enhancement of a $^7T_1(\pi,\pi^*) \rightarrow {}^5CT$ 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 ↔ 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 ↔ 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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(19) (a) Cornelius, P. A.; Steele, A. W.; Chernoff, D. A.; Hochstrasser, R. M. *Chem. Phys. Lett.* **1981**, *82*, 9-14. (b) Dixon, D. W.; Kirmaier, C.; Holten, D. *J. Am. Chem. Soc.* **1985**, *107*, 808-813.

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

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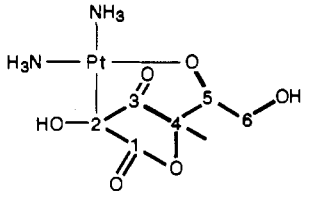
The electronic structure of the *cis*-$Pt(NH_3)_2$(ascorbate) molecule has been studied by valence-electron self-consistent-field calculations. A simpler molecule, *cis*-$Pt(NH_3)_2(CH_2OH)(OCH_3)$, is used to model the ascorbate in a calculation of ligand binding energies. A comparison of localized 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*-$Pt(NH_3)_2(CH_2OH)(OCH_3)$ (II), which



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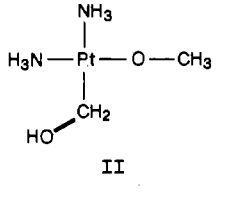

II

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.

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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‡ National Bureau of Standards.

(1) Hollis, L. S.; Amundsen, A. R.; Stern, E. W. *J. Am. Chem. Soc.* **1985**, *107*, 274.
(2) Martell, A. E. In *Ascorbic Acid: Chemistry, Metabolism, and Uses*; Seib, P. A., Tolbert, B. M., Eds.; Advances in Chemistry 200; American Chemical Society: Washington, DC, 1982; pp 153-178.
(3) Mason, R.; Robertson, G. B.; Pauling, P. L. *J. Chem. Soc. A* **1969**, 485.
(4) (a) Lippard, S. J., Ed. *Platinum, Gold, and Other Metal Chemotherapeutic Agents*; ACS Symposium Series 209; American Chemical Society: Washington DC, 1983. (b) Hacker, M. P., Doyle, E. B., Krakoff, I. H., Eds. *Platinum Coordination Complexes in Cancer Chemotherapy*; Martinus-Nijhoff: Boston, MA, 1984.
(5) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.
(6) Pidcock, A.; Richards, R. E.; Venanzi, L. M. *J. Chem. Soc. A* **1966**, 1797.

0020-1669/86/1325-4777$01.50/0

Table I. Compact Effective Potential for Pt[a]

CEP	a_k	n_k	B_k
V_g	-9.798 54	1	3.908 13
V_{s-g}	5.798 43	0	1.362 79
	247.969 06	2	3.911 36
	-187.515 94	2	3.342 27
V_{p-g}	3.670 55	0	1.075 86
	151.559 15	2	3.524 91
	-93.020 55	2	2.804 43
V_{d-g}	13.093 53	0	42.631 16
	80.293 85	2	4.744 68
V_{f-g}	6.138 70	0	1.589 88

[a] The form of the analytic representation is

$$r^2V_l(r) = \sum_k A_{lk} r^{n_{lk}} e^{-B_{lk}r^2}$$

Table II. Energy-Optimized Shared-Exponent Gaussian Basis Set for Pt[a]

shell	type (ij)	α_i	c_i	c_j
1	SP	6.6530	0.282 256	0.036 575
	SP	3.9950	-1.075 967	-0.284 606
	SP	1.5410	1.131 255	0.752 346
	SP	0.5599	0.478 240	0.476 585
2	SP	1.3410	-0.161 817	-0.038 798
	SP	0.1436	0.570 083	0.223 969
3	SP	0.04721	1.000 000	1.000 000
4	D	4.8670	-0.018 388	
	D	1.4650	0.400 756	
	D	0.5473	0.516 735	
5	D	0.1772	1.000 000	

