but may simply mean the two quantities should not be plotted.

The *E*, *C*, and *W* analysis of these data reveals that more bases in the *E* and *C* correlation with a wider range of *C*/*E* values should be studied to accurately characterize the alkyl-substituted bis(dimethylglyoximato)cobalt(II) system. The problem is one of solving for three unknowns with four pieces of data. Thus, the parameters we reported above for the $(DH)_2CoR$ system are not well-defined and must be considered tentative. We do know from the value reported for the 4-CN derivative that the cobalt–carbon bond dissociation energy for the complex with no base attached must be less than 18 kcal mol^{-1}. We also note that both the covalent and electrostatic properties of the ligand are important in stabilizing the cobalt–carbon bond. If these conclusions on model compounds carry over to biological systems, hydration and dehydration could play an important role in stabilizing and destabilizing the cobalt–carbon bond.

In conclusion, we would emphasize that our treatment of the $(DH)_2CoR$ system clearly shows the need for more data to accurately define the parameters for this system and leads to confidence in the prediction of ΔH^{A} when any of the 48 different types of bases incorporated into the *E* and *C* equation are coordinated as axial bases. A more accurate definition of *E*, *C*, and *W* would also permit a more quantitative comparison of the influences of O_2 and methyl radical coordination to cobalt(II) on the acidity of the resulting compound. Our above analysis of the $(DH)_2CoR$ system indicates the insight in both the interpretation and design of experiments that can be accrued if one treats data of this sort with the *E* and *C* analysis.

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Registry No. DOE, 629-82-3; MoPFB, 5163-43-9; MeCoDMG, 36609-02-6; CoPPIXDME, 14932-10-6; ZnTPP, 14074-80-7; Cu(HFAcAc)$_2$, 14781-45-4; [Ni(TFACCAM)$_2$]$_2$, 62081-96-3; [Rh(COD)Cl]$_2$, 12092-47-6; [Pd(π-Allyl)Cl]$_2$, 12081-18-4; Zn[N(SiMe$_3$)$_2$]$_2$, 3999-27-7; Cd[N(SiMe$_3$)$_2$]$_2$, 3323-04-4; $Rh_2(CO)_4Cl_2$, 14523-22-9; I_2, 7553-56-2; IBr, 7789-33-5; ICl, 7790-99-0; C_6H_5SH, 108-98-5; 4-*t*-$C_4H_9C_6H_4OH$, 98-54-4; 4-$CH_3C_6H_4OH$, 106-44-5; C_6H_5OH, 108-95-2; 4-FC_6H_4OH, 371-41-5; 4-ClC_6H_4OH, 106-48-9; 3-FC_6H_4OH, 372-20-3; 3-$CF_3C_6H_4OH$, 98-17-9; $(CH_3)_3COH$, 75-65-0; CF_3CH_2OH, 75-89-8; $(CF_3)_2CHOH$, 920-66-1; C_4H_4NH, 109-97-7; $B(CH_3)_3$, 593-90-8; $Al(CH_3)_3$, 75-24-1; $Al(C_2H_5)_3$, 97-93-8; $Ga(C_2H_5)_3$, 1115-99-7; $(CH_3)_3SnCl$, 1066-45-1; SO_2, 7446-09-5; $SbCl_5$, 7647-18-9; $HCCl_3$, 67-66-3; $CF_3(CF_2)_6H$, 375-83-7; HNCO, 75-13-8; HNCS, 3129-90-6; $Ga(CH_3)_3$, 1445-79-0; $In(CH_3)_3$, 3385-78-2; BF_3, 7637-07-2; H_2O, 7732-18-5; C_8OH, 111-87-5; $(CF_3)_3COH$, 2378-02-1; 4-BrC_6H_5OH, 106-41-2; CH_3OH, 67-56-1; C_5H_5N, 110-86-1; NH_3, 7664-41-7; CH_3NH_2, 74-89-5; $(CH_3)_2NH$, 124-40-3; $(CH_3)_3N$, 75-50-3; $(C_2H_5)NH_2$, 75-04-7; $(C_2H_5)_2NH$, 109-89-7; $(C_2H_5)_3N$, 121-44-8; CH_3CN, 75-05-8; $ClCH_2CN$, 107-14-2; $(CH_3)_2NCN$, 1467-79-4; $HC(O)N(CH_3)_2$, 68-12-2; $CH_3C(O)N(CH_3)_2$, 127-19-5; $CH_3C(O)OC_2H_5$, 141-78-6; $CH_3C(O)OCH_3$, 79-20-9; $CH_3C(O)CH_3$, 67-64-1; $(C_2H_5)_2O$, 60-29-7; $(C_3H_7)_2O$, 111-43-3; $(C_4H_9)_2O$, 142-96-1; $(CH_2)_4O_2$, 123-91-1; $(CH_2)_4O$, 109-99-9; $(CH_2)_5O$, 142-68-7; $(CH_3)_2SO$, 67-68-5; $(CH_2)_4SO$, 1600-44-8; $(CH_3)_2S$, 75-18-3; $(C_2H_5)_2S$, 352-93-2; $(CH_2)_3S$, 287-27-4; $(CH_2)_4S$, 110-01-0; $(CH_2)_5S$, 1613-51-0; C_5H_5NO, 694-59-7; 4-$CH_3C_5H_4NO$, 1003-67-4; 4-$CH_3OC_5H_4NO$, 1122-96-9; $(CH_3)_3P$, 594-09-2; C_6H_6, 71-43-2; $HC(C_2H_4)_3N$, 100-76-5; $C_6H_{10}O$, 279-49-2; $(CH_3)_2Se$, 593-79-3; $C_9H_{18}NO$, 2564-83-2; $[(CH_3)_2N]_3PO$, 680-31-9; $C_2H_5C(CH_2O)_3P$, 824-11-3; $(CH_3)_2O$, 115-10-6; 4-$CH_3C_5H_4N$, 108-89-4; $(C_2H_5)_3PO_4$, 78-40-0; $C_5H_{11}N$, 110-89-4; CH_3-Im, 616-47-7; 3-$CH_3C_5H_4N$, 108-99-6; 3-ClC_5H_4N, 626-60-8; 4-$OCH_3C_6H_4OH$, 150-76-5; 3-$N(CH_3)_2C_6H_4OH$, 99-07-0; 3-$CH_3C_6H_4OH$, 108-39-4; 3-$OCH_3C_6H_4OH$, 150-19-6; 3-ClC_6H_4OH, 108-43-0; 3-BrC_6H_4OH, 591-20-8; 3-CNC_6H_4OH, 873-62-1; 4-CNC_6H_4OH, 767-00-0; 3-$NO_2C_6H_4OH$, 554-84-7; 4-$NO_2C_6H_4OH$, 100-02-7; 4-$NH_2C_5H_4N$, 504-24-5; 4-$C(CH_3)_3C_5H_4N$, 3978-81-2; 4-$OCH_3C_5H_4N$, 620-08-6; 4-$C_6H_5C_5H_4N$, 939-23-1; 3-$C_6H_5C_5H_4N$, 1008-88-4; 3-$OCH_3C_5H_4N$, 7295-76-3; 3-IC_5H_4N, 1120-90-7; 3-BrC_5H_4N, 626-55-1; 3-$CF_3C_5H_4N$, 3796-23-4; 4-$CF_3C_5H_4N$, 3796-24-5; 3-CNC_5H_4N, 100-54-9; 4-CNC_5H_4N, 100-48-1.

