Reductive Photochemistry of *cis*-Dichlorobis(1,10-phenanthroline)rhodium(III) Chloride

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The relative quantum efficiencies for loss of *cis*-$Rh(phen)_2Cl_2^+$ (where phen = 1,10-phenanthroline) in the presence of dA (deoxyadenosine), dG (deoxyguanosine), and uric acid have been measured in phosphate buffer. The relative reactivity was uric acid > dG > dA with the quantum efficiency in the presence of uric acid (under argon) approximately unity and that in the presence of dA essentially equal to that for *cis*-$Rh(phen)_2Cl_2^+$ alone. The product distribution was found to be oxygen dependent. *cis*-$Rh(phen)_2Cl_2^+$ aquation products were primarily formed in the presence of oxygen while adduct formation was the primary chemistry in the absence of oxygen. Reductive quenching mechanisms are invoked to account for the increased reactivity in the presence of dG (one electron) and uric acid (two electron). Such a mechanism provides a rationale for the previously observed site of covalent binding of the metal to dG.

Introduction

The photophysics and photochemistry of *cis*-dichlorobis(1,10-phenanthroline)rhodium(III) chloride (cis-$Rh(phen)_2Cl_2^+$) have been of interest to us because this complex can serve as a prototype for a concept of photochemotherapy modeled after the chemical reactions of *cis*-dichlorodiammineplatinum(II) (*cis*-platinum) with DNA. Thus, we have reported the photochemically induced covalent binding of *cis*-$Rh(phen)_2Cl_2^+$ to calf thymus DNA as well as to several nucleosides and nucleotides.[1] We observed that the complex binds more efficiently to the purine bases than the pyrimidines and, of the purines, to guanosine more so than adenosine (e.g. 1.6:1 for polyG vs polyA). Spectral data obtained for two isolated rhodium dG and dA adducts support the assignment of the sites of metalation in these products as N1 for dG and N3 for dA.[1]

The selectivity for purines vs pyrimidines is not surprising in light of the known base selectivity of *cis*-platinum. However, we were struck by the extent of selectivity for dG over dA. The lowest lying excited state of *cis*-$Rh(phen)_2Cl_2^+$ has been assigned as metal-centered (^{3}d−d) from the absorption and low-temperature (77 °K) emission spectra[2] and the generally accepted mechanism for substitution of this state is a dissociation/addition mechanism, which has been substantiated for *cis*-dichlorobis(2,2′-bipyridine)rhodium(III).[3] The sites for metalation of dG and dA (e.g. N1 and N3, respectively; see above) would be expected to have comparable nucleophilicity. One would therefore expect similar binding efficiencies to these purines. The fact that this is not observed implies that a second mechanism may be contributing to the binding reaction.

We now present evidence that this is indeed the case and that this mechanism involves reductive quenching of *cis*-$Rh(phen)_2Cl_2^+$ by dG, followed by electron donor−rhodium bond formation. There is precedent for this proposal, i.e. reductive quenching of the ^{3}d−d excited state of *cis*-dichlorobis(2,2′-bipyridine)rhodium(III) chloride (cis-$Rh(bpy)_2Cl_2^+$) leads to the photosubstitution of the chlorides by water.[4]

Experimental Section

The metal complexes, *cis*-$[Rh(phen)_2Cl_2]Cl{\cdot}2H_2O$, *cis*-$[Rh(phen)_2Cl(OH_2)](ClO_4)_2$, and *cis*-$[Rh(phen)_2(OH_2)_2]$ $(ClO_4)_3{\cdot}2H_2O$ were prepared following published procedures.[5,6] 2′-Deoxyguanosine was purchased from Sigma, 2′-deoxyguanosine from U.S. Biochemical Corp., and uric acid from Aldrich. pH measurements were carried out as previously described.[1] All water was distilled as described previously[1] and the phosphate buffer (pH 7) was prepared from NaH_2PO_4 and Na_2HPO_4 which were purchased from J. T. Baker.

Photolyses were carried out in matched Pyrex photolysis tubes held in a turntable with a Canrad-Hanovia 450 W medium pressure Hg lamp encased in a uranium yellow filter (transmitting >330 nm) at 12−15 °C. "Anaerobic" solutions were bubbled with argon for 20 min in the dark prior to photolysis.

HPLC analyses were performed on 100 μL aliquots with a Varian 9010 Star pump equipped with a Rheodyne 7125 injection port, a Varian 9050 Star variable wavelength detector set at 336 nm, and a HP 3395 integrator. Separations were made on a Hamilton PRP-1 semipreparative column eluted with a 48% HPLC grade methanol (from Mallinckrodt) and 52% 0.1 M ammonium acetate (J. T. Baker) solution at a flow rate of 1.5 mL/min, except where noted.