[a] Each shell is represented as contracted set of Gaussian functions

$$\sum_i c_i e^{-\alpha_i r^2}$$

Table III. Pt Excitation Energies (eV)

state	E(Desclaux)[a]	E(CEP)
$(5s^2)(5p^6)(5d^{10})$	0.00	0.00
$(5s^2)(5p^6)(5d^8)(6s^2)$[b]	0.49	0.63
$(5s^2)(5p^6)(5d^9)$[b]	6.80	6.72
$(5s^2)(5p^6)(5d^8)$[b]	24.75	24.58
state	E(Martin, Hay)[c]	E(CEP)
$(5s^2)(5p^6)(5d^8)(6s^2)$ (^{3}F)	0.00	0.00
$(5s^2)(5p^6)(5d^{10})$ (^{1}S)	0.50	0.40
$(5s^2)(5p^6)(5d^9)$ (^{2}D)	7.26	7.11

[a] Reference 8. [b] Energy of average of configuration; see ref 8 for definition. [c] Reference 9.

Method of Calculation

Valence-electron SCF calculations were performed by using the HONDO code,[7] which had been modified to use effective core potentials[8] in place of the chemically unimportant core electrons. For the Pt-containing molecules of interest, the effective potentials prove advantageous in both reducing the number of electrons, and therefore the size of the expansion basis set used to represent the molecular orbital, and including the dominant part of the relativistic contribution to the electronic structure in heavy metals such as Pt. A set of compact effective potentials (CEP) and concomitant basis sets have been reported for Li through Ar.[8] All-electron calculations at the double-ζ basis level of accuracy are reproducable by using these CEP and orbital bases. The C, N, and O CEP and bases were used in the present calculation. Relativistic CEP have also been generated for the elements from K through Rn, and the CEP, bases, and atomic excitation energies for Pt are reported in Tables I, II, and III, respectively. The atomic energies are compared in a variety of states containing 8, 9, or 10 Pt 5d electrons, with comparable relativistic Dirac–Fock[9] and relativistic Hartree–Fock calculations that neglect the spin–orbit interaction.[10] Considering the wide range of d occupancies and ionicities for these states, the agreement is good, reflecting the accurate representation of the relativistic effects. The 5s and 5p electrons are included in both the atomic and molecular wave functions since the 5s, 5p, and 5d orbitals overlap. However, the 5s and 5p orbital energies are so much greater than the 5d that there is no need to consider excitations out of these subshells. They are always completely occupied as $(5s^2)(5p^6)$ but evaluated self-consistently.

The geometry of the *cis*-Pt$(NH_3)_2$(ascorbate) complex was obtained primarily from the reported conformation of Pt(*cis*-1,2-diaminocyclohexane (*cis*-dach))(ascorbate)[1] by retaining the Pt(ascorbate) geometry and positioning the N atoms for the two ammonia ligands at the reported positions of N1 and N2 in the Pt(*cis*-dach) complex. This geometry may not be optimal for the diammine, which would lead to a small underestimate for the calculated bond energies. The N–H bond in the ammonia ligand was fixed at 1.021 Å, and one hydrogen was placed in the plane defined by the atoms bonded to Pt while the remaining two hydrogens were placed symmetrically above and below this plane with the ∠HNH equal to 109.4°.

Table IV. Centroids and Dissociation Energies for Pt$(NH_3)_2(CH_2OH)(OCH_3)$

	Pt–O	Pt–C	Pt–N_o	Pt–N_c
	Ascorbate Geometry			
R[a]	2.034	2.138	2.047	2.100
centroid (II)[b]	0.49	0.81	0.50	0.45
centroid (I)[b]	0.51	0.68	0.51	0.48
D_e[c]	170.5	212	36	15
	Optimized Geometry			
R	2.024	2.046	2.137	2.224
centroid (II)	0.52	0.95	0.44	0.30
D_e	158	202	42.5	27.5

[a] All distances in Å. [b] Centroid for bonding orbitals, Pt–A, in compound I or II relative to A. Centroid for bonding lone pair: CH_2OH, 0.39 Å; OCH_3, 0.32 Å; NH_3, 0.32 Å. [c] Dissociation energy in kcal/mol.