Supplementary Material Available: Tables of thermodynamic and spectroscopic data for an updated *E* and *C* fit (18 pages). Ordering information is given on any current masthead page.

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Experimental and Theoretical Study of the Nascent Photoredox Behavior of the Aqueous Hexachloroplatinate(IV) Ion

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The nascent photoredox behavior of aqueous ammonium hexachloroplatinate(IV) has been studied following picosecond laser excitation at 355 nm. The observed species exhibits two absorption bands with peaks near 640 and 440 nm, which decay via a first-order rate law with a common lifetime of 210 ± 10 ps. The quasi-relativistic version of the multiple-scattering Xα molecular orbital theory has been used to predict the absorption spectra for various possible transients for comparison to the experimental observations. The experimental and calculated information leads to the assignment of the transient as being $PtCl_5^{2-}$ of a square-pyramidal structure with elongated Pt–Cl bond lengths although the possibility exists that the species could be an electronically excited state of $PtCl_6^{2-}$.

The increased use of fast reaction techniques such as flash laser photolysis and pulse radiolysis has opened up broad new horizons to the study of the chemical and physical properties of short-lived species. In many instances, these techniques afford unique opportunities to investigate substances of unusual formal oxidation states and of less common structures; however, the evolution of our capacity to achieve faster resolution in time has been inevitably accompanied by an increase in the difficulty of identifying in a specific manner what species is being observed. This arises in part because the species becomes more closely associated with its mode of generation as one progresses to shorter time scales, and the use of alternative experimental routes to its formation (and thus to an aid in its identification) is less feasible. Consequently for studies involving ever shorter time scales, alternative means, particularly those based upon theoretical predications and interpretations as employed in this work, will assume an increasingly important role in the characterization of transitory entities.

