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Cis–Trans Photoisomerization in $Ru(bpy)_2(OH_2)_2{}^{2+}$. Crystal Structure of *trans*-$[Ru(bpy)_2(OH_2)(OH)](ClO_4)_2$

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Abstract: The cis ⇌ trans photoisomerization of $Ru(bpy)_2(OH_2)_2{}^{2+}$ in acidic aqueous solution has been investigated. The reaction is independent of the wavelength of irradiation and occurs with quantum yields of 0.043 (cis → trans) and 0.025 (trans → cis). In the presence of $ClO_4{}^-$ the photochemical oxidation of $Ru(bpy)_2(OH_2)_2{}^{2+}$ to $Ru(bpy)_2(OH_2)(OH)^{2+}$ occurs and the quantum efficiency for this reaction is linearly dependent on $[ClO_4{}^-]$. The isomerization and oxidation reactions are interpreted as occurring by a dissociative pathway which results from the thermal population of a low lying d–d state which lies above a lowest lying metal–ligand charge-transfer state. The crystal structure of *trans*-$[Ru(bpy)_2(OH_2)OH](ClO_4)_2$ has been determined from three-dimensional X-ray counter data. The complex crystallizes in the trigonal space group $P3_121$ with three formula units in a cell of dimensions a = 10.902 (2), c = 17.070 (4) Å. The structure has been refined to a final value of the conventional R factor of 0.031 based on 2259 independent observations. The geometry of the complex is roughly octahedral, with Ru–N bonds of 2.090 (3) and 2.099 (3) Å. The Ru atom lies on a twofold axis, which constrains the two coordinated oxygen atoms to be equivalent; the additional hydrogen atom formally associated with the water ligand forms a symmetrical hydrogen bond to the hydroxyl ligand on an adjacent ion. The Ru–O distance is 2.007 (3) Å.

Introduction

The recent photochemistry of ruthenium complexes has been dominated by investigations based on $Ru(bpy)_3{}^{2+}$.[1] Most of the work has been directed toward the electron-transfer reactions of $Ru(bpy)_3{}^{2+}$ in its electronically excited, luminescing state.[2] Very little work has been reported dealing with other photochemical reactions of 2,2′-bipyridyl complexes. Watts et al. have investigated the photochemistry of $Ru(bpy)_3{}^{2+}$ in aqueous media[3,4] and recently the results of a series of investigations in nonaqueous solvents have appeared.[5-7] An obvious extension of the work with $Ru(bpy)_3{}^{2+}$ from our point of view is to the study of complexes of the type $[Ru^{II}(bpy)_2L_2]$ where L is a unidentate ligand. No systematic studies of the photochemistry of such complexes have been reported, although their photophysical properties have been reported in a number of investigations.[8-10]

Much of our work on $Ru(bpy)_3{}^{2+}$, as well as the work of others, has been undertaken in search of potential solar energy conversion systems. A good part of our research will ultimately involve the use of related complexes such as those with modified bipyridine rings as well as complexes of the type $[Ru^{II}(bpy)_2L_2]$. In the work it will be essential to establish the photochemical properties of modified $Ru(bpy)_3{}^{2+}$-like complexes. With this in mind, we have undertaken a systematic study of the photochemistry of complexes of the type $[Ru^{II}(bpy)_2L_2]$ in both aqueous and nonaqueous media.

We wish to report here some surprising and novel results observed in the photochemistry of *cis*-$Ru(bpy)_2(OH_2)_2{}^{2+}$ in acidic aqueous solution. A cis ⇌ trans photoisomerization has been observed and characterized:

$$cis\text{-}Ru(bpy)_2(OH_2)_2{}^{2+} \overset{h\nu}{\rightleftharpoons} trans\text{-}Ru(bpy)_2(OH_2)_2{}^{2+} \quad (1)$$

as has the photochemical oxidation of Ru(II) to Ru(III) by $ClO_4{}^-$. We have been able to grow crystals of the salt *trans*-$[Ru(bpy)_2(OH_2)(OH)](ClO_4)_2$ and to prove the trans stereochemistry by X-ray crystallography.

