strongly on spin changes. The hydrogen-bonding effects seem to be more important in kinetics than in thermodynamics.

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A Picosecond Study of Rapid Multistep Radiationless Decay in Manganese(III) Porphyrins

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Picosecond transient absorption studies of two Mn(III) porphyrins in coordinating and noncoordinating solvents have revealed two resolvable transient states in each case. The lifetimes of the transients are ≤30 ps and 80 or 140 ps, the faster component being instrument-limited and the slower one depending on the complex. We attribute the transients to the two lowest energy tripmultiplet states that arise from coupling of the ring (π,π^*) triplet and the unpaired metal electrons. The rapid deactivation of both tripmultiplets probably proceeds via lower energy CT or (d,d) excited states.

Introduction

Manganese(III) porphyrins[1] are generally considered to be nonluminescent,[2,3] although a weak ($\phi \sim 10^{-5}$) "phosphorescence" has been reported at low temperature.[4] This essentially nonemissive behavior has been attributed to quenching of the ring (π,π^*) states by lower energy metal ↔ ring charge-transfer (CT) states.[2,3,5–7] Two recent picosecond transient absorption studies have revealed very fast decay of the absorption changes in the 450–600-nm region following photoexcitation, with lifetimes of 17 ps[5] for $\mathrm{Mn^{III}TPP(Cl)}$ and 55 ps[6] for $\mathrm{Mn^{III}Meso(Cl)}$. These time constants were attributed to radiationless decay of a ring (π,π^*) "tripmultiplet" state. Here we report the results of a picosecond study in which we monitored the absorption changes and kinetics over a more extensive spectral region (500–900 nm). For *both* $\mathrm{Mn^{III}TPP(Cl)}$ and $\mathrm{Mn^{III}OEP(Cl)}$ in CH_2Cl_2 and in pyridine we observed two transients: one has a fast (≤30 ps) decay and the other a slower relaxation (80 ps for TPP, 140 ps for OEP). We suggest that the short-lived component is the "tripquintet", $^5T_1(\pi,\pi^*)$, a fraction of which relaxes to the longer lived "tripseptet", $^7T_1(\pi,\pi^*)$. Decay of both tripmultiplets probably proceeds via lower energy CT or (d,d) excited states.

Experimental Method

The dual-beam picosecond transient absorption spectrometer used in this work has been described previously.[8] Samples flowing through a 2 mm path length cell at room temperature were excited with a 30-ps flash at either 355 nm (~200 μJ) or 532 nm (up to 1.5 mJ) and probed at various delay times with a 30-ps "white-light" (450–950 nm) pulse. $\mathrm{Mn^{III}TPP(Cl)}$ and $\mathrm{Mn^{III}OEP(Cl)}$ from Aldrich Chemical Co. were checked by thin-layer chromatography and absorption spectroscopy and were used without further purification. Spectral grade solvents were employed.

Results

Figure 1 shows transient difference spectra from 500 to 640 nm for $\mathrm{Mn^{III}OEP(Cl)}$ (A) and $\mathrm{Mn^{III}TPP(Cl)}$ (B) in CH_2Cl_2 at two time delays. For both complexes the 7- and 13-ps spectra (acquired during the 30-ps, 355-nm excitation flash) exhibit strong excited-state absorption to the blue of 520 nm, bleaching of the absorption bands in the visible region, and weaker excited-state absorption extending to longer wavelengths. After the excitation flash (67- and 73-ps spectra) much of the strong absorption near 500 nm and a sizable fraction of the bleachings have decayed. Only small, but resolvable, absorption changes remain. Thus, there appear to be two observable transients for each complex; from the 500–640-nm data of Figure 1 the longer lived component is more apparent for the OEP complex than for the TPP complex.

