must undergo two nitrogen inversions during isomerization. However, unlike the 14aneN$_4$ complex, the 13aneN$_4$ complex provides the first example of a configurational isomer intermediate that is observable during the course of the isomerization reaction. The slightly lower energy of λ_{max} for the intermediate α complex (435 nm), compared to that of the stable β isomer, is consistent with a somewhat poorer match between metal ion and macrocycle cavity size.

The trans-V or (+−++) isomer, which differs from the cis complex by inversion of a single nitrogen and which in turn yields the trans-II β isomer by subsequent inversion of a second nitrogen, appears to be a likely structure for the α isomer.

One final point must be mentioned. Although the kinetic scheme shown in eq 1 is consistent with the observed biphasic kinetics, another kinetic scheme (eq 4) is also possible. Here the

$$\alpha\text{-Ni(13aneN}_4)^{2+} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} cis\text{-Ni(13aneN}_4)(\text{H}_2\text{O})_2^{2+} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \beta\text{-Ni(13aneN}_4)^{2+} \quad (4)$$

species α-Ni(13aneN$_4$)$^{2+}$ is not an intermediate, but a dead-end species formed in a relatively rapid equilibrium and then disappearing as the more stable product β-Ni(13aneN$_4$)$^{2+}$ is formed. Computer simulation of absorbance–time data sets similar to that in Figure 1 showed that, with only minor adjustment of the rate constants k_1, k_2, k_3, and k_4, either kinetic scheme was able to reproduce the data equally well. At the present time no way of resolving this case of kinetic indistinguishability seems apparent.

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Binuclear Platinum(II) Photochemistry. Nucleophile-Induced Reduction of Electron Acceptors by Electronically Excited $Pt_2(P_2O_5H_2)_4^{4-}$

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The electronic excited states of a number of inorganic complexes have been used as reagents to induce electron-transfer reactions.[2,3] In such reactions, a powerful oxidant (reductant) is generated by oxidative (reductive) quenching of the excited state of the metal complex with a one-electron acceptor A (donor D), and this species generally back-reacts rapidly with photogenerated A$^-$ (D$^+$). Here we describe several oxidative quenching reactions of a strongly emissive complex, Pt$_2$(pop)$_4^{4-}$ (pop = P$_2$O$_5$H$_2$);[3-9] the most important result is that the back-reaction between photogenerated Pt$_2$(pop)$_4^{3-}$ and A$^-$ can be inhibited by axial–ligand binding.

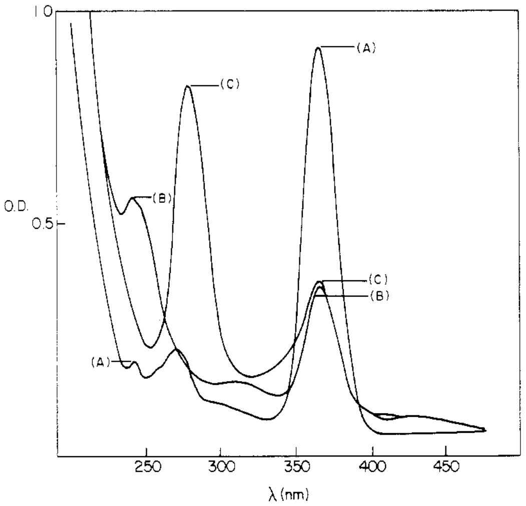

Figure 1. UV–vis spectral changes for the photolysis of Pt$_2$(pop)$_4^{4-}$ in an air-saturated 0.1 M HClO$_4$ aqueous solution: (a) before photolysis; (b) after photolysis for ~0.5 h; (c) after photolysis for the product with added KCl.

Experimental Section

Materials. K$_4$[Pt$_2$(pop)$_4$]·3H$_2$O and K$_4$[Pt$_2$(pop)$_4$X$_2$]·2H$_2$O (X = Cl,Br,SCN) were prepared and purified by standard procedures.[10-12] The structures of all four compounds have been determined by X-ray crystallographic methods.[4,11-15] The complexes *trans*-[Ru(en)$_2$Cl$_2$]ClO$_4$[16a] (en = 1,2-diaminoethane), [Ru(NH$_3$)$_5$His]Cl$_3$[16b] (His = histidine), and *trans*-[Os(NH$_3$)$_4$Cl$_2$]ClO$_4$[16c] were synthesized by published procedures. Horse heart cytochrome *c* (type VI) was purchased from Sigma and used without further purification. The protein as received contained (11.0 ± 0.5)% ferrocytochrome *c* (Cyto-C^{2+}) as determined by the addition of a slight excess of K$_3$Fe(CN)$_6$ to several concentrations of protein while optical changes were monitored at 550 nm. Other reagents were of analytical grade and doubly deionized water was used throughout the experiments.