Viewed in this context, the principal objectives of this study are twofold. First, we have used picosecond flash photolysis

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coupled with UV–visible absorption detection to investigate the nascent photoredox behavior of the hexachloroplatinate(IV) ion, $PtCl_6^{2-}$, in acidic aqueous media. Then we have applied a relatively new theoretical approach (namely the quasi-relativistic version of the multiple-scattering $X\alpha$ molecular orbital model that has been shown in the last few years to give a realistic description of the electronic structures of stable complex ions such as $PtCl_6^{2-}$)[2] to calculate the charge-transfer absorption spectra of probable products to compare to the experimental spectrum. To the extent to which this latter endeavor is successful, it provides insight into the composition and structure of the entity being observed and, at a minimum, serves to clarify the possibilities, which must be considered.

Previous chemical scavenging and EPR spin-trapping experiments, carried out under steady-state conditions, have shown that the near-UV–visible photolysis of $PtCl_6^{2-}$ generates chlorine atom and not hydroxyl radical.[3,4] These features make it highly probable that the nascent photoredox act involves homolytic bond cleavage as in

$$PtCl_6^{2-} \xrightarrow{h\nu} PtCl_5^{2-} + Cl \qquad (1)$$

rather than the intermolecular electron-transfer process

$$PtCl_6^{2-} + H_2O \xrightarrow{h\nu} PtCl_6^{3-} + OH + H^+ \qquad (2)$$

Earlier flash photolysis and pulse radiolysis findings serve to exemplify the difficulties encountered in identifying the primary platinum(III) species because more than one product is observed in the micro- and millisecond time frames.[5-9] The molar absorptivity of these species (ϵ 2000–4000 M^{-1} cm^{-1}) in the near-UV–visible region establishes the absorption character as being of a charge-transfer type, but the bands are relatively broad (fwhm ca. 50–80 nm) and devoid of fine structure. More specifically, Wright and Laurence observed in the flash photolysis of $PtCl_6^{2-}$ on the millisecond scale a transient with a peak at ca. 410 nm.[9] This same or very similar species has been found by pulse radiolysis in the reactions of e_{aq}^- with $PtCl_6^{2-}$ and of OH and $PtCl_4^{2-}$.[5-7] In the latter case, a precursor with a peak maximum near 450 nm occurred. Recently we have located in the photochemistry of $PtCl_6^{2-}$ such a band as a precursor to the one absorbing at 410 nm, using the quadrupled output of a Nd-YAG laser; however, there were spectral indications in the 300–500-nm region of earlier events although the low signal levels and laser pulse duration (ca. 20 ns) precluded accurate measurements being made of them.[10] Using the facilities at the Canadian Picosecond Laser Flash Photolysis Centre, we have now investigated the transient behavior on the picosecond time scale to seek species that could give rise to the longer term events.

Computational Method

The "quasi-relativistic" $X\alpha$ method has been used.[11,12] The effects of the mass-velocity and Darwin corrections are included self-consistently, while those of the spin–orbit operator are neglected. Generally, the spin–orbit effects are taken into account after self-consistency, by first-order perturbation theory. However, in the present case, the spin–orbit coupling has been neglected since it vanishes to first order for the ground and ligand-to-metal charge-transfer (LMCT) states. The Pt–Cl bond length of 2.32 Å for both $PtCl_6^{2-}$ and $PtCl_4^{2-}$ has been chosen for the undeformed model of $PtCl_5^{2-}$.[13,14] For deformed $PtCl_5^{2-}$, various elongations of the bond lengths up to 0.5 Å (50 pm or 0.945 au) have been considered in the calculations along with changes to the Cl–Pt–Cl bond angles. Elongations of the bond lengths have been performed in the context of the a_{1g} mode (symmetrical elongation) and of the e_g mode (four bonds shortened and one extended). The radii of the Pt and Cl atomic spheres are the same as those used previously.[13,14] An external tangent outer sphere has been employed, which also serves as a Watson sphere on which a positive charge of +2 is distributed.[15] The values of the atomic exchange parameters for Pt (0.693 06) and for Cl (0.723 25) have been taken from the compilation by Schwarz.[16] A weighted average of the atomic values (0.718 22) has been used for the interatomic and extramolecular regions. In the solution of the secular equations, spherical harmonics up to $l = 4$ are included in the Pt sphere and the extramolecular region and up to $l = 1$ for the chlorine spheres. The transition-state method has been employed in the calculations of the charge-transfer (CT) energies, without spin polarization.[17]