The solid squares in the inset of Figure 2 show that the strong 500-nm absorption for $\mathrm{Mn^{III}OEP(Cl)}$ develops and decays essentially with the excitation pulse, placing a time constant of ≤30 ps on the relaxation.[9] The 620-nm absorption of $\mathrm{Mn^{III}OEP(Cl)}$ (triangles in Figure 2 inset) clearly decays more slowly, as suggested by the time evolution of the spectra (Figure 1A) and by the data after the excitation flash (and up to 1 ns, not shown); the time constant for the relaxation is 150 ± 30 ps. $\mathrm{Mn^{III}TPP(Cl)}$ also exhibits an instrument-limited ≤30-ps decay of the strong absorption near 500 nm, but the residual absorption changes shown in Figure 1B are so small that the kinetics of their disappearance cannot be measured accurately.

In order to measure the decay kinetics of the slower component more accurately, and to search for additional resolvable spectral features, we measured the time evolution of the transient difference spectra between 640 and 900 nm on samples 2–3 times more concentrated than those employed above and excited with stronger flashes at 532 nm. The absorption changes between 640 and 900 nm at 27 ps (solid) and 147 ps (dashed) for both complexes in CH_2Cl_2 are shown in Figure 3. $\mathrm{Mn^{III}OEP(Cl)}$ shows a broad transient absorption centered near 690 nm and a trough near 775

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[1] Abbreviations used for porphyrin macrocycles: TPP (tetraphenylporphyrin), OEP (octaethylporphyrin), Meso (mesoporphyrin), PPDME (protoporphyrin IX dimethyl ester).

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[9] Because of possible recycling of molecules that have returned to the ground state during the 30-ps excitation flash, we did not attempt to deconvolute the excited-state decay from the instrument response. We estimate the lifetimes of the short-lived component for both complexes to be 5–30 ps.

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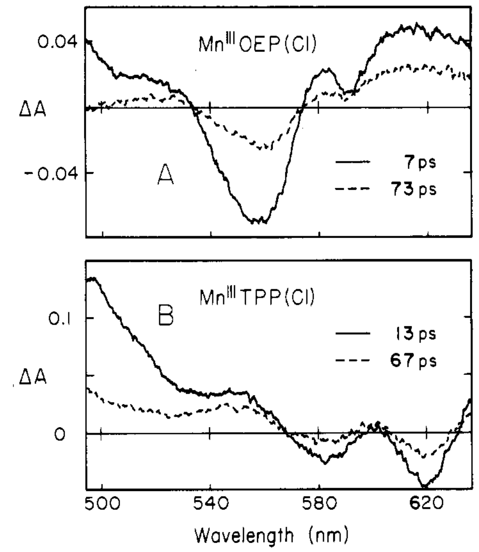

Figure 1. Transient difference spectra of Mn^{III}OEP(Cl) (A) and Mn^{III}TPP(Cl) (B) in CH_2Cl during (—) and after (- - -) a 30-ps, 355-nm flash.

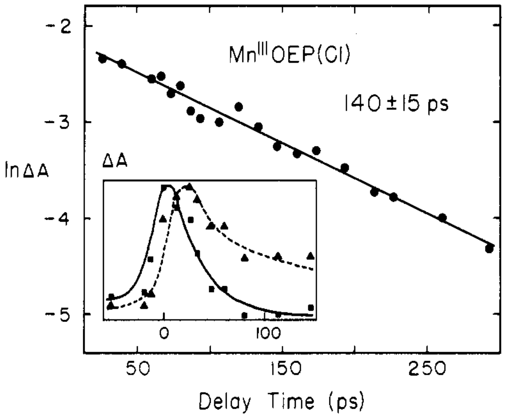

Figure 2. Kinetics for decay of transient absorption at 690 nm for Mn^{III}OEP(Cl) in CH_2Cl_2 following 532-nm excitation. Inset: Decay profiles of the transient absorption at 500 (■) and 620 nm (▲) for Mn^{III}OEP(Cl) in CH_2Cl_2 following 355-nm excitation. Note the ordinate of the inset is not a log scale.

nm that reflects the bleaching in the 780-nm ground-state absorption band. Mn^{III}TPP(Cl) shows transient absorption near 650 nm tailing to longer wavelengths.