Photochemistry. Photolyses were performed with a 350-W high-pressure mercury short-arc lamp (Illumination Industries, Inc.) coupled with a high-intensity monochromator (Bausch and Lomb). Incident light intensities were taken from average values measured just before and after each photolysis experiment by using ferrioxalate actinometry.[17] Electronic absorption spectra were measured with a Beckman Acta CIII spectrophotometer. To minimize any effects arising from secondary photolysis, quantum yields (excitation at 367 nm) were determined within

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Table I. Quantum Yields for the Photooxidation of $Pt_2(pop)_4^{4-}$ in Aqueous Solution

medium[a]	pH	$10^5[Pt_2(pop)_4^{4-}]$/ mol dm^{-3}	product	Φ_{ox}
0.1 M $HClO_4$	1.1	2.8	$Pt_2(pop)_4(H_2O)_2^{2-}$	7.3×10^{-4}
0.1 M H_2SO_4	1.1	3.3	$Pt_2(pop)_4(H_2O)_2^{2-}$	6.2×10^{-4}
0.1 M HCl	1.1	1.3	$Pt_2(pop)_4Cl_2^{4-}$	4.4×10^{-2}
0.1 M HCl	1.1	2.7	$Pt_2(pop)_4Cl_2^{4-}$	3.7×10^{-2}
0.1 M HCl	1.1	5.3	$Pt_2(pop)_4Cl_2^{4-}$	2.7×10^{-2}
0.01 M NaCl[b]	4.5	3.8	$Pt_2(pop)_4Cl_2^{4-}$	1.3×10^{-4}
0.02 M NaCl[b]	4.5	3.8	$Pt_2(pop)_4Cl_2^{4-}$	2.0×10^{-4}
0.04 M NaCl[b]	4.5	3.8	$Pt_2(pop)_4Cl_2^{4-}$	3.1×10^{-4}
0.06 M NaCl[b]	4.6	3.9	$Pt_2(pop)_4Cl_2^{4-}$	4.0×10^{-4}
0.08 M NaCl[b]	4.6	3.9	$Pt_2(pop)_4Cl_2^{4-}$	5.0×10^{-4}
0.10 M NaCl	4.7	3.8	$Pt_2(pop)_4Cl_2^{4-}$	5.7×10^{-4}
0.20 M NaCl	4.7	3.9	$Pt_2(pop)_4Cl_2^{4-}$	8.6×10^{-4}
0.30 M NaCl	4.7	3.7	$Pt_2(pop)_4Cl_2^{4-}$	9.4×10^{-4}
0.50 M NaCl	4.8	3.9	$Pt_2(pop)_4Cl_2^{4-}$	10.5×10^{-4}
0.005 M NaBr[b]	4.5	3.4	$Pt_2(pop)_4Br_2^{4-}$	3.5×10^{-4}
0.01 M NaBr[b]	4.5	3.4	$Pr_2(pop)_4Br_2^{4-}$	7.1×10^{-4}
0.02 M NaBr[b]	4.6	3.4	$Pt_2(pop)_4Br_2^{4-}$	1.2×10^{-3}
0.04 M NaBr[b]	4.8	3.4	$Pt_2(pop)_4Br_2^{4-}$	1.6×10^{-3}
0.06 M NaBr[b]	4.9	3.5	$Pt_2(pop)_4Br_2^{4-}$	1.9×10^{-3}
0.08 M NaBr[b]	5.0	3.5	$Pt_2(pop)_4Br_2^{4-}$	2.3×10^{-3}
0.10 M NaBr	5.2	3.6	$Pt_2(pop)_4Br_2^{4-}$	2.6×10^{-3}
0.005 M KNCS[b]	4.5	3.8	$Pt_2(pop)_4(SCN)_2^{4-}$	9.7×10^{-3}
0.01 M KNCS[b]	4.6	3.9	$Pt_2(pop)_4(SCN)_2^{4-}$	1.7×10^{-2}
0.02 M KNCS[b]	4.8	3.9	$Pt_2(pop)_4(SCN)_2^{4-}$	2.7×10^{-2}
0.04 M KNCS[b]	5.0	3.8	$Pt_2(pop)_4(SCN)_2^{4-}$	4.4×10^{-2}
0.06 M KNCS[b]	5.2	3.6	$Pt_2(pop)_4(SCN)_2^{4-}$	5.2×10^{-2}
0.08 M KNCS[b]	5.4	3.9	$Pt_2(pop)_4(SCN)_2^{4-}$	6.4×10^{-2}
0.10 M KNCS	5.7	3.8	$Pt_2(pop)_4(SCN)_2^{4-}$	6.7×10^{-2}
0.20 M KNCS	5.7	3.7	$Pt_2(pop)_4(SCN)_2^{4-}$	8.7×10^{-2}
0.30 M KNCS	5.7	3.9	$Pt_2(pop)_4(SCN)_2^{4-}$	9.7×10^{-2}
0.50 M KNCS	5.8	3.8	$Pt_2(pop)_4(SCN)_2^{4-}$	10.7×10^{-2}