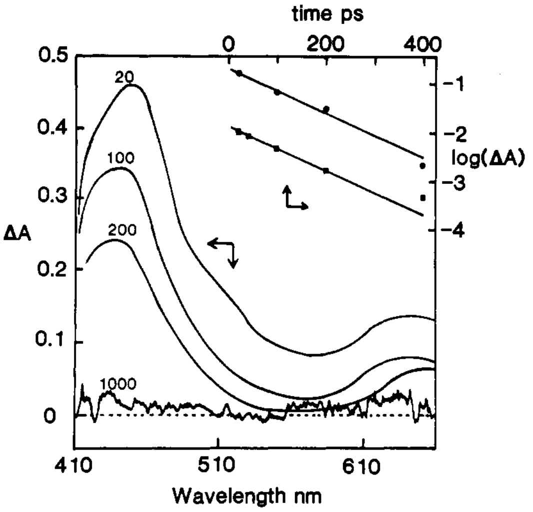

Figure 1. Time evolution of transient absorption of ammonium hexachloroplatinate(IV) in pH 2 aqueous solution. The lower portion shows the smoothed spectra at various picosecond intervals following a 30-ps flash at 355 nm, and the curve at 1000 ps has been reproduced directly from the original data to give an indication of the noise level. The curves in the upper right corner show the plots of the first-order decay kinetics for absorption: ●, 450–460 nm; ■, 635–644 nm.

Experimental Section

Ammonium hexachloroplatinate(IV) was obtained from K and K Laboratories, and it was recrystallized several times from aqueous hydrochloric acid media. The solution contained 5 mM $PtCl_6^{2-}$ at pH 2 (10 mM perchloric acid), and it was irradiated under aerated conditions by using the tripled frequency output of a Nd-YAG laser at 355 nm (30-ps-pulse half-width 2.75 mJ (average)/pulse). Details of the laser and optical recording systems are given elsewhere.[18] Permanent photochemistry was monitored via the absorption spectrum: The solution was refreshed as necessary to avoid errors from this factor, and the sample was also mixed between flashes.

Results and Discussion

Irradiation of $PtCl_6^{2-}$ at 355 nm involves an overlapping absorption region between ligand field and LMCT bands.[2] It also lies in the region where the quantum yields for both photoaquation

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Table I. Electronic Energy Levels and Charge Distributions for $PtCl_5^{2-}$ [a]

		Pt							Cl_{eq}			Cl_{ax}				
MO	*E*, Ry	s	p	d_{z^2}	$d_{x^2-y^2}$	d_{xy}	$d_{xz,yz}$	f	s	p_σ	p_π	s	p_σ	p_π	INT	OUT
$4b_1$	−0.406				43				1	49					5	2
$6a_1$	−0.464	2	1	41						13			33		9	1
$2b_2$	−0.529					47					43				9	1
6e	−0.532						38				51			1	9	1
$1a_2$	−0.540										89				10	1
5e	−0.552						7				31			50	11	1
$3b_1$	−0.559										86				13	1
4e	−0.562		1							40	41			6	11	1
$5a_1$	−0.576			2							80 (p_z)				17	1
3e	−0.592		2				5			47	25			6	14	1
2e	−0.637						43				20			22	15	
$1b_2$	−0.642					46					39				15	
$4a_1$	−0.667	7		20						6			52 (p_z)		13	2
$3a_1$	−0.684	8		27						52					11	2
$2b_1$	−0.686				51					41					7	1
$1b_1$	−1.424								95						4	1
1e	−1.425								95						5	
$2a_1$	−1.432								85			9			5	1
$1a_1$	−1.448								9			86			5	

[a] The point group is C_{4v}. The C_4 axis of symmetry is collinear with the *z* axis and the *z*0*x* and *z*0*y* planes are σ_v mirrors. Each Pt–Cl bond length is 5.088 au.

and photoexchange achieve values greatly in excess of unity.[3,19] Consequently, it is in this spectral area that irradiation is likely to be maximal in terms of the formation of the platinum(III) species that are postulated to be the chain carriers in the photochemistry.

Upon pulsed irradiation of $PtCl_6^{2-}$, there was a prompt development on the picosecond scale of two absorption bands with peak maxima near 440 and 640 nm. Figure 1 shows the time evolution of the smoothed spectra, and the curve at 1000 ps gives an indication of the noise level encountered and also suggests the occurrence of some residual absorption at the longer wavelength. In the upper right portion of the figure, plots for the first-order kinetic decay of the two bands are given. The fact that the lifetimes calculated from the plots are the same ($\tau = 210 \pm 10$ ps) is a good indication that the two bands are associated primarily with a single species. Under the assumption that its quantum yield is *1*, we estimate the molar absorptivity to be about 3000 M^{-1} cm^{-1} for the more intense peak; however, as the quantum yield is in all probability considerably less than 1 (perhaps $\Phi < 0.1$),[9,10] the actual value is likely to be in the tens of thousands range. These two bands are thus indicative of highly allowed charge-transfer type of transitions.