A log plot for decay of the absorption increase near 690 nm for Mn^{III}OEP(Cl) is shown in Figure 2 (circles). The time constant is calculated to be 140 ± 15 ps, in excellent agreement with that of 150 ± 30 ps obtained in the 620-nm region from the measurements employing 355-nm excitation pulses. Mn^{III}TPP(Cl) in CH_2Cl_2 showed a somewhat faster decay of 80 ± 20 ps measured at 650 nm following excitation with 532-nm flashes (log plot not shown).

Both complexes gave similar transient spectra between 640 and 900 nm in CH_2Cl_2 and in pyridine, and for Mn^{III}OEP(Cl) we measured the same decay times ($\leq$30 and ~150 ps) in the two solvents. Previous work has suggested that complexes such as Mn^{III}OEP(Cl) and Mn^{III}TPP(Cl) exist as the monopyridinate complex in pyridine with the chloride counterion not being strongly associated with the metal.[10]

Discussion

Excited-State Manifold for Mn(III) Porphyrins. Mn^{III}OEP(Cl) and Mn^{III}TPP(Cl) have a d^4 ground-state electronic configuration ($S = 2$). Therefore, the "(π,π^*)" states of these complexes are not the normal singlets and triplets because of coupling of the unpaired metal electrons with the ring π electrons. The ground state is a quintet ($^5S_0$), and a quintet excited state ($^5S_1$) is derived from the lowest excited ring (π,π^*) singlet; a "tripmultiplet" manifold ($^3T_1$, $^5T_1$, $^7T_1$) is derived from the lowest ring (π,π^*) triplet.[2] The essentially nonluminescent behavior of these complexes is generally attributed to quenching of the normally emissive (π,π^*) excited states by CT or (d,d) states at lower energy. Calculations suggest that the four half-filled metal orbitals, d_{xy}, $d\pi(d_{xz},d_{yz})$, and d_{z^2} lie between the two highest filled ring orbitals, $a_{1u}(\pi)$ and $a_{2u}(\pi)$, and the two lowest empty ring orbitals, $e_g(\pi^*)$, with the empty metal $d_{x^2-y^2}$ lying above the $e_g(\pi^*)$ orbitals.[2,3,11] The red ground-state absorption bands in the "octaalkyl-substituted" complexes, such as Mn^{III}OEP(Cl), have been ascribed to transitions $a_{2u}(\pi) \rightarrow a_{1g}(d_{z^2})$ (near 680 nm) and $[a_{1u}(\pi), a_{2u}(\pi)] \rightarrow e_g(d_\pi)$ (near 780 nm). The 620-nm band in Mn^{III}TPP(Cl) probably represents a CT transition. For the Mn(III) porphyrins, there are undoubtedly a large number of (π,d) CT, (d,π^*) CT, and (d,d) states not evident from the ground-state absorption spectrum that may also act to quench emission.[2,3,11] Finally, relatively strong (π,d) CT transitions appear to contribute significantly to the near-UV–visible ground-state absorption spectrum normally dominated by the ring (π,π^*) transitions, and these may mix substantially.[2,3] For example, both complexes studied here exhibit a split "Soret" band with peaks near 350 and 470 nm.[3] Thus, the presence of allowed CT transitions extending from the near-UV to near-IR region potentially complicates not only the interpretation of the ground-state spectra but also that of the excited-state difference spectra of Figures 1 and 3.