[a] All the solutions were saturated with air prior to photolysis. [b] Ionic strength of the solution = 0.1 M (maintained with $NaClO_4$).

the first 10% of the photolysis experiments. They were found to be dependent on acid concentrations, complex concentrations, and the presence or absence of oxygen in the reaction solutions. For the quantum yield determinations of the photooxidation of $Pt_2(pop)_4^{4-}$ to $Pt_2(pop)_4X_2^{4-}$ by O_2, the solutions were saturated with air prior to the photolysis experiments. All deoxygenated solutions were prepared by degassing in five freeze-pump-thaw cycles.

Flash photolyses were performed with standard instrumentation; the excitation source was the 355-nm output of a Quanta-Ray DCR-2 Nd:YAG laser. The optical path of the flash-photolysis cell was 1 cm.

Electrochemistry. Cyclic voltammograms (cv) were obtained with Princeton Applied Research (PAR) instruments: Model 175 (universal programmer) and Model 173 (potentiostat-galvanostat). Pyrolytic graphite and glassy-carbon electrodes were used as the working electrode. The reaction cell was a standard PAR Model K64 three-electrode jacketed polarographic cell that was maintained to ±0.1 °C by thermostated water. Cyclic voltammograms were recorded with a Houston Model 100 X-Y recorder at slow scan rates (<1 V s^{-1}) and with a Tektronix Model 5103N storage oscilloscope at high scan rates (>1 V s^{-1}). All reaction solutions were deaerated before the cv scans.

Results and Discussion

The UV-vis spectral changes of air-saturated, aqueous $HClO_4$ (0.1 M) solutions of $Pt_2(pop)_4^{4-}$ upon excitation at 367 or 450 nm are shown in Figure 1. The peak at 367 nm ($^1A_{1g} \rightarrow {}^1A_{2u}$ transition of $Pt_2(pop)_4^{4-}$) disappears, and a peak at 245 nm (estimated $\epsilon_{max} \sim 2.1 \times 10^4$ M^{-1} cm^{-1})[18] develops. The 245-nm species, which subsequently degrades, can also be generated by treating $Pt_2(pop)_4^{4-}$ with 2 equiv of $[NH_4]_2[Ce(NO_3)_6]$ in water. Addition of Cl^- to the solution after photolysis leads to an immediate red shift of the 245-nm band to 282 nm, indicating the formation of $Pt_2(pop)_4Cl_2^{4-}$.[10,11] We tentatively identify the 245-nm species as $Pt_2(pop)_4(H_2O)_2^{2-}$. The observed red shift of the $d\sigma \rightarrow d\sigma^*$ transition from 245 nm in $Pt_2(pop)_4(H_2O)_2^{2-}$ to 282 nm in $Pt_2(pop)_4Cl_2^{4-}$ accords with an MO model in which the $d\sigma$ level has appreciable σ(Cl) character in the latter case.[10,12] The quantum yield for the formation of $Pt_2(pop)_4(H_2O)_2^{2-}$ (Φ_{ox}) is insensitive to the nature of the acid present (Table I). We have found that Φ_{ox} is smaller than the quantum yield for the disappearance of $Pt_2(pop)_4^{4-}$ (Φ_{DE}), indicating the presence of a secondary process. For example, in 0.1 M $HClO_4$, $[Pt_2(pop)_4^{4-}] = 2.8 \times 10^{-5}$ M, Φ_{ox} and Φ_{DE} are 7.3×10^{-4} and 1.7×10^{-3}, respectively. Prolonged photolysis of $Pt_2(pop)_4^{4-}$ in 0.1 M $HClO_4$ or 0.1 M H_2SO_4 leads to complete destruction of the $Pt_2(pop)_4$ unit.

