) (Fe(PPIXDME)(NO)) complexes with various N-, O-, and S-donor bases (B) as an axial ligand trans to a nitrosyl group.[16-20] It was shown that these spectral parameters are dependent upon the electronic and stereochemical properties of the axial ligands, and in particular, the g values and NO stretching frequencies (ν_{NO}) in the complexes with unhindered imidazoles and pyridines vary linearly with the basicity of the base ($pK_a(BH^+)$).[21] During the course of these studies, we have found that Fe(PPIXDME)(NO) complexes with azolates are formed by the reaction of NO with the systems consisting of (protoporphyrin IX dimethyl esterato)iron(II) complexes with various azoles and tetraalkylammonium hydroxide. The present work reports on attempts to estimate the basicity of the azolates from the EPR g values of the complexes thus formed and to elucidate the bond strength of the iron to axial ligands.

Experimental Section

Materials and Methods. Fe(PPIXDME)Cl and Fe(PPIXDME)(NO) were prepared as described before.[22,23] Nitric oxide, purchased from Takachiho Trading Co., was passed through a KOH column to remove higher nitrogen oxides. The azoles were obtained commercially. The liquid bases were distilled by flowing N_2 under reduced pressure, and the solid bases were recrystallized or sublimed. All the solvents were dried and distilled by usual methods. The solvents and liquid bases were deoxygenated by bubbling with pure N_2 prior to use. Tetramethylammonium hydroxide (2.7 M) and tetrabutylammonium hydroxide (0.40 M) in methanol were purchased from Eastman Kodak Co. and Tokyo Chemical Industry, respectively. All other chemicals used were obtained as the best available grade and were used without further purification.

EPR measurements were carried out on a JES-ME-3X spectrometer with 100-kHz field modulation at about 20 °C and at 77 K, which was calibrated with a Takeda-Riken frequency counter Model TR-5211A and 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical powder (g = 2.0036) and

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