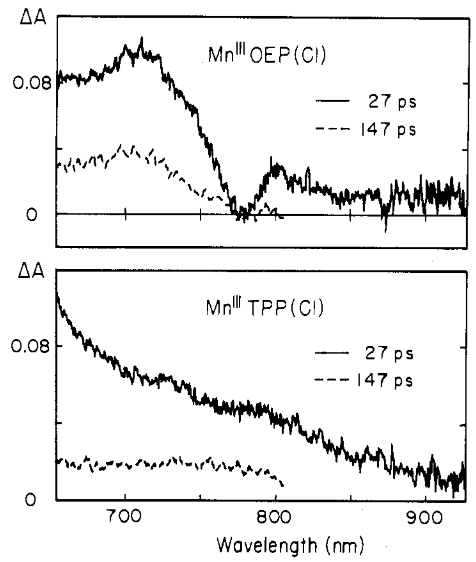

Figure 3. Near-infrared transient difference spectra of Mn^{III}OEP(Cl) and Mn^{III}TPP(Cl) in CH_2Cl_2 at delay times of 27 (—) and 147 ps (- - -) with respect to the 30-ps, 532-nm excitation flash.

Comparison with Earlier Picosecond Studies. In previous work, absorption changes were measured between 450 and 600 nm.[5,6] The 13-ps spectrum for Mn^{III}TPP(Cl) in Figure 1B agrees well with those reported by Irvine et al. who used 1-ps excitation flashes at 597 nm.[5] Our estimated lifetime of 5–30 ps[9] for decay of the strong absorption increase near 500 nm is consistent with their value of 17 ps, measured in both CH_2Cl_2 and pyridine. They measured bleaching in the strong 470-nm Soret band and resolved the strong transient absorption near 500 nm. It may not be surprising that they did not see the much weaker absorption changes to longer wavelengths due to the second component (Figure 1B), which are better resolved with more concentrated samples than can be used for probing through the strong 470-nm ground-state absorption band. In addition, potential recycling during our long-duration excitation flashes could permit buildup

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of the second, longer lived transient, making its detection easier. The lifetime of 55 ps reported by Chirvonyi and Dzhagarov[6] for Mn$^{\rm III}$Meso(Cl) is intermediate between the two time constants of $\leq$30 and 140 ± 15 ps found here for Mn$^{\rm III}$OEP(Cl). Normally, Meso and OEP complexes show similar photophysical behavior.[2,7] This similarity, together with our results, and the 17-ps decay observed by Irvine et al.,[5] suggested that Mn$^{\rm III}$Meso(Cl) should exhibit both fast and slow decay components. Possibly the previously observed 55-ps decay[6] is an average value.

In both earlier picosecond studies the authors attributed the observed decays, 17 ps for Mn$^{\rm III}$TPP(Cl) and 55 ps for Mn$^{\rm III}$Meso(Cl), to relaxation of a "tripmultiplet" state. Irvine et al.[5] based this assignment largely on the observation that many porphyrin (π,π^*) states,[7] such as the triplet (π,π^*) of Zn$^{\rm II}$TPP,[12] show strong absorption near 500 nm (i.e. to the red of the Soret band); such absorption is seen in the Mn(III) porphyrin transient spectra at short time delays (Figure 1 and ref 5 and 6). Unfortunately, this spectral assignment is not unique; (π,d) states are also expected to have relatively strong absorption to the red of the Soret band, since their spectra should resemble those of porphyrin π cation radicals.[7] However, in agreement with the general conclusion by Irvine et al., we believe that the most consistent interpretation of the results is that the fast ($\leq$30 ps) transient is a tripmultiplet state. More specifically we assign it as the tripquintet, $^5T_1(\pi,\pi^*)$, which apparently forms rapidly via intersystem crossing from the lowest singquintet, $^5S_1(\pi,\pi^*)$. The most pronounced spectral effects of the $^5T_1(\pi,\pi^*)$ decay are a substantial decrease in the strong absorption between 500 and 530 nm and a partial decay of the ground-state bleachings (Figure 1 and squares in Figure 2 inset). The relatively broad transient absorption at longer wavelengths (Figures 1 and 3) decays also, but by a smaller degree (triangles in Figure 2 inset). These observations, along with the fact that the bleachings do not change shape, lead us to believe that the decay of the bleachings indeed reflects the return of some fraction of molecules to the ground state as the $^5T_1(\pi,\pi^*)$ relaxes and is not simply due to the growth of new absorption by the longer lived transient in the same regions. On the basis of the magnitude of the decay of the bleachings near 550 nm for Mn$^{\rm III}$OEP(Cl) and near 580 and 620 nm for Mn$^{\rm III}$TPP(Cl), we estimate that at least 60% of the $^5T_1(\pi,\pi^*)$ decay results in repopulation of the ground state in $\leq$30 ps. Since there is the possibility of recycling during the 30-ps excitation flash, the contribution of this pathway to $^5T_1(\pi,\pi^*)$ decay could be greater than 60%.