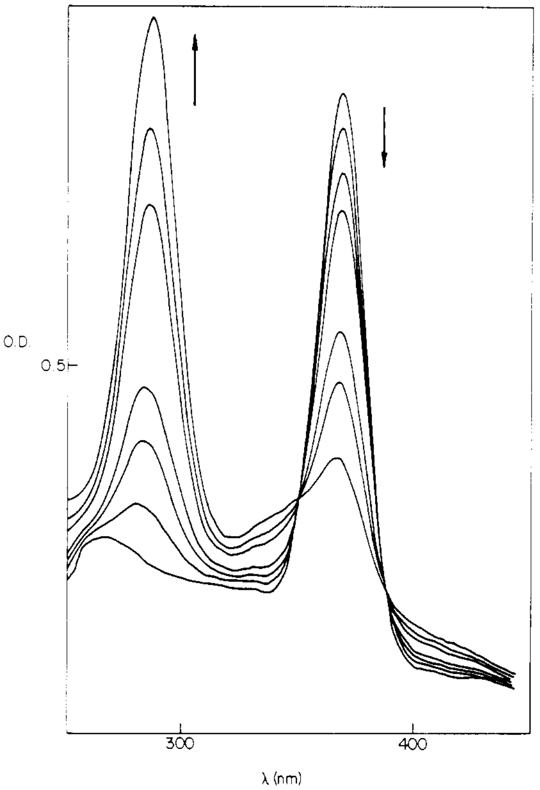

Figure 2. UV-vis spectral changes for the photolysis of $Pt_2(pop)_4^{4-}$ in 0.1 M HCl.

In the presence of added nucleophile X^- (X = Cl, Br, SCN), UV-vis excitation of $Pt_2(pop)_4^{4-}$ in neutral or acidic solution results in rapid and clean aerial oxidation to $Pt_2(pop)_4X_2^{4-}$. The UV-vis spectral changes during the course of the photoreaction in HCl (0.1 M) (Figure 2) (isosbestic points at 387 and 350 nm) are identical with those for the corresponding thermal reaction.[10] The quantum yields for formation of $Pt_2(pop)_4X_2^{4-}$ (Φ_{ox}) measured under various experimental conditions are given in Table I. In general, Φ_{ox} increases with decreasing pH of the solution. It also increases with increasing nucleophilicity and concentation of X^-. At sufficiently high concentrations of X^- ($[X^-] > 0.1$ M), Φ_{ox} reaches a limiting value, designated Φ_{max}, where Φ_{max} is much greater for SCN^- than for Cl^- (Figure 3). From Table I, it is evident that Φ_{ox} increases with decreasing concentration of $Pt_2(pop)_4^{4-}$, indicating the importance of self-quenching in the deactivation of the phosphorescence.

Flash photolysis of a sample containing 25 μM $Pt_2(pop)_4^{4-}$ and 40 μM *trans*-$[Ru(en)_2Cl_2]ClO_4$ in 0.1 M deoxygenated KSCN solution gave a prompt signal that decayed after several milliseconds. The transient absorption difference spectra recorded at 10 μs (prompt spectrum) and 10 ms (delayed spectrum) after the laser flash are shown in Figures 4 and 5, respectively. The delayed spectrum, which was unchanged over a period of 100 ms, is the same as the $Pt_2(pop)_4(SCN)_2^{4-}$ ($\lambda_{max} \sim 337$ nm)/$Pt_2(pop)_4^{4-}$ difference spectrum. This is consistent with steady-state photolysis experiments, where irradiation of $Pt_2(pop)_4^{4-}$ in KSCN solution in the presence of *trans*-$[Ru(en)_2Cl_2]ClO_4$ led to the formation of $Pt_2(pop)_4(SCN)_2^{4-}$. The prompt spectrum (Figure 4) is that of the $Pt^{II}Pt^{III}$ mixed-valence intermediate, $Pt_2(pop)_4(SCN)^{4-}$,

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(18) The ϵ_{max} of $Pt_2(pop)_4(H_2O)_2^{2-}$ was determined by measuring the amount of $Pt_2(pop)_4Cl_2^{4-}$ produced upon addition of Cl^- to the $Pt_2(pop)_4(H_2O)_2^{2-}$ solution.