The isolation of the trans complex is surprising since complexes of the type $[M(bpy)_2L_2]$ both for Ru and other metals have been widely accepted as existing only in the cis geometry. The rationale behind this notion has been the severe steric crowding which exists between the hydrogen atoms at the α positions in the bipyridine rings when the geometry is trans.[11] As far as we know there are no structurally confirmed examples of octahedral coordination complexes where the bipyridyl ligands are in the trans configuration. Recently Krause[12] has reported the synthesis of *trans*-$Ru(bpy)_2(py)_2{}^{2+}$ and a series of related complexes. However, the proposed *trans*-bipyridyl structure has not been confirmed crystallographically nor is there convincing spectral evidence especially in view of the large number of mistaken structural assignments in this area in the past.[11,13] Four somewhat related structures are known, the distorted square planar complexes, $[Pd(bpy)_2](NO_3)_2$,[14] $[Pt(bpy)_2][TCNQ)_2]$,[15] and $[Pt(bpy)_2][(TCNQ)_3]$,[16] and the distorted octahedral complex $Cu(bpy)_2(ClO_4)_2$[17] in which the Cu–O distances are 2.45 and 2.73 Å in the solid state. However, none of the known structures involve cases where the *trans*-bpy geometry is found at a metal site where a strong preference exists for a regular octahedral coordination environment.

Experimental Section

Materials. $Ru(bpy)_2CO_3$ was prepared according to published procedures.[18] All other chemicals were reagent grade and used without further purification. The water was doubly distilled, lastly from $KMnO_4$ in an all-glass apparatus. The $K_3[Fe(ox)_3]$ actinometer solutions were prepared and used as described originally by Hatchard and Parker.[19] The actinometer, Reinecke's salt, was prepared and used according to Adamson.[20] Nitrogen gas was purified by passing through a series of two Cr(II) scrubbers.

***cis*-$[Ru(bpy)_2(OH_2)_2](PF_6)_2$.** The source of the cis isomer used in all of the experiments described was $Ru(bpy)_2CO_3$ dissolved in acidic solution. This isomer is extremely difficult to isolate as a solid because of its high solubility. A solid sample was obtained, however, by adding a slight excess of 65% HPF_6 to a concentrated aqueous solution of $Ru(bpy)_2(CO_3)$. The solution volume was then reduced to a few milliliters under vacuum and allowed to stand for several hours, whereupon the desired product crystallized out. All of the above operations were carried out in subdued light to avoid obtaining the trans isomer, whose $PF_6{}^-$ salt is much less soluble.

***trans*-$[Ru(bpy)_2(OH_2)_2](ClO_4)_2$.** A concentrated solution of $Ru(bpy)_2CO_3$ (150 mg in 50 mL of H_2O) was filtered and then acidified with 50 mL of 1 M $HClO_4$. The solution was photolyzed with a 250-W sunlamp until precipitation appeared complete, about 1.5 h. The solid product was filtered off, washed with 2-propanol followed by ether, and finally air dried. Anal. Calcd for $RuC_{20}H_{20}N_4Cl_2O_{10}$: C, 37.05; H, 3.11; N, 8.64. Found: C, 37.09; H, 3.06; N, 8.58.

***trans*-$[Ru(bpy)_2(OH_2)OH](ClO_4)_2$.** Crystals of the salt were prepared by allowing a concentrated acidic solution of *trans*-$[Ru(bpy)_2(OH_2)_2](ClO_4)_2$ to stand in air overnight. The mother liquor of the photolysis solution from the previous preparation may also

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be used if it is exposed to room lights for a few days. The crystals were filtered off and air dried. Anal. Calcd for $RuC_{20}H_{19}N_4Cl_2O_{10}$: C, 37.11; H, 2.96; N, 8.65. Found: C, 36.83; H, 2.86; N, 8.48.

Apparatus. Quantum yields were determined using a 1000-W Xe–Hg compact arc lamp, housed in a Schoeffel lamp housing (LH151N). The light beam was passed through a Bausch and Lomb high-intensity monochromator (catalog no. 33-86-79). Photolyses were carried out in 1-cm spectrophotometric cells which facilitated absorbance readings of the reaction solutions. The cell was positioned approximately 1 in. from the exit slit of the monochromator in a large aluminum block fitted with a water jacket. An additional Corning 3-74 filter was placed in front of the sample cell for irradiations at wavelengths above 400 mm. The bandwidth of the monochromator with a 3-mm exit slit was calculated to be 20 nm. Typical intensities obtained were 2×10^{-8} einstein/s at 436 nm, 4×10^{-9} einstein/s at 334 nm, and 8×10^{-9} einstein/s at 297 nm.