HPLC analyses of 8-hydroxydeoxyguanosine (8-OH-dG) were performed using a previously published technique.[7] In this technique an electrochemical detector was placed in series before the UV detector which was set at 245 nm. The electrochemical detector consisted of a BAS LC-4C controller and a BAS thin layer cell equipped with a glassy carbon working electrode and a silver−silver chloride reference electrode. The detector response was analyzed by an HP-3393A integrator. Analyses of the 8-OH-dG standard were performed with 25 μL injections with the detector sensitivity set at 100 nA. Analyses of the photolysis solutions were made with 100 μL injections with the detector set at 10 nA. Separations were made on a 4.6 mm × 25 cm Microsorb-MV C18 column (100 Å) eluted with a flow rate of 0.5 mL/min of 20% methanol and 80% of a solution (pH 5.3) 12.5 mM in citric acid (Mallinckrodt), 10 mM in acetic acid (Mallinckrodt), 25 mM in sodium acetate (Matheson Coleman & Bell), and 30 mM in sodium hydroxide (J. T. Baker).

Lyophilization was performed on a Neslab Cryocool equipped Vitris benchtop freeze dryer in Labconco lyophilization flasks.

For the anaerobic irradiations two sets of four 2 mL solutions were prepared which were 1.02 mM in *cis*-$Rh(phen)_2Cl_2^+$ and 20 mM phosphate buffer (pH 7). One solution contained no substrate while

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(1) Mahnken, R. E.; Billadeau, M. A.; Nikonowicz, E. P.; Morrison, H. *J. Am. Chem. Soc.* **1992**, *114*, 9253. See also R. E. Mahnken, Doctoral Dissertation, Purdue University, May, 1991.
(2) Carstens, D. H. W.; Crosby, G. A. *J. Mol. Spectrosc.* **1970**, *34*, 113.
(3) Weiland, S.; DiBenedetto, J.; vanEldik, R.; Ford, P. C. *Inorg. Chem.* **1986**, *25*, 4893.
(4) Kalyanasundaram, K. *Nouv. J. Chim.* **1979**, *3*, 512.
(5) Gillard, R. D.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc.* **1965**, 1951.
(6) Gidney, P. M.; Gillard, R. D.; Heaton, B. T. *J. C. S. Dalton* **1972**, 2621.
(7) Floyd, R. A.; Watson, J. J.; Wong, P. K.; Altmiller, D. H.; Richard, R. C. *Free Rad. Res. Comms.* **1986**, *1*, 163.

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the others were either 4.9 mM in uric acid, 4.98 mM in dG, or 4.98 mM in dA. The solutions were irradiated for 2, 3, and 6 min, with HPLC analyses performed prior to, and following, photolysis. Comparable solutions were irradiated for 4 h when air was present, with analyses at 15, 30, 60, 120, and 240 min.

Photolysis solutions for 8-OH-dG detection were 1.00 mM in *cis*-$Rh(phen)_2Cl_2^+$ and 5.10 mM in dG in 20 mM Trizma buffer (pH 7.2). Two photolyses were performed, one aerobically for 260 min and one anaerobically for 6.5 min (following bubbling with argon for 30 min.).

A 5 mL preparative photolysis solution was prepared which was 1.20 mM in *cis*-$Rh(phen)_2Cl_2^+$, 6.01 mM in uric acid, and 25 mM phosphate buffer (pH 7). This solution was bubbled with argon for 20 min and irradiated for 10 min. The photolysate was bubbled with air for 15 min and lyophilized, and the residue was dissolved in 1 mL of water. After filtration the filtrate was separated by HPLC in 48% methanol and 52% 30 mM ammonium acetate. The longest retained photoproduct (t_r = 15.5 min) was collected and lyophilized. The molecular weight of the photoproduct was determined using both fast atom bombardment (FAB) and plasma desorption (PD). The FAB experiments were carried out on a MS50 mass spectrometer (Kratos Analytical, Inc., Ramsey, NJ) equipped with a Kratos FAB ion source. The sample was dissolved in water and approximately 1 μL was added to the FAB probe tip which contained *m*-nitrobenzyl alcohol as the matrix. The FAB atom gun used xenon and produced a neutral atom beam at 7–8 keV with an ion current of approximately 1 mA. The high-resolution mass measurements were obtained using conventional peak matching procedures. For these measurements, the MS50 mass spectrometer was tuned for a resolution of 10 000. The PD experiments were carried out using a Bioion 20R (Applied Biosystems Sweden AB; Foster City, CA) plasma desorption mass spectrometer. This instrument utilizes a ^{252}Cf ionizing source which produces MeV fission fragments. The interaction of the fission fragments with the sample produces ions which are mass analyzed with a time-of-flight mass spectrometer.[8] The photoproduct was applied to a nitrocellulose-coated Mylar target and allowed to dry prior to being put into the mass spectrometer. The accelerating potential was set at 17 000 kV, with data being collected for 30 min.