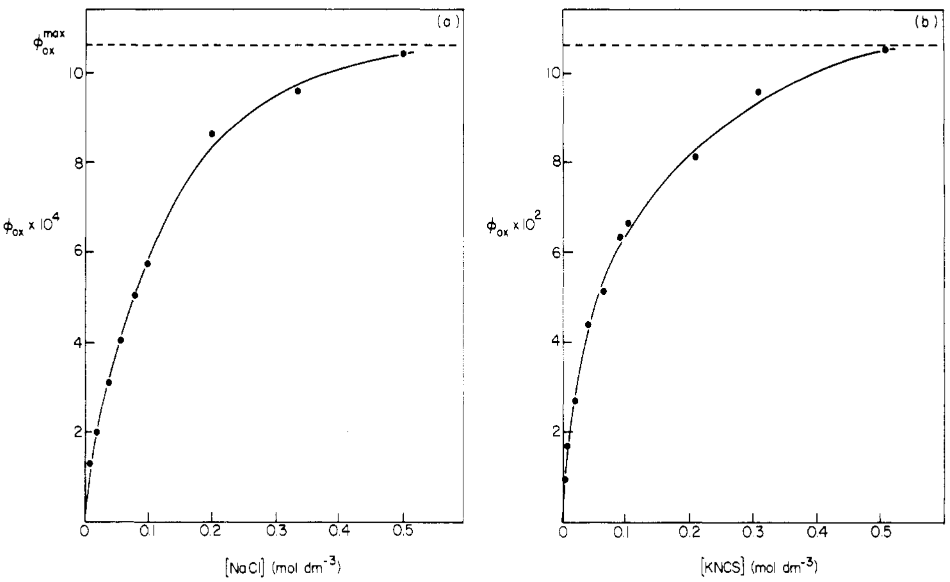


Figure 3. Φ_{ox} vs. [X$^-$] plots for the photooxidation of $Pt_2(pop)_4^{4-}$: (a) X = Cl; (b) X = SCN.

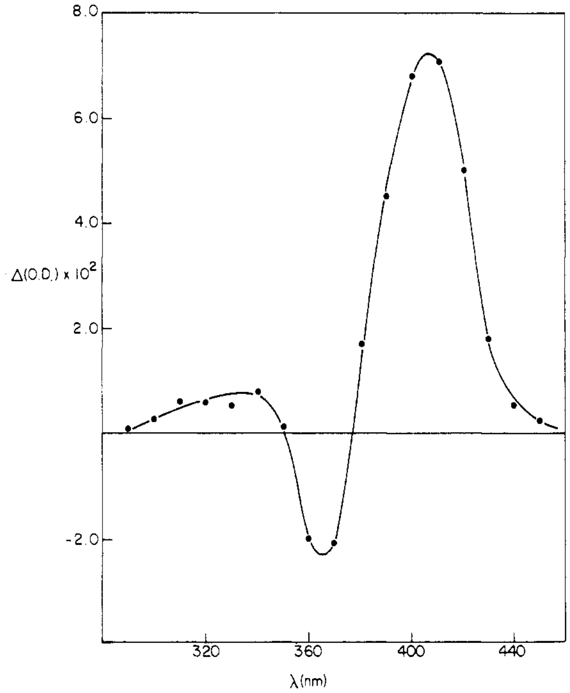


Figure 4. Prompt (recorded 10 μs after the laser flash) transient absorption difference spectrum of a 25 μM $Pt_2(pop)_4^{4-}$ solution containing KSCN (0.1 M) and *trans*-[Ru(en)$_2$Cl$_2$]ClO$_4$ (40 μM).

minus that of $Pt_2(pop)_4^{4-}$. After correction for $Pt_2(pop)_4^{4-}$ absorption, the spectrum of $Pt_2(pop)_4(SCN)^{4-}$ agrees with that found by pulse radiolysis of $Pt_2(pop)_4(SCN)_2^{4-}$ in aqueous solution (λ_{max} for $Pt_2(pop)_4(SCN)^{4-}$ ~ 390 nm).[19] Similar results also have been obtained in flash photolysis experiments on $Pt_2(pop)_4^{4-}$/SCN$^-$ solutions with O_2 as the electron acceptor.