The foregoing spectral and kinetic features show that this species is not one of those observed on the micro- and millisecond time scales although it is likely to be precursor to them: The small amount of residual absorption is suggestive of this possibility. In addition, these features in conjunction with spectral information reported in the literature provide the basis for eliminating a number of species as the one giving rise to the spectrum of Figure 1. Although chlorine atom and Cl_2^- are formed along with the aquation product $PtCl_5(H_2O)^-$, they do not absorb to any significant extent above 400 nm.[3,9,20,21] The occurrence of ground-state $PtCl_6^{3-}$ seems improbable on the basis of the absence of hydroxyl radical formation (eq 2), and also both theoretical and experimental results point to its charge-transfer spectrum being below 350 nm.[8,13,14] Similarly, such results indicate that longer lived products absorbing around 450 nm are of a distorted octahedral type such as $PtCl_4(H_2O)(OH)^{2-}$: Theory in agreement with experiment indicates the absence of any major absorption band in the 600-nm region. Calculations performed during the course of this study also suggest that the platinum(IV) fragment $PtCl_5^-$ (C_{4v}) and the aquated platinum(III) species of the type $PtCl_5O$ or $PtCl_4O$ (C_{4v}; O stands for OH or H_2O) will not account for the presence of absorption in the 600-nm region.

In consideration of the foregoing information and the short lifetime of the species, we have been led to consider in detail by the Xα method two possible cases, namely that the absorption in Figure 1 is the ground-state absorption spectrum of $PtCl_5^{2-}$ or alternatively an excited-state absorption (ESA) of $PtCl_6^{2-}$ with the spectrum consisting of LMCT transitions.[22] In essence, these two cases represent the natural time evolution of the system upon excitation since the creation of a CT excited state of $PtCl_6^{2-}$ will obey the Franck–Condon principle and be followed by the slower formation of $PtCl_5^{2-}$ (eq 1). In addressing these alternatives, three features have served as the criteria of selection: (1) the location of the low-energy band, (2) the energy difference between the two CT transitions, and (3) the nature of the MO's involved in these transitions, which provide insight into their relative intensities.

The results of the calculations indicate that both cases can provide viable explanations for the observed spectrum. We first consider the ESA possibility and then focus in detail on the ground-state $PtCl_5^{2-}$ species. For the former, the nascent CT configuration for $^*PtCl_6^{2-}$ has been assumed to be $(3t_{1u})^5(2t_{2g})^6(3e_g)$, corresponding to its population by irradiation of the tail of the first intense LMCT (peak 262 nm).[2] Calculations have been performed within the frameworks of O_h and C_{4v} symmetries, the latter corresponding to a model where the "hole" is localized on one chlorine atom. Both symmetries lead to the same type of results, namely transitions at 620 nm ($1t_{2g} \rightarrow 3t_{1u}$), 400 nm ($2a_{1g} \rightarrow 3t_{1u}$), and 430 nm ($2e_g \rightarrow 3t_{1u}$). Three transitions are involved; however, the latter two could appear as a single broad band. The wave function for the $3t_{1u}$ level is comprised of 60% $p_\pi(p_z)$ Cl_{eq} and 40% $p_\sigma(p_z)$ Cl_{ax}. Contributions for the other levels are as follows respectively: $1t_{2g}$, $5d_\pi(d_{xz})$ Pt + p_π Cl; $2a_{1g}$, 6s Pt + p_π Cl; $2e_g$, $5d_\sigma(d_{z^2})$ Pt + p_σ Cl. The excellent overlap between $5d_{z^2}$ and $3p_z$ Cl_{ax} is somewhat better than that for $5d_{xz}$ and $3p_z$ Cl_{ax} so that, if the higher energy transitions (400, 430 nm) appear as one band, it should be more intense than the one predicted at 620 nm. This is in agreement with the observed spectrum (Figure 1); however, one also needs to consider the possible lifetime of the species. In this regard, emission has been observed from crystalline salts of $PtCl_6^{2-}$ at low temperature,[23,24] but this has been assigned to phosphorescence from the LF spin-forbidden

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transition $^3T_{1g} \rightarrow {}^1A_{1g}$. The nascent excited state formed in the intense CT absorption with a maximum at 262 nm, $^1T_{1u}$, must have a radiative lifetime of a few nanoseconds according to the integrated absorption coefficient. No emission can be detected in the appropriate spectral region from this CT excited state,[25] and thus the fluorescence quantum yield must be less than about 10^{-5}. Combining this yield with the estimate of the radiative lifetime implies that the $^1T_{1u}$ state must have a lifetime less than 1 ps. The transient observed in this work cannot therefore be identified with this CT excited state.