Results

A. Photoaquation of *cis*-$Rh(phen)_2Cl_2^+$. The photolysis of *cis*-$Rh(phen)_2Cl_2^+$ under aerobic conditions proceeds with the sequential substitution of Cl^- by water. This photoaquation, as monitored by HPLC, shows a loss in *cis*-$Rh(phen)_2Cl_2^+$ (t_r = 21.3 min) throughout the photolysis concomitant with a growth in *cis*-$Rh(phen)_2Cl(OH_2)^{2+}$ (t_r = 11.0 min) and, after 120 min of photolysis, a growth in *cis*-$Rh(phen)_2(OH_2)_2^{3+}$ (t_r = 6.5 min). These retention times (t_r) were confirmed with authentic samples of the rhodium complexes.[5,6] A small quantity of an unidentified species was also observed (t_r = 7.8 min).

In the anaerobic case, after 6 min of irradiation, about 29% of the *cis*-$Rh(phen)_2Cl_2^+$ had been converted to two products, *cis*-$Rh(phen)_2Cl(OH_2)^{2+}$ and an unidentified species (t_r = 7.5 min) we presume to be identical with that noted above.[9]

B. Photolyses of *cis*-$Rh(phen)_2Cl_2^+$ with dA. An aerobic photolysis of *cis*-$Rh(phen)_2Cl_2^+$ in the presence of dA gave a rate of loss of starting material comparable to that for photolysis of *cis*-$Rh(phen)_2Cl_2^+$ alone and produced the same products. Under argon, photolysis of the complex with dA also proceeded similarly to that of *cis*-$Rh(phen)_2Cl_2^+$ alone but at a slightly slower rate (ca. 0.7). Based upon the reported[10] quantum efficiency (0.02) for photoaquation of the complex we estimate the quantum efficiency for loss of *cis*-$Rh(phen)_2Cl_2^+$ in the presence of dA to be 0.01.

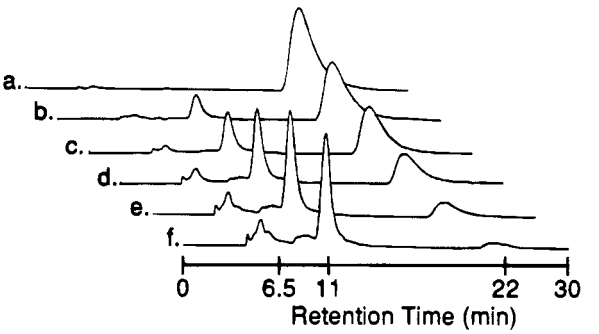


Figure 1. HPLC traces of the photolysis of *cis*-$Rh(phen)_2Cl_2^+$ with dG in the presence of oxygen after 0 min (a), 15 min (b), 30 min (c), 60 min (d), 120 min (e), and 240 min (f) of photolysis.

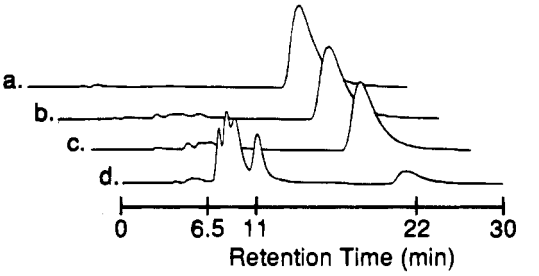


Figure 2. HPLC traces of the argon-degassed photolysis of *cis*-$Rh(phen)_2Cl_2^+$ with dG after 0 min (a), 2 min (b), 3 min (c), and 6 min (d) of photolysis.