The proposed mechanism for the photochemical oxidation of $Pt_2(pop)_4^{4-}$ by various acceptors, A, is outlined in Scheme I. Previous studies have shown that the $^3A_{2u}$ state of $Pt_2(pop)_4^{4-}$ is an extremely powerful one-electron reductant and that this state is oxidatively quenched very rapidly by many molecules and ions.[3,6a] In the presence of excess nucleophile X$^-$, the photogenerated $Pt_2(pop)_4^{3-}$, which is coordinatively unsaturated, is converted into $Pt_2(pop)_4X^{4-}$, whose presence for X = SCN has been confirmed in the flash photooxidation of $Pt_2(pop)_4^{4-}$ to $Pt_2(pop)_4(SCN)_2^{4-}$. These mixed-valence diplatinum(II,III) species are unstable and react as follows: For cases in which $E_f°(A/A^-)$ is

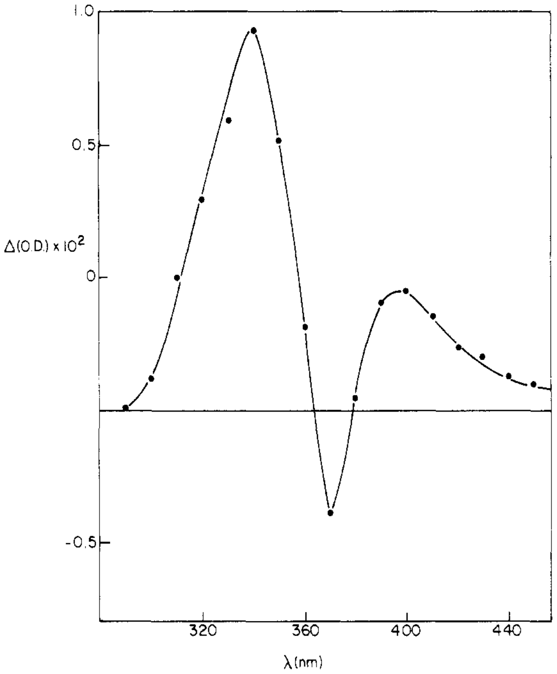
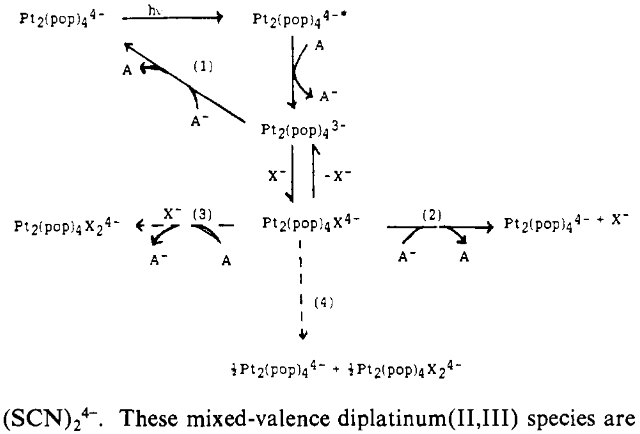


Figure 5. Delayed (recorded 10 ms after the laser flash) transient absorption difference spectrum of a 25 μM $Pt_2(pop)_4^{4-}$ solution containing NaSCN (0.1 M) and *trans*-[Ru(en)$_2$Cl$_2$]ClO$_4$ (40 μM).

Scheme I. Proposed Mechanism for the Photooxidation of $Pt_2(pop)_4^{4-}$ to $Pt_2(pop)_4X_2^{4-}$ by A



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[19] Che, C.-M.; Gray, H. B.; Atherton, S. J.; Lee, W. M. *J. Phys. Chem.*, in press.

less than $E_f^\circ(Pt_2(pop)_4X^{4-}/Pt_2(pop)_4^{4-})$ or $E_f^\circ(Pt_2(pop)_4^{3-}/Pt_2(pop)_4^{4-})$, $Pt_2(pop)_4X^{4-}$ and $Pt_2(pop)_4^{3-}$ back-react with A^- (pathways 1 and 2 to regenerate the starting material, $Pt_2(pop)_4^{4-}$, as observed when A is one of a number of osmium(III) complexes (vide infra). The fully oxidized species, $Pt_2(pop)_4X_2^{4-}$, is produced (pathways 3 and 4 when $E_f^\circ(A/A^-)$ is greater than $E_f^\circ(Pt_2(pop)_4X^{4-})$ or $E_f^\circ(Pt_2(pop)_4^{3-}/Pt_2(pop)_4^{4-})$, as observed for A = *trans*-$Ru(en)_2Cl_2^+$ or O_2 and X = SCN.