Absorbance measurements were performed on a Bausch and Lomb Spectronic 210 UV spectrophotometer and a Cary 17 spectrophotometer. Emission measurements were performed on a Hitachi Perkin-Elmer fluorescence spectrophotometer MPF-2A.

Quantum Yield Measurements. Light intensities were measured with 3-mL aliquots of actinometer solution in the same cell and under the same conditions as the reaction measurements. Over a period of several months and numerous measurements, the lamp intensity varied by only a few percent. The quantum yields for cis → trans and trans → cis isomerizations were determined from the initial slopes of plots of the isomer concentration vs. time. The isomer concentrations were obtained by solving simultaneous equations for the absorbance readings at 480 and 495 nm. The following extinction coefficients for the Ru(II) complexes were used in the calculations: at 480 nm, trans, 10 100 ± 1000, cis, 8500 ± 200; at 495 nm, trans, 11 800 ± 1000, cis, 7300 ± 200. The reproducibility of the quantum yield measurements was good, with a standard deviation of ±0.005; however, a systematic error of as much as ±0.01 may be present owing to inaccuracies of the extinction coefficients. The solutions to the simultaneous equations are very sensitive to small errors in extinction coefficients. In particular the extinction coefficients for the trans isomer may be in error because of the sensitivity of this isomer to molecular oxygen.

All photolyses were carried out under N_2. The reactions were followed to completion at intervals from 30 s to 3 min depending on the lamp intensity. The [isomers] vs. time plots were only gently curving for the first four to five data points which defined the initial slopes. A variety of initial concentrations were used with no detectable variation in quantum yield after corrections were made for the fraction of light absorbed.

The quantum yield for the appearance of $Ru(bpy)_2(OH_2)(OH)^{2+}$ in 1 N $HClO_4$ was determined from the initial slope of a plot of [Ru(II)] vs. time. Its concentration was determined by subtracting the total Ru(II) isomer concentration at each point from the initial concentration.

Crystallographic Data. Weissenberg and precession photographs indicated that the crystals of $[Ru(bpy)_2(OH_2)(OH)](ClO_4)_2$ belong to the noncentrosymmetric trigonal space group D_3^4-$P3_121$. The cell constants, obtained by least-squares methods, are $a = b = 10.902$ (2) and $c = 17.070$ (4) Å. The observations were made at 22 °C using Mo Kα_1 radiation with an assumed wavelength of 0.709 26 Å. A calculated density of 1.835 g cm^{-3} for three monomeric units in the cell was not in good agreement with the observed value of 1.778 g cm^{-3} measured by flotation in iodomethane and carbon tetrachloride. Since the two values were measured from different crystals, the discrepancy may indicate the existence of a polymorphism, which has a considerable precedence in the structural chemistry of metal complexes of 2,2′-bipyridine and 1,10-phenanthroline.[21,22]

Diffraction data were collected from a prismatic crystal mounted roughly parallel to the crystallographic c axis with faces (100), $(\bar{1}00)$, (010), $(0\bar{1}0)$, $(1\bar{1}0)$, $(\bar{1}10)$, (001), and $(00\bar{1})$. The separations between opposite pairs of faces follow: (100) and $(\bar{1}00)$, 0.015 cm; (010) and $(0\bar{1}0)$, 0.014 cm; (110) and $(\bar{1}10)$, 0.013 cm; (001) and $(00\bar{1})$, 0.060 cm. The data were collected on a Picker four-circle automatic diffractometer equipped with a graphite monochromator using Mo Kα radiation at a takeoff angle of 1.5°. The receiving aperture was 5.0 × 5.0 mm and was placed 35 cm from the crystal. Data were collected in the θ–2θ scan mode at a rate of 1°/min; peaks were scanned from 0.80° in 2θ below the calculated Mo Kα_1 peak position to 0.80° in 2θ above the calculated Mo Kα_2 peak position. Stationary-counter, stationary-crystal backgrounds were collected at both ends of each scan for 10 s out to a 2θ value (Mo Kα) of 45°, and for 20 s thereafter.