The remaining <40% of the $^5T_1(\pi,\pi^*)$ decay gives rise to the longer lived transient, which has smaller absorption than $^5T_1(\pi,\pi^*)$ near 500 nm but comparable absorption past 650 nm (to the red of bleaching in the ground-state visible bands, as in Figure 3). This general spectral behavior is similar to that reported for the tripmultiplets, $^2T_1(\pi,\pi^*)$ and $^4T_1(\pi,\pi^*)$, for Cu(II) porphyrins.[13,14] The main difference is that in the Cu(II) complexes the magnitudes of the transient absorption just to the red of the Soret-band bleaching is more similar for the two tripmultiplets than observed here and previously[5] for the Mn(III) complexes. However, this spectral difference may not be unexpected since the 350–500-nm region for the Mn(III) porphyrins may contain contributions from both CT and (π,π^*) transitions that may mix and cause spectral shifts. To longer wavelengths, the broad absorption centered near 700 nm for Mn$^{\rm III}$OEP(Cl) in Figure 3 is similar to that seen for Cu$^{\rm II}$OEP,[13] but it is difficult to determine where the excited-state absorption maximum is located in this region for the Mn(III) complex, because of the bleaching in the ground-state band near 780 nm. The near-infrared spectrum for Mn$^{\rm III}$TPP(Cl) is less similar to that for Cu$^{\rm II}$TPP, which has a small but resolvable feature near 820 nm.[13] The general comparisons, particularly for Mn$^{\rm III}$OEP(Cl), are consistent with the longer lived component also being a tripmultiplet state, although one cannot rule out the possibility that this transient could contain some CT character. There are other possibilities, but they are not considered very likely on spectral and kinetic grounds: (1) The transient absorption beyond 650 nm for the two Mn(III) porphyrins is not consistent with either the $\leq$30-ps or 80–140-ps transient being a (d,d) excited state; such ligand field states for Ni(II)[8,15] and Co(III)[16] porphyrins show absorptions similar to but red-shifted 15–20 nm from the ground-state spectrum and do not show any absorption beyond 600 nm. (2) The longer lived transient is not likely to be a deligated state, since similar spectral and kinetic behavior was observed in CH_2Cl_2 and in pyridine where the axial ligand and the coordinating properties of the solvent are different.

Proposed Deexcitation Pathways. Thus, on the basis of the available spectral data and comparisons with the kinetic results on other metalloporphyrins,[7] we propose the following scheme for the excited-state deactivation of Mn(III) porphyrins: Excitation of the $^5S_0$ ground state populates the $^5S_1(\pi,\pi^*)$ lowest excited singquintet, either directly with 532-nm flashes or following rapid radiationless decay of a higher energy excited state produced with 355-nm pulses. From excitation pulse intensity measurements Irvine et al.[5] estimated that $^5S_1(\pi,\pi^*)$ lives 0.1–0.5 ps. From the magnitude of the initial absorption changes observed here and previously,[5] it appears that much of the singquintet decays by internal conversion to the ground state rather than by intersystem crossing to the lowest tripquintet, $^5T_1(\pi,\pi^*)$. $^5T_1(\pi,\pi^*)$, which has a lifetime of 5–30 ps, also decays by at least two pathways. We estimate that at least 60% of the decay of this state also results in $\leq$30-ps repopulation of the ground state ($^5S_0$), probably via (π,d) CT, (d,π^*) CT, or (d,d) states having the same multiplicity. The lowest energy state of each type would appear to be $(a_{2u}(\pi),d_{xy})$, $(d_{z^2},e_g(\pi^*))$, and $(d_{z^2},d_{x^2-y^2})$, respectively.[2,11] The energies of these states are not known, but to participate in the $^5T_1(\pi,\pi^*)$ decay they must be lower than 1.5–2 eV, the approximate energy of the tripquintet based on tripmultiplet energies in a variety of metalloporphyrins;[2,4] Harriman[4] places $^5T_1(\pi,\pi^*)$ at 1.8 eV and $^7T_1(\pi,\pi^*)$ at 1.6 eV for Mn$^{\rm III}$TPP(Cl).