It is difficult to estimate the E_f° value for the $Pt_2(pop)_4^{3-}/Pt_2(pop)_4^{4-}$ couple because the electrochemistry of $Pt_2(pop)_4^{4-}$ is not reversible. The cyclic voltammograms of $Pt_2(pop)_4^{4-}$ in $HClO_4$ (1.0 M) and NaX (0.1 M) solutions are characterized by an irreversible anodic wave, the potential (E_{pa}) of which decreases with increasing concentration and nucleophilicity of X^- (in 0.1 M NaX solutions, E° is 0.7, 0.5, and 0.4 V vs. SCE for X = Cl, Br, and SCN, respectively). However, as evidence for the thermal oxidation of $Pt_2(pop)_4^{4-}$ by one-electron acceptors[20] such as Cyto-C^{3+}, $Co(EDTA)^-$, $Ru(NH_3)_5His^{3+}$, and *trans*-$Ru(NH_3)_4Cl_2^+$ has not been found, it is likely that E_f° for $Pt_2(pop)_4^{3-}/Pt_2(pop)_4^{4-}$ is >0.15 V vs. SCE. This value is in reasonable agreement with that reported by Roundhill and co-workers.[21]

One-electron acceptors such as $Co(EDTA)^-$, $Ru(NH_3)_5His^{3+}$, $Co(ox)_3^{3-}$, *trans*-$Os(NH_3)_4Cl_2^+$, BSEP (BSEP = 1,1′-bis(α-sulfoethyl)-4,4-bipyridinium inner salt), O_2, and *trans*-$Ru(en)_2Cl_2^+$ have been found to quench the phosphorescence of $Pt_2(pop)_4^{4-}$ efficiently.[6a,20] The photoformation of $Pt_2(pop)_4X_2^{4-}$ has been induced by *trans*-$Ru(en)_2Cl_2^+$, whose thermal reaction with $Pt_2(pop)_4^{4-}$ apparently does not proceed at room temperature.[20] With reagents such as *trans*-$Os(NH_3)_4Cl_2^+$, which possess very negative E_f° values, net photoformation of $Pt_2(pop)_4X_2^{4-}$ was not observed upon steady-state irradiation. This is understandable in terms of rapid back-decay of photogenerated $Pt_2(pop)_4^{3-}$ (or $Pt_2(pop)_4X^{4-}$) to $Pt_2(pop)_4^{4-}$ through pathway (1 or 2, because of the large driving force of the reaction.

With A = O_2, nucleophile-induced photooxidation of $Pt_2(pop)_4^{4-}$ occurs with no observable degradation of the $Pt_2(pop)_4$ unit. The E_f° of the O_2/O_2^- couple at 25 °C in water (pH 7) has been found to be −0.155 V vs. NHE.[21] As the E_f° value for $Pt_2(pop)_4^{3-}/Pt_2(pop)_4^{4-}$ is <−1 V vs. NHE,[6a] oxidative quenching of excited $Pt_2(pop)_4^{4-}$ by O_2 is expected to be nearly diffusion-controlled, because of the large driving force of the reaction ($\Delta E^\circ > 0.8$ V). Experimentally, O_2 quenches the phosphorescence of $Pt_2(pop)_4^{4-}$ efficiently ($\sim 10^9$ M^{-1} s^{-1}),[6a,20] although energy as well as electron transfer may contribute significantly to the observed rate.

The involvement of O_2 as a one-electron acceptor also may be inferred from the dramatic increase in Φ_{ox} with increasing acidity of the solution (Table I). Increasing the concentration of H^+, which tends to remove O_2^- by protonation to $^\bullet HO_2$, can inhibit the back-reaction of O_2^- with $Pt_2(pop)_4^{3-}$ (or $Pt_2(pop)_4X^{4-}$) and also lead to the formation of $Pt_2(pop)_4X_2^{4-}$ through $^\bullet HO_2$ oxidation. The increase in Φ_{ox} with increasing concentration and nucleophilicity of X^- is in accord with the corresponding increase in the concentration of $Pt_2(pop)_4X^{4-}$ in the photooxidation process.