However, since there must also be a triplet-excited-state manifold corresponding to the excited singlets, the transient might be the lowest CT triplet, $^3T_{1u}$. By arguments similar to those above, and including a factor of about 10^{-3} for the spin prohibition, it would have a maximum lifetime of about 1 ns, long enough to represent the transient. We feel, nevertheless, that since this is not the lowest triplet state, extremely rapid internal conversion to the lowest triplet would restrict the lifetime of the CT triplet to a value appreciably less than the 210 ps found here for the transient. Consequently, ESA is not a reasonable interpretation for the transient absorption observed.

We now turn to the consideration of the second case, namely that the observed spectrum correlates with the presence of the pentachloroplatinate(III) ion. For $PtCl_5^{2-}$, two limiting structures with square-pyramidal (C_{4v}) and trigonal-bipyramidal (D_{3h}) geometries can be envisioned. Previously reported results from Xα calculations on these structures predict a spectrum for the trigonal-bipyramidal form that is quite different from the observed spectrum, but a slightly distorted version of square-pyramidal $PtCl_5^{2-}$ offers the potential for a realistic explanation.[13,14] We have therefore investigated in detail the effects of changes in bond angles and lengths on the predicted spectrum for square-pyramidal $PtCl_5^{2-}$. The results from variations in bond angles from 90° up to 120° (with and without bond length modifications) in general do not support a major contribution from this type of deformation. When the Cl_{ax}–Pt–Cl_{eq} angle is increased from 90°, there is a decrease in the energy difference between the two transitions $5a_1 \rightarrow 6a_1$ and $4a_1 \rightarrow 6a_1$, these being predicted to have considerable intensity (see below). At an angle of about 110°, the transitions become isoenergetic, and with subsequent angular increase, the energy gap rapidly widens; however, the more intense transition is now the one at longer wavelength, which is not in agreement with the experimental observation.

The focus is thus on changes in bond lengths with little deviation from 90° (±5°) angles, and it is pertinent to note that in the analysis of the ligand field spectrum of the similar d^7 ion $Co(CN)_5^{3-}$(aq), significant angular departure (> 98°) from C_{4v} symmetry leads to lack of agreement with the experiment.[26] While we find cases where some differences in Pt–Cl_{ax} and Pt–Cl_{eq} bond lengths can accommodate our spectral results, the most satisfactory solution is one in which all bond lengths are kept equal and are increased by 0.37 Å (0.7 au) relative to the 2.32 Å found for $PtCl_6^{2-}$. In Table I, the electronic energy levels and charge distributions for such a geometry for $PtCl_5^{2-}$ (C_{4v}) are presented: The highest occupied level is $6a_1$, which accommodates one electron. As has been discussed elsewhere,[13,14] the lowest CT transitions that are expected to be intense are $4a_1 \rightarrow 6a_1$ and $5a_1 \rightarrow 6a_1$, which both involve shifts of electron density from the chlorine atoms (p_σ Cl_{ax} and p_π Cl_{eq}, respectively) toward the platinum center (d_{z^2}). In Figure 2, the wave function contours of the three orbitals are shown in the xz plane with the metal center at the origin. Superimposing the contours of $4a_1$ and $5a_1$, respectively, on that of $6a_1$ shows that the overlap of $4a_1$ and $6a_1$ is significantly larger than that of $5a_1$ and $6a_1$, implying that the latter transition will be weaker in intensity. The $4a_1 \rightarrow 6a_1$ transition is of the $p_\sigma \rightarrow d_\sigma$ type whereas $5a_1 \rightarrow 6a_1$ is in the $p_\pi \rightarrow d_\sigma$ category. As has been discussed by Jørgensen,[27] the former type of transition is expected to be very intense and the latter to be less so. The calculated positions are 620 nm ($5a_1 \rightarrow 6a_1$) and 460 nm ($4a_1 \rightarrow 6a_1$). Both the estimated relative intensities and the calculated positions of the two bands are commensurate with the observed spectral features (Figure 1).