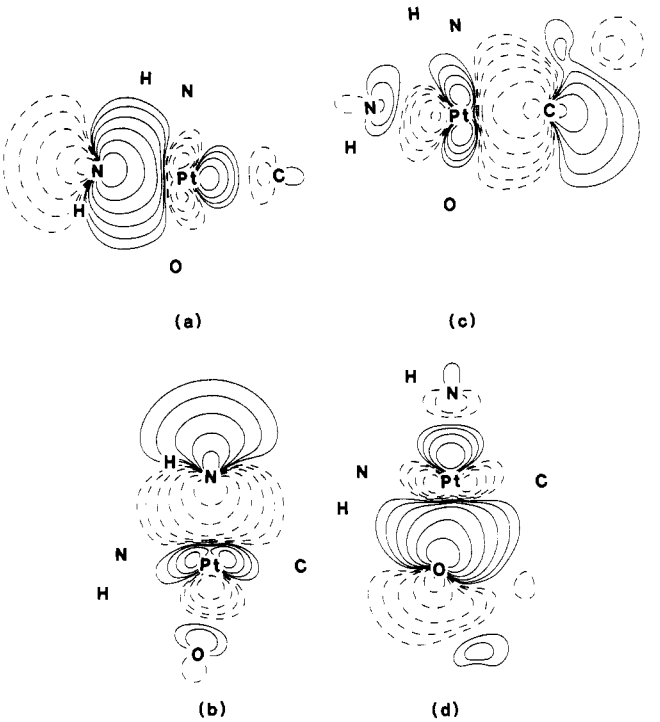

Figure 1. Charge amplitude contour plots for the localized bonding orbitals in Pt$(NH_3)_2$(ascorbate): (a) Pt–N bond trans to C; (b) Pt–N bond trans to O; (c) Pt–C bond; (d) Pt–O bond.

Results and Discussion

There are 188 electrons in this molecule, but the use of the CEP reduces the double-ζ (DZ) basis to 160 functions that represent 100 valence electrons. However, the calculation of the dissociation

(7) Dupuis, M.; King, H. F. *Int. J. Quantum Chem.* **1977**, *11*, 613; *J. Chem. Phys.* **1978**, *68*, 3998.
(8) Stevens, W. J.; Basch, H.; Krauss, M. *J. Chem. Phys.* **1984**, *81*, 6026.
(9) Desclaux, J. P. *At. Data* **1973**, *12*, 312.
(10) Martin, R. L.; Hay, P. J. *J. Chem. Phys.* **1981**, *75*, 4539.

energy of each of the four ligand bonds was done with the model compound II, which contains only 60 electrons and requires 96 basis functions. The accuracy of the model-compound representation of the charge distribution in I is supported by the similarity in the centroids of the localized orbitals, obtained by Boys' method,[11] that are summarized in Table IV. Plots of the charge densities of the bonding orbitals in the plane of the complex were also compared. The similarity is almost complete between the orbitals for compounds I and II, and only the orbitals for the ascorbate molecule are depicted in Figure 1.

Compound II was studied both at the conformation of the ascorbate molecule and at a fully optimized geometry. The Pt–C distance in the model compound, as seen in Table IV, is reduced by almost 0.1 Å upon energy optimization of the geometry, and there are comparable increases in both of the Pt–N bond distances. The geometry optimization substantially enhances the interligand hydrogen bonding by reducing the distance from the O atom in each of the CH_2OH and OCH_3 ligands to an H atom on the respective cis-ammonia ligand from 2.67 to 1.99 Å.

The bond dissociation energies are summarized in Table IV. These values are the in vacuo bond energies and are a measure of the intrinsic bond strength without consideration of solvation. The large bond energies for dissociating the ionic ligands, CH_2OH^- and OCH_3^-, reflect the electrostatic binding of the charged fragments. Covalent binding also contributes significantly to the Pt–C bond, which is over 40 kcal/mol stronger than the Pt–O bond. The dissociation energy of the ammonia ligands shows a substantial trans influence. The model calculation at the ascorbate geometry yields a very low dissociation energy of 15 kcal/mol for the ammonia ligand trans to Pt–C. Optimizing the geometry increases the dissociation energy to 27.5 kcal/mol. This increase is attributable in part to the calculated weakening of the trans Pt–C bond, but the ionic H-bond interactions between the anionic ligands and the protons on the ammonia ligands are also significant. These ionic H-bond interactions are not as likely in the ascorbate; therefore, we can predict a low bond energy for NH_3 trans to the Pt–C bond in *cis*-$Pt(NH_3)_2$(ascorbate).