C. Photolyses of *cis*-$Rh(phen)_2Cl_2^+$ with dG. The aerobic photolysis of *cis*-$Rh(phen)_2Cl_2^+$ with dG is shown in Figure 1. There was a more rapid loss (ca. 1.3-fold) of the complex, and more rapid growth in *cis*-$Rh(phen)_2Cl(OH_2)^{2+}$ (t_r = 10.8 min), than was observed for photolysis of the complex alone. Several additional products are seen in the HPLC trace, one group with retention times (4.9–6.5 min) similar to *cis*-$Rh(phen)_2(OH_2)_2^{3+}$ and a second (t_r = 8.8–9.5 min) which we assign to the previously observed rhodium–dG adducts.[1]

Analysis of the 260 min aerobic photolysis for 8-OH-dG indicated that a trace amount of 8-OH-dG was produced. The identification was made by matching the retention times from electrochemical detection (822 mV vs NHE) and oxidation potentials of a species in the photolysate (t_r = 11.9 min) and the authentic 8-OH-dG (t_r = 11.9 min). The oxidation potentials were determined from hydrodynamic voltammograms (822, 772, 722, 672, and 622 mV vs NHE) for both the authentic 8-OH-dG (707 mV vs NHE) and the photolysate (708 mV vs NHE).

Photolysis of the complex in the presence of dG under argon (Figure 2) increases the rate of loss by ca. 2.7-fold but with less formation of the chloroaquo product (t_r = 10.6 min) than was seen in air. Also, there were substantial amounts of products at t_r = 8.8, 8.2, and 7.6 min.[11] Based upon the rate enhancement, we estimate the quantum efficiency for loss of starting material to be 0.05.

The 6.5 min anaerobic photolysis also contained a trace amount of 8-OH-dG as determined by matching the retention times of the photolysate species and the authentic 8-OH-dG observed by electrochemical detection (822 mV vs NHE).[12]

(8) Roepstorff, P. *Accts. Chem. Res.* **1989**, *22*, 421.
(9) There are several possible structures for this unidentified species, the most notable being *trans*-$Rh(phen)_2XY^{n+}$. While trans isomers have been reported for ethylenediammine and 2,2′-bipyridine analogs, no such report has appeared for a phenanthroline complex.
(10) Muir, M. M.; Huang, W.-L. *Inorg. Chem.* **1973**, *8*, 1831.
(11) There are preliminary spectral data that indicates at least two of these products have the formula *cis*-$Rh(phen)_2Cl(dG)^{n+}$. Such products could be formed by a coupling of the photochemically produced ion pair (see Scheme 1 and Discussion).

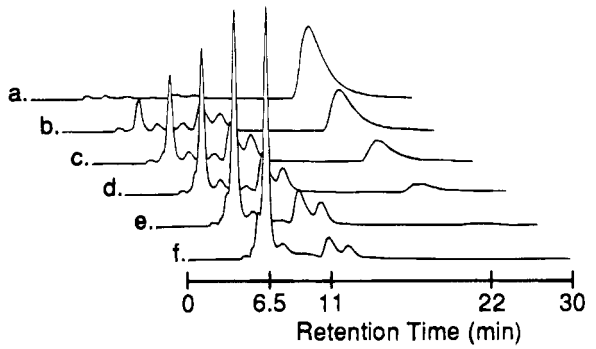


Figure 3. HPLC traces of the photolysis of *cis*-Rh(phen)$_2$Cl$_2^+$ with uric acid in the presence of oxygen after 0 min (a), 15 min (b), 30 min (c), 60 min (d), 120 min (e), and 240 min (f) of photolysis.

D. Photolyses of *cis*-Rh(phen)$_2$Cl$_2^+$ with Uric Acid. The results of an aerobic photolysis of *cis*-Rh(phen)$_2$Cl$_2^+$ with uric acid are shown in Figure 3. The rate of loss of *cis*-Rh(phen)$_2$Cl$_2^+$ was ca. 4.6-fold that observed with dG, with a concomitant increased rate of growth of the major product, *cis*-Rh(phen)$_2$(OH$_2$)$_2^{3+}$ (t_r = 6.1 min). Two unidentified products were also formed. One (t_r = 7.4 min) had a concentration which remained fairly constant after 30 min of photolysis. The concentration of the other (t_r = 12.4 min) mirrored that of *cis*-Rh(phen)$_2$Cl(OH$_2$)$^{2+}$.

The anaerobic photolysis of *cis*-Rh(phen)$_2$Cl$_2^+$ with uric acid (Figure 4) produced four products analogous to those formed in air but with a greatly different distribution. After 6 min the primary aerobic product, the diaquo complex (t_r = 6.1 min), was negligible, but there was a slight increase in the chloroaquo product (t_r = 10.8 min). A small quantity of the t_r = 7.7 min product was seen, and the major product corresponded to the t_r = 12.3 min peak. The rate of loss of the *cis*-Rh(phen)$_2$Cl$_2^+$ was dramatically enhanced, being 50-fold that observed for the complex alone. We estimate the quantum efficiency for disappearance of *cis*-Rh(phen)$_2$Cl$_2^+$ in the presence of uric acid to be ca. 1.0!