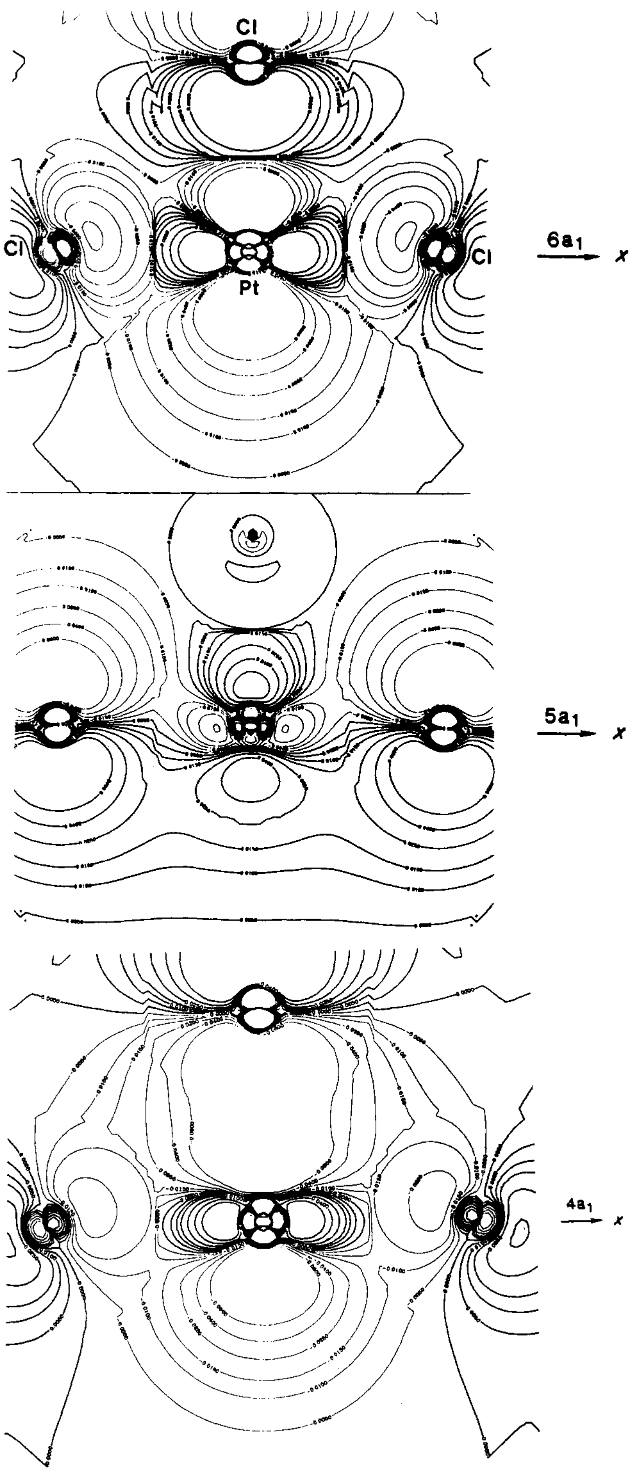

Figure 2. Wave function contours of the $4a_1$, $5a_1$, and $6a_1$ MO's of $PtCl_5^{2-}$ (C_{4v}; elongated Pt–Cl bonds). $6a_1$ is the HOMO, where the electron is transfered from $5a_1$ (620 nm) or $4a_1$ (460 nm). All contours are in the xz plane, containing the platinum center (as the origin), two equatorial chlorines, and the axial one (z axis).

These results in conjunction with the experimental information provide a consistent picture of the nascent photoredox behavior

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(25) Attempts to locate such emission in aqueous solutions of K_2PtCl_6 at room temperature using a SPEX Fluorolog 222 fluorometer were unsuccessful in detecting its presence. At the highest sensitivity level, there may have been some very weak emission near 450 nm; however, the excitation spectrum was not that of $PtCl_6^{2-}$ so this may have been an adventitious impurity.

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of $\mathrm{PtCl_6^{2-}}$ (eq 1) in terms of an excited state with a subpicosecond lifetime, not observed in this work, forming $\mathrm{PtCl_5^{2-}}$ with a 210-ps lifetime. The latter is anticipated intuitively on the basis of the homolytic bond cleavage action. Presumably the decay of the $\mathrm{PtCl_5^{2-}}$ represents its solvation or aquation leading to the formation of the longer lived and less strongly absorbing platinum(III) aquo species, and the presence of some residual absorption is suggestive of this.