The remaining <40% of the $^5T_1(\pi,\pi^*)$ decay gives rise to the longer lived 80- or 140-ps component, which we assign as $^7T_1(\pi,\pi^*)$. Under this interpretation, the rapid 5–30-ps decay can be viewed in part as the time for equilibration of the tripmultiplets. Such rapid equilibration has been proposed for Ag(II) and Mo(IV) porphyrins (<10 ps)[14a,17] and Cu(II) porphyrins (100–500 ps).[14,18] The longer lifetime of $^7T_1(\pi,\pi^*)$ compared to that of $^5T(\pi,\pi^*)$ can be rationalized on the basis of spin selection: First, direct relaxation of the tripseptet to the quintet ground state is spin-forbidden. Second, no low-energy septet CT or (d,d) excited state to which $^7T(\pi,\pi^*)$ could decay rapidly are expected. The septet (d,d) excited states are simply nonexistent. No metal ↔ ring CT transition involving the half-filled d orbitals can lead to septet excited states. Thus, the only possible septet CT states are $^7(\pi,d_{x^2-y^2})$, and these will be very high in energy and unlikely to participate in decay of $^7T_1(\pi,\pi^*)$.

We note, however, that the proposed 80–140-ps relaxation $^7T_1 \rightarrow {}^5S_0$ in the Mn(III) porphyrins is significantly faster than the relaxation $^4T_1 \rightarrow {}^2S_0$ in Cu(II) porphyrins, even though the tripmultiplets in the two complexes are probably at comparable energy. Thus the tripseptet decay in the Mn(III) complexes may involve a spin-forbidden relaxation (slower than the spin-allowed decay of the tripquintet) via a quintet CT state. Some likely CT states are generated by electron promotions to or from the half-filled metal dπ orbitals, which could give rise to a spin–orbit

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enhancement of a ${}^7T_1(\pi,\pi^*) \rightarrow {}^5$CT relaxation. The faster relaxation for Mn^{III}TPP(Cl) of 80 ps compared to the 140-ps decay of Mn^{III}OEP(Cl) could be due to the lower energy ${}^7T_1(\pi,\pi^*)$ in the TPP complex, with a concomitant smaller energy gap between this state and the ground state or CT quenching levels; triplet and tripmultiplet excited states of TPP complexes are always at lower energy than for the comparable OEP complexes.[2]

Thus, the striking differences between the photophysical behavior in Cu(II) and Mn(III) porphyrins, both of which have a tripmultiplet manifold, probably can be traced to the relative energies of metal $\leftrightarrow$ ring CT states. Such CT states are above the tripmultiplet manifold in the Cu(II) complexes, although they do appear to participate in the tripmultiplet decay.[14,18] On the other hand, the numerous possible low-energy CT states in the Mn(III) porphyrins appear to provide effective routes for rapid radiationless decay. Similarly, the rapid deexcitation of the Fe(II) and Fe(III) porphyrins apparently involves low-energy metal $\leftrightarrow$ ring CT and/or (d,d) excited states. Interestingly, the finding here in the Mn(III) porphyrins of a comparatively long-lived (80–140 ps) "bottleneck" state, assigned as ${}^7T_1(\pi,\pi^*)$, is reminiscent of the 30–50-ps decay assigned to a spin-forbidden (π,π^*) bottleneck state in iron porphyrins.[19] Thus, it appears to be a general phenomenon for transition-metal porphyrins that some fraction of the excited-state decay proceeds through the lowest spin-forbidden "(π,π^*)" state, even when the excited state that feeds it lives for only tens of picoseconds or less.