Low-resolution FAB-MS analysis of the major photoproduct gave a molecular ion at *m/z* 655 with a corresponding ^{37}Cl isotope peak at *m/z* 657. Several other notable peaks were *m/z* 620, 576, 498, 463, and 283. High-resolution FAB-MS on the *m/z* 655 peak yielded a mass of 655.0472 (calculated 655.0473 for RhC$_{28}$H$_{21}$N$_8$O$_3$Cl). The plasma desorption mass spectrum contained peaks at *m/z* 656, 498, and 463 which correlate to the observed peaks in the FAB mass spectrum.

Discussion

Photoaquation of *cis*-Rh(phen)$_2$Cl$_2^+$. The ability to follow the mono- and diaquation of the metal complex by HPLC affords a unique insight into the details of this chemistry. As noted in the Introduction, the now classical mechanism for photosubstitution of d^6 rhodium complexes involves dissociation/addition from the ^{3}d−d excited state. Excitation into this state leads to substitution of the weakest ligand, chloride, by water. We observed that the conversion of *cis*-Rh(phen)$_2$Cl$_2^+$ to *cis*-Rh(phen)$_2$Cl(OH$_2$)$^{2+}$ is quenched by molecular oxygen. The second photoaquation step is also quenched by oxygen, even more so than the first step. This classical mechanism appears to be also operating when *cis*-Rh(phen)$_2$Cl$_2^+$ is photolyzed with dA since the photoaquation of the complex is essentially unaffected by the presence of this base. Extended photolysis does eventually produce a rhodium−dA adduct.[1]

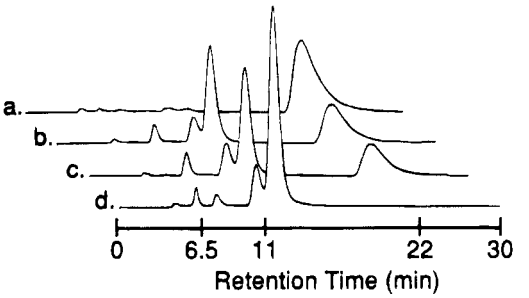


Figure 4. HPLC traces of the argon-degassed photolysis of *cis*-Rh(phen)$_2$Cl$_2^+$ with uric acid after 0 min (a), 2 min (b), 3 min (c), and 6 min (d) of photolysis.

Table 1. Relevant Electrochemical Data[a]

compound	E_{ox} (v)	E_{red} (V)	$^*E_{red}$ (eV)
adenine	1.30[b]		
guanine	1.07[b]		
guanosine	1.03[c]		
uric acid	0.67[b,g]		
cis-Rh(phen)$_2$Cl$_2^+$		−0.57[d,g]	1.18[e]
O$_2$		−0.076[f,g]	

[a] Potentials are reported vs NHE and are one-electron processes except where noted. [b] Reference 28. [c] Reference 18. [d] Reference 14. [e] $^*E_{red} = E_{red} + E^{o-o}$, E^{o-o} was estimated from the emission maximum reported in ref 2. The formula was taken from ref 15. [f] Reference 29. [g] A two-electron process.

Photoaquation in the Presence of dG. There are three key observations that the classical mechanism is not the sole source of substitution by dG. Thus, the presence of dG increases the ϕ_{dis} in argon from 0.02 to 0.05, the product distribution is affected by the presence of oxygen (both phenomena being absent with dA), and an oxidation product of dG is formed.