The centroid positions of the localized ligand bonding orbitals are related to the amount of covalent character in the ligand–metal bond. A large covalent mixing will cause a substantial shift of the centroid away from the ligand atom, relative to the centroid position for the isolated ligand lone-pair orbital. Smaller shifts, due to polarization of the ligand lone pair by the positively charged Pt, can be expected for ligands with little covalent bonding. Centroid positions and shifts from isolated-ligands values are summarized for all four ligand lone pairs in Table IV. In the strong Pt–C bond, the centroid shift is larger than in any other bond. The centroid shifts in the Pt–O and Pt–N bonds are significantly smaller, indicating less covalent character in the bonds. The nitrogen trans to the carbon shows the smallest centroid shift, indicating weak covalent interactions that correlate with the small ligand binding energy. Geometry optimization does not change the relative values of these centroids greatly but the Pt–N centroids move away from Pt as larger Pt–N bond energies are calculated, suggesting that the increase is not due to an increase in covalent bonding but to internal hydrogen bonding. The centroid shifts for the Pt–C bond are larger in both model compound II calculations than those found for the ascorbate molecule I, suggesting that the calculated Pt–C bond energy is an overestimate for the ascorbate molecule.

There are two conclusions to be drawn from these calculations: (1) The covalent contribution to the trans influence correlates with the differences between the centroid positions of the localized bonding orbitals, and the overall trans influence is quantitatively measured by using the dissociation energy of the trans ligand. (2) Pt–C bonds are strong and have a large trans influence. The large trans influence for a σ-bonding carbon ligand is well-known experimentally.[5] The covalent bonding to the ligand makes use of the formally unoccupied Pt $5d(x^2 - y^2)$, Pt $6p\sigma$, and Pt 6s orbitals. The earliest analyses focused on the $6p\sigma$ and 6s participation in the bond,[12,13] but a more recent analysis concluded the trans influence correlates better with the population of the Pt $5d(x^2 - y^2)$ orbital.[14] The present calculations find that the Pt $5d(x^2 - y^2)$ contribution is largest in the overlap with the ligand, and the movement of the ligand bonding orbital centroids toward Pt is determined by the magnitude of the Pt 5d population in the bond.

The reduction in the dissociation energy, D_e, for the Pt–N trans to C is so large that it is likely to contribute to labilization of this ligand. Release of ammonia from the diammine has recently been noted by Hollis et al. in ligand-exchange reactions.[15] This suggests that in solution the Pt–N bond trans to the Pt–C bond can be broken. We could then speculate that the *cis*-Pt(C)(N) fragment can bind in an intrastrand chelate to DNA.[4] This leaves the ascorbate anion still bound to Pt, which reduces the binding energy to nucleic acid bases by reducing the effective charge of the cation interacting with the lone-pair electrons of the base. The binding energy of $Pt(NH_3)_3^{2+}$ to NH_3 is calculated to be 72 kcal/mol.[16] When bound to DNA, the ascorbate anion must also avoid the negatively charged phosphate moiety. In addition, the trans influence will reduce the binding of the base trans to the Pt–C bond. The binding energy of the $Pt(NH_3)_2$ fragment to DNA will be significantly reduced by replacing one ammonia ligand by the ascorbate anion.

Registry No. I, 105164-55-4; Pt, 7440-06-4; C, 7440-44-0.

(11) Boys, S. F. In *Quantum Theory of Atoms, Molecules and the Solid State*; Lowdin, P. O., Ed.; Academic: New York, 1966; pp 253–262.

(12) Langford, C. M.; Gray, H. B. *Ligand Substitution Processes*; Benjamin: New York, 1965.

(13) McWeeny, R.; Mason, R.; Towl, A. D. C. *Discuss. Faraday Soc.* **1969**, *47*, 20.

(14) Armstrong, D. R.; Fortune, R.; Perkins, P. G.; Dickinson, R. J.; Parish, R. V. *Inorg. Chim. Acta* **1976**, *17*, 73.

(15) Hollis, L. S., private communication.

(16) Basch, H.; Krauss, M.; Steven, W. J.; Cohen, D. *Inorg. Chem.* **1986**, *25*, 684.