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Electronic Structure of Diammine(ascorbato)platinum(II) and the Trans Influence on the Ligand Dissociation Energy

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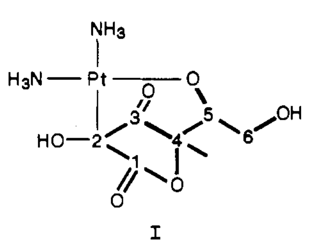
The electronic structure of the *cis*-Pt(NH$_3$)$_2$(ascorbate) molecule has been studied by valence-electron self-consistent-field calculations. A simpler molecule, *cis*-Pt(NH$_3$)$_2$(CH$_2$OH)(OCH$_3$), is used to model the ascorbate in a calculation of ligand binding energies. A comparison of localized ligand bonding orbital charge centroids and density plots supports the validity of the model compound to represent the bonding in the ascorbate. The Pt–C bond energy is calculated to exceed that for Pt–O by about 40 kcal/mol. The dissociation energies for the NH$_3$ ligands exhibit a strong trans influence with a low dissociation energy for the NH$_3$ trans to the Pt–C bond. These results suggest that this NH$_3$ ligand is suitable for exchange in these molecules.

Introduction

Recently, the structures of *cis*-diammineplatinum complexes of ascorbic acid have been reported[1] in which the ascorbate dianion is found to be bound to the Pt at the C2 and O5 sites. These are unusual binding sites since transition metal chelation by ascorbate is usually reported to occur at the O2 and O3 sites.[2] However, binding to both carbon and oxygen sites has been observed in platinum binding to the acetylacetonate anion.[3] In addition to the unusual Pt–C bond, interest in this molecule is stimulated by the antitumor properties of *cis*-diammineplatinum complexes.[4] In order to obtain insight into the platinum–ligand bonding, we have initiated self-consistent-field (SCF) calculations of the electronic structure of *cis*-Pt(NH$_3$)$_2$(ascorbate) (I) and the ligand dissociation energies of *cis*-Pt(NH$_3$)$_2$(CH$_2$OH)(OCH$_3$) (II), which is used to model the ascorbate–ligand binding. The model compound allows the study of the Pt–C and Pt–O bonds, with a carbon bound to oxygen in both bonds providing a part of the environment found in the ascorbate molecule. We have tested the validity of the model by comparing localized orbitals of the Pt–ligand bonds in the model compound II with the comparable localized orbitals in the ascorbate molecule I. The relationships of the localized electron-pair charge centroids and their orbital density plots compared well for the model and ascorbate compounds. These results show that the model compound adequately describes the binding of the ascorbate compound to Pt.



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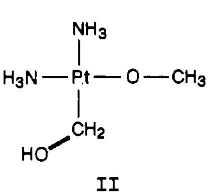

II

The trans influence in square-planar Pt(II) complexes is a well-known effect[5] and is defined in terms of the dependence of a bond strength on the nature of the ligand trans to that bond.[6] Although the effect is defined in terms of a bond strength, the relative measure of that strength is usually determined indirectly, through the variation of spectroscopic parameters such as bond lengths, vibrational frequencies, and NMR coupling constants.[5] Intrinsic bond dissociation energies provide the most direct connection to the definition. It is found that for the ascorbate model the difference in the dissociation energies of the two NH$_3$ ligands is quite large compared to the relatively slight shifts in equilibrium bond distances. The strong binding of C to Pt is connected to the weak binding of N to Pt trans to the C binding site. These results can be used to infer a mechanism for the binding of *cis*-Pt(NH$_3$)$_2$(ascorbate) to DNA.

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