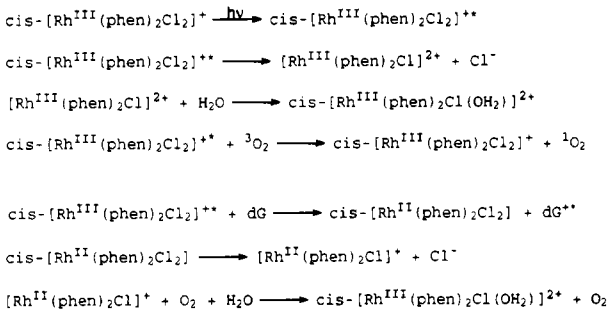
There are several potential ways by which dG could influence photosubstitution of *cis*-Rh(phen)$_2$Cl$_2^+$. These include energy transfer, oxidative quenching, and reductive quenching. In the rhodium case studied here, energy transfer between the ^{3}d−d excited state and the organic substrates would be endothermic and unlikely. Oxidative quenching is likewise unlikely since the Rh$^{IV/III}$ electrochemical couple has not been observed for *cis*-Rh(phen)$_2$Cl$_2^+$. This leaves reductive quenching of the excited state by dG as the most reasonable mechanism for interaction. In fact, such quenching is known, i.e. the efficiencies of reductive quenching of a series of rhodium(III) complexes, including *cis*-Rh(phen)$_2$Cl$_2^+$, by various aromatic compounds, have been reported.[13] The photochemical products which result were not detailed but *cis*-Rh(bpy)$_2$(OH)$_2^+$ (where bpy is 2,2′-bipyridine) has been reported as the ultimate rhodium product of the UV photolysis of aqueous solutions of *cis*-Rh(bpy)$_2$Cl$_2^+$ with the electron donor triethanolamine.[4]

The electrochemistry of *cis*-Rh(phen)$_2$Cl$_2^+$ shows two overlapping one-electron reductions. The loss of Cl$^-$ accompanies each reduction, so the ultimate product is Rh^I(phen)$_2^+$.[14] An analogous reduction of the excited state is possible if the potential donor has an oxidation potential less than the excited state reduction couple (Rh$^{III*/II}$) of *cis*-Rh(phen)$_2$Cl$_2^+$. We can estimate this couple to be 1.18 eV vs NHE by using a procedure described elsewhere.[15] Several relevant oxidation potentials for potential quenchers in this study are shown in Table 1.

(12) Based upon the detector responses for the injected standard (25 μL of a 4 μM solution) and photolysates (100 μL), the upper limit of the 8-OH-dG concentration was estimated to be 1 μM, a small fraction of all "Rh(phen)$_2$"-containing products.

(13) Ohno, T. *Coord. Chem. Rev.* **1985**, *64*, 311.
(14) Kew, G.; DeArmond, K.; Hanck, K. *J. Phys. Chem.* **1974**, *78*, 727.
(15) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; VonZelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85.

Scheme 1. Photochemical Pathways for *cis*-$Rh(phen)_2Cl_2^+$ with and without Deoxyguanosine (dG)



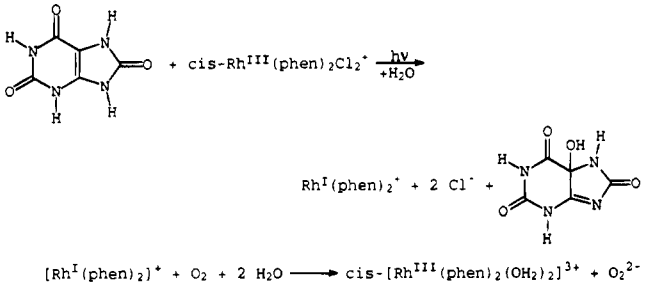
It is clear from these data that, as between guanine and adenine, only guanine has an oxidation potential appropriate for reducing the *cis*-$Rh(phen)_2Cl_2^+$ excited state. We expect the same to be true of the nucleosides since guanosine has an ionization potential 0.4 eV lower than that for adenosine (8.0 vs 8.4 eV, respectively).[16] *We therefore propose that the dG-induced enhancement in ϕ for aquation of cis-$Rh(phen)_2Cl_2^+$ is due to reductive quenching of the excited state by the base.* The resulting one-electron transfer process would yield *cis*-$Rh^{II}(phen)_2Cl_2$ and $dG^{+\bullet}$, with the rhodium complex then dissociating to Cl^- and $Rh^{II}(phen)_2Cl^+$. Interception of this species by water, with concomitant electron transfer to oxygen, would provide the chloraquo product and superoxide anion. Either *cis*-$Rh(phen)_2Cl(OH_2)^{2+}$ or *cis*-$Rh(phen)_2(OH_2)_2^{3+}$ could then be the source of the previously isolated *cis*-$Rh(phen)_2(OH_2)(dG)^{n+}$ adducts.[1] These steps are summarized in Scheme I.