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Resonance Raman Spectra of the Ground and Charge-Transfer Excited State of Pentaammine(4,4'-bipyridine)ruthenium(II) and Pentaammine(4,4'-bipyridinium)ruthenium(II)

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Resonance Raman (RR) spectra are reported for aqueous $\mathrm{Ru^{II}(NH_3)_5}$(4,4'-bipyridine) (I) and $\mathrm{Ru^{II}(NH_3)_5}$(4,4'-bipyridine-$\mathrm{H^+}$) ($\mathrm{IH^+}$) in resonance with their charge-transfer absorptions (480 and 570 nm) using CW ($\mathrm{Kr^+}$, 530.9 nm) and pulsed (YAG, 532 nm) laser excitation. Several RR bands are observed, which are assignable to symmetric and antisymmetric combinations of pyridine ring modes by comparison with the biphenyl vibrational spectrum. The previously reported RR spectra of Ru(2,2'-bipyridine)$_3^{2+}$ and of its charge-transfer excited state are also assigned in this framework. At high pulsed laser power levels new Raman bands grow in, which are attributed to ring modes in the charge-transfer excited states by analogy with the biphenyl radical anion RR spectrum. Even though the lifetimes of the charge-transfer states are known from transient absorption spectroscopy to be 36 and 230 ps for I and 30 ps for $\mathrm{IH^+}$, the photon flux is estimated to be sufficient to produce a detectable steady-state population of excited molecules. The excited-state RR spectrum for I at pH 7 appears to contain overlapping contributions from protonated and unprotonated molecules. Although this behavior is not unexpected in view of the enhanced basicity anticipated for the uncoordinated pyridine N atom in the charge-transfer state, for which a $\mathrm{p}K_\mathrm{a}$ of 11.4 is estimated, the short excited-state lifetimes imply that protonation must occur more rapidly than the equilibrium rate.

Introduction

Ruthenium(II) complexes of nitrogen heterocycles have attracted much interest because of the rich photophysical and photochemical phenomena associated with the Ru → heterocycle charge-transfer interactions. Ru(bpy)$_3^{2+}$ (bpy = 2,2'-bipyridine) has been especially popular as a photoelectron-transfer agent because of its strong charge-transfer absorption in the visible region and the relatively long life of its charge-transfer excited state.[1-4] The nature of this state has been probed extensively, and has recently been determined, via analysis of its resonance Raman (RR) spectrum by Woodruff and co-workers[5,6] and by Forster and Hester,[7] to involve localization of charge on one of the bipyridine ligands. Localization has also been explored in mixed-ligand complexes involving 2,2'-bipyridine.[8-10]

In pentaammineruthenium(II) heterocycle complexes, the energy of the metal → ligand charge-transfer (MLCT) state has been shown by Malouf and Ford[11] to control the photochemistry. When the MLCT absorption is to the blue of ~460 nm (in water), photoexcitation leads to ligand replacement by solvent via population of a lower lying ligand field state. For longer wavelength MLCT absorption the photosolvation yield drops sharply, the MLCT state now falling below the photoactive ligand field state.[11] The complex with 4-acetylpyridine ($\lambda_{\max}$ = 523 nm) falls in the latter group. Leroi and co-workers[12] have recently shown it possible to obtain the excited-state RR spectrum of this complex but not of the complex with pyridine itself ($\lambda_{\max}$ = 405 nm), whose charge-transfer state lies above the ligand field state; the lifetime of the charge-transfer state was presumably too short to permit its RR spectrum to be recorded (although weak enhancement due to the mismatch of the 532-nm laser line with the MLCT transition can also account for the absence of an observable spectrum).

In this study we report RR spectra of $\mathrm{Ru^{II}(NH_3)_5}$(4,4'-bpy) (I) and of $\mathrm{Ru^{II}(NH_3)_5}$(4,4'-bpy$\mathrm{H^+}$) ($\mathrm{IH^+}$) in its ground and excited states, using 532-nm excitation from a pulsed YAG laser. These complexes show long-wavelength MLCT absorption (480 and 570 nm) and low photoaquation quantum yields.[13] The excited-state RR frequencies are interpreted as arising from the MLCT state, in which the transferred electron is delocalized over the two bipyridine rings, supporting a quinoid-like resonance structure. In this structure a negative charge is concentrated on the N atom not coordinated to Ru. Consistent with the enhanced basicity expected for this state, the excited-state RR spectrum at pH 7 indicates partial protonation of the complex. Recent picosecond absorption transient measurements by Winkler et al.[13] have shown short lifetimes for the MLCT states and support a more detailed model of excited-state ordering. The pumping of the excited-state RR spectra despite the short lifetimes is attributable to the high photon flux in the 10-ns YAG pulses and high RR cross sections

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