In irradiated Cyto-$C^{3+}/Pt_2(pop)_4^{4-}$/NaX (0.1 M) solutions,[22] decay of photogenerated Cyto-C^{2+} to Cyto-C^{3+} is much slower for X = Cl than for X = H_2PO_4, thereby indicating that the back-reaction can be inhibited by axial-ligand binding. With a better nucleophile, SCN^-, the back-decay of Cyto-C^{2+} is strongly inhibited. Such inhibition is important, because it means that $Pt_2(pop)_4^{4-}$ can be used as an efficient photoreduction initiator of intramolecular electron-transfer reactions in multisite proteins and protein complexes.[23] Replacement of the standard $Ru(bpy)_3^{2+}$/EDTA photoreducing system[2] with $Pt_2(pop)_4^{4-}/SCN^-$ will facilitate certain types of transient absorption spectroscopic measurements, because the binuclear Pt^{II} complex does not absorb as strongly as $Ru(bpy)_3^{2+}$ at wavelengths above 400 nm.

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Registry No. $Pt_2(pop)_4^{4-}$, 80011-25-2; $Pt_2(pop)_4(H_2O)_2^{2-}$, 99546-98-2; $Pt_2(pop)_4Cl_2^{4-}$, 87355-26-8; $Pt_2(pop)_4Br_2^{4-}$, 87374-25-2; $Pt_2(pop)_4(SCN)_2^{4-}$, 102133-43-7; *trans*-$[Ru(en)_2Cl_2]ClO_4$, 56172-97-5; $HClO_4$, 7601-90-3; HCl, 7647-01-0; NaCl, 7647-14-5; NaBr, 7647-15-6; KNCS, 333-20-0; cytochrome *c*, 9007-43-6.

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[22] Flash photolysis of a sample containing 50 μM cytochrome *c* in 0.1 M Na_2HPO_4 solution (11% reduced) gives a prompt signal that decays on a millisecond time scale following excitation. The magnitude of the prompt signal was studied at constant laser power between 500 and 600 nm, where the platinum complexes have little absorption. The spectrum thus obtained agrees closely with that predicted from the difference spectra of Cyto-C^{3+}/Cyto-C^{2+}, indicating that the prompt signal corresponds to the photoinduced reduction of the protein. In 0.1 M NaCl, the rate of decay of the signal (or the back-reaction) decreases by more than tenfold. In 0.1 M NaSCN, the prompt signal remains relatively constant over 200 ms, indicating that essentially no back-decay of Cyto-C^{2+} to Cyto-C^{3+} takes place in this time interval.

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Use of NMR Chemical Shifts To Study the Bonding in Mixed-Ligand-Metal Complexes

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In our previous studies of mixed chelates (MXY, where X and Y are bidentate ligands), the properties of the metal ion such as the ionization potentials, optical spectra, and electron spin resonance spectra were reported.[1-3] In general, the above metal properties turned out to be the average of the properties observed for the two nonmixed chelates, MX_2 and MY_2. In order to determine the effects on the ligands themselves, proton and carbon nuclear magnetic resonance can be used. Although the chemical shifts are sensitive to small changes in bonding, the interpretation of the changes is not always straightforward. In this paper, molecular orbital calculations are utilized to interpret the experimental NMR data of platinum(II) acetylacetonate type complexes.

Experimental Section

The calculation procedure was to use the INDO method[4] to determine the geometry of the complexes and then to use the CNDOS method as modified by Rajzmann and Francois[5] to calculate the atomic charges and chemical shifts. A standard program with no reparameterization was utilized so that the results would be as universally applicable as possible. Due to program size limitations H and F atoms were used to place of CH_3 and CF_3 groups, respectively. Also, Be was used in place of the actual metal atom in the calculations. Because of these approximations, only the methine position would be expected to have a high theoretical–experimental correlation. The experimental platinum(II) proton and carbon chemical shift data were taken from a recent paper.[6] This paper reported data for both the palladium(II) and platinum(II) complexes. The correlation coefficient between the two sets of complexes is 0.9998 for the proton data and 0.9997 for the carbon data. Thus, our conclusions

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