Once formed, $dG^{+\bullet}$ can deprotonate or add water. The addition of water ultimately yields 8-OH-dG, which was detected in trace amounts electrochemically. Kasai et al. have shown that riboflavin will also sensitize the formation of trace amounts of 8-OH-dG from dG by a redox process which does not involve the hydroxyl radical.[17]

It is interesting that the electrochemical observations indicate that guanosine is oxidized in a one-electron−one-proton wave and that the radical site in $G^{\bullet}$ is initially at C8.[18] Rearrangement then occurs such that the radical resides on N1 or the exocyclic amine (NH).[18] The structure of the radical obtained by chemical oxidation−deprotonation of guanosine is disputed. Three sites have been proposed: C8, exocyclic oxygen, and exocyclic amine.[19,20] *Placement of the radical site at N1 would explain the formation of the cis-$Rh(phen)_2(N1\text{-}dG)(OH_2)^{n+}$ product alluded to in the Introduction.*[1,21] Coupling at the amine site has been previously postulated to explain the second, as yet unidentified product, isolated from the same reaction.[1]

The effect of oxygen on the photochemistry observed for *cis*-$Rh(phen)_2Cl_2^+$ with dG supports the electron transfer proposal. Oxygen increases the amount of *cis*-$Rh(phen)_2Cl(OH_2)^{2+}$ while quenching the formation of the radical coupling products. Since the reduction potential of molecular oxygen is more positive than the $Rh^{III/II}$ couple, once $Rh(phen)_2Cl^+$ is formed by reductive quenching it will be oxidized to form *cis*-$Rh(phen)_2Cl(OH_2)^{2+}$ (cf. Scheme I). The oxidation of another reduced rhodium complex, $Rh(bpy)_2^+$, by oxygen has been suggested.[22] Interestingly, oxygen has essentially no effect on the formation of 8-OH-dG. This observation supports the previously proposed mechanism which does not involve reactive oxygen species but merely addition of water to the radical cation of dG.[17]

Scheme 2. Photochemical Reaction of *cis*-$Rh(phen)_2Cl_2^+$ with Uric Acid in the Presence of Oxygen



The proposed reductive quenching mechanism by deoxyguanosine is of biological importance in that it has been invoked for the photochemical cleavage of DNA by two tris(polypyridyl)ruthenium(II) complexes.[23,24]

Two-Electron Processes. *cis*-$Rh(phen)_2Cl_2^+$ was irradiated with uric acid, a more easily oxidizable quencher (Table 1), to substantiate the proposed reductive quenching photochemistry. The important observations from these photolyses are (1) the increased rate of loss of *cis*-$Rh(phen)_2Cl_2^+$ under aerobic (6-fold) and anaerobic (50-fold) conditions; (2) in the latter case, the large quantum efficiency for disappearance of the complex (1.0) versus that observed in the presence of dG; (3) the conversion of *cis*-$Rh(phen)_2Cl_2^+$ directly to *cis*-$Rh(phen)_2(OH_2)_2^{3+}$ when the photolysis is carried out with oxygen present; and (4) the formation of a new rhodium species which contains a uric acid derived ligand.

The correlation between substrate oxidation potential and quantum efficiency for disappearance of *cis*-$Rh(phen)_2Cl_2^+$ substantiates the rationale that the previously discussed rhodium−dG interaction (and the adducts isolated therefrom) involve reductive quenching. One could therefore rationalize the formation of the diaquo product by two sequential one-electron transfer processes. However, one would then expect that there would be a buildup in the concentration of *cis*-$Rh(phen)_2Cl(OH_2)^{2+}$. This did not occur! We therefore propose a two-electron transfer process to form $Rh(phen)_2^+$, which is then oxidized by oxygen to give *cis*-$Rh(phen)_2(OH_2)_2^{3+}$ directly (Scheme 2). The electrochemical oxidation of uric acid has been shown to be a two-electron process,[25] and we estimate that such a two-electron transfer to the metal complex excited state is exothermic by 0.46 eV.

A rhodium−uric acid adduct is the major product under argon. The identity of the rhodium−uric acid photoadduct can be addressed by analysis of the mass spectral data. The FAB and PD mass spectra contain a similar fragmentation pattern. The highest mass peaks correspond to $Rh(phen)_2(L^-)Cl$, where L^- is the deprotonated form of a ligand derived from uric acid (the identity of L is discussed below). The presence of Cl^- is indicated by the isotopic pattern observed in the FAB-MS at *m/z* 655 and 498 as well as the loss of Cl indicated from the fragmentation pattern: *m/z* 655 to 620 and 498 to 463. The presence of $Rh(phen)_2$ is indicated by the observed absorbance

(16) Yu, C.; O'Donnell, T. J.; LeBreton, P. R. *J. Phys. Chem.* **1981**, *85*, 3851.
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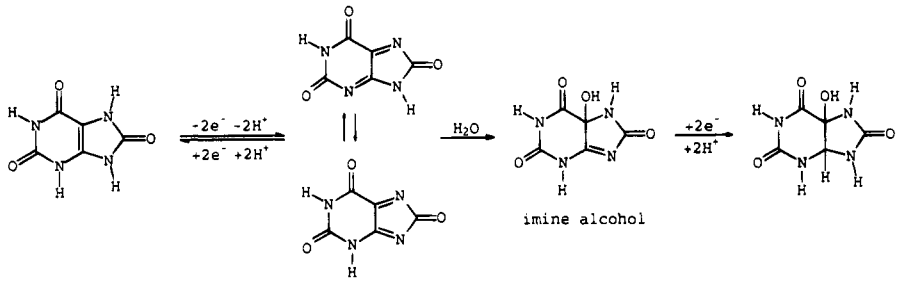
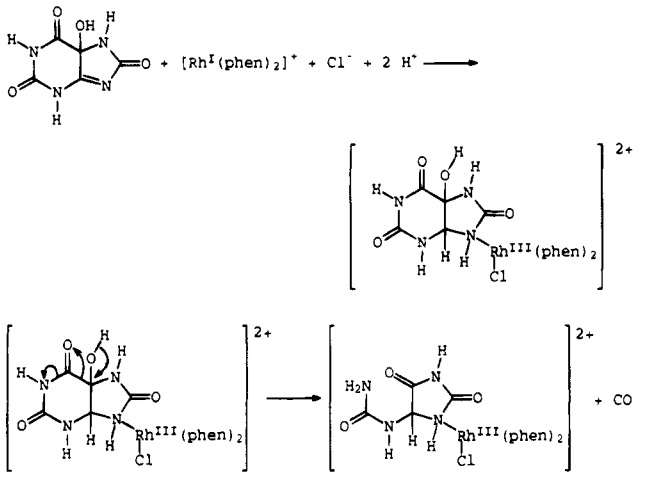
Scheme 3. Electrochemical Oxidation of Uric Acid and Reduction of the Resultant Imine Alcohol[15]



Scheme 4. Oxidative Addition of the Imine Alcohol to $Rh(phen)_2^+$ and CO Elimination



at 336 nm (HPLC) and the MS peaks: *m/z* 498, $Rh(phen)_2Cl$; *m/z* 463, $Rh(phen)_2$; and *m/z* 283, Rh(phen). The peak at *m/z* 576 corresponds to a loss of H_2NCO from the $Rh(phen)_2L^-$ fragment.

With the mass of the molecular ion (655.0472) and the mass of $Rh(phen)_2Cl$ (498.0111), the mass of L has been calculated to be 157.0361, which corresponds to $C_4H_6O_3N_4$ (calculated mass of 157.0362). We propose that L is allantoin, a major product of the electrolysis of uric acid.[25,26] Upon electrolysis uric acid is oxidized in a two-electron–two-proton process to produce an intermediate as an equilibrium mixture of two tautomers. The addition of water yields an imine alcohol which is reducible in a two-electron–two-proton process. These processes are summarized in Scheme 3.

Photolysis of uric acid with *cis*-$Rh(phen)_2Cl_2^+$ gives reduction of the complex to $Rh(phen)_2^+$ concomitant with loss of two Cl^-. Uric acid is oxidized and hydrolyzed, yielding the imine alcohol. These redox active species, $Rh(phen)_2^+$ (−0.57 V vs NHE)[14] and the imine alcohol (ca. −0.7 V vs NHE),[27] undergo a two-electron back-transfer during which the imine alcohol oxidatively adds to $Rh(phen)_2^+$ with incorporation of Cl^- in the coordination sphere. The site of ligation is not known, but it is reasonable to expect ligation to occur near to, or at, the site of reduction, the imine. We therefore postulate that ligation occurs at the imine nitrogen. Once ligated the alcohol undergoes rearrangement, eliminating CO and yielding ligated allantoin. These reactions are summarized in Scheme 4.

Conclusions

We have demonstrated that reductive quenching of the ^3d-d excited state occurs when *cis*-$Rh(phen)_2Cl_2^+$ is photolyzed with dG or uric acid. The former leads to the chloroaquo product and involves a one-electron transfer process. We propose that the same chemistry produces the coupling products previously reported. When uric acid is present a two-electron transfer leads directly to the diaquo product in the presence of oxygen or to a coupling product under argon. These photochemical reactions are summarized in Scheme 1.

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