A unique data set $(-h, k, l)$ was collected having $2° < 2\theta < 56°$, beyond which there was little intensity above background. Three standard reflections were monitored and showed no systematic decline as a function of exposure time. The data were processed by the method of Ibers and co-workers[23] using their formula for the estimated standard deviation:

$$\sigma(I) = [C + 0.25(t_s/t_b)^2(B_H + B_L) + p^2I^2]^{1/2}$$

the value of p being assigned as 0.04.[24] The values of I and $\sigma(I)$ were corrected for Lorentz-polarization (Lp) using the expression[25]

$$\frac{1}{Lp} = \frac{2 \sin 2\theta}{\cos^2 2\theta_m + \cos^2 2\theta}$$

where the angle of the monochromator, $2\theta_m$, was 12°. The data were also corrected for absorption.[26] The attenuation coefficient for Mo Kα radiation was 17.40 cm^{-1}, and the transmission coefficients ranged from 0.78 to 0.83. There were 2259 independent data collected with intensity greater than three times their estimated standard deviations; only these data were used in the structure analysis and refinement.

Solution and Refinement of Structure. All least-squares refinements in this analysis were carried out on F, the function minimized being $\sum w(|F_o| - |F_c|)^2$ and the weights w being taken as $4F_o^2/\sigma^2(F_o^2)$. In all calculations of F_c the atomic scattering factors for all nonhydrogen atoms were taken from ref 26 and those for hydrogen were taken from Stewart, Davidson, and Simpson.[27] The effects of the anomalous dispersion of Ru, Cl, and O were included in F_c, the values for $\Delta f'$ and $\Delta f''$ being taken from ref 26.

The position of the ruthenium atom was determined from a three-dimensional Patterson function and refined by the method of least squares. The locations of the remaining nonhydrogen atoms were obtained from subsequent difference Fourier syntheses; anisotropic least-squares refinement of these 19 atoms led to values of the unweighted and weighted solutions, $R_1 = \sum|(|F_o| - |F_c|)|/|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$, of 0.040 and 0.048, respectively. The ten independent hydrogen atoms (one of which is constrained to lie on a twofold axis) were located in subsequent difference Fourier syntheses, and a least-squares calculation in which the hydrogen atoms were refined isotropically while all other atoms were refined anisotropically gave values of R_1 and R_2 of 0.031 and 0.033, respectively. The data were corrected for secondary extinction but this did not improve the model significantly.[28,29]

Since only a single form $(\bar{h}kl)$ of the data had been collected, in order to test the enantiomeric model a least-squares calculation was run in which the Miller indices hkl were replaced by $\overline{hkl}$ for all reflections. This test produced residuals of $R_1 = 0.034$ and $R_2 = 0.038$, which indicates that the original model selected is correct.

In the final cycle of least-squares refinement, no atomic parameter underwent a shift of more than 0.12 times its estimated standard deviation, which was taken as evidence that the refinement had converged. The value of R_2 showed no abnormal dependence on $\sin\theta$ or $|F_o|$, which suggested that our weighting scheme was appropriate. A final difference Fourier contained peaks as high as 0.76 e Å^{-3} in the vicinity of the metal atom, but was otherwise featureless. The final value of the extinction coefficient was 1.8 (3) $\times 10^{-7}$. The positional parameters derived from the final least-squares cycle are presented in Table I. The atomic thermal parameters and a list of observed and calculated structure amplitudes are available.[30]

Results

Visible photolysis of *cis*-$Ru(bpy)_2(OH_2)_2^{2+}$ in aqueous solution leads to spectral changes which very slowly revert to the original spectrum after a few days in the dark (under purified N_2). The origin of the color change is a cis ⇌ trans photoisomerization which reaches a photostationary state after a short period of photolysis (eq 1). A justification for the stereochemistry of the trans product based on X-ray crystallography will be presented in a later section.

Quantum yields for both the cis → trans and trans → cis conversions were found to be independent of wavelength and experimental Φ values are given in Table II as a function of wavelength. The same results were obtained in either 1 N H_2SO_4 or 1.0–0.5 N CF_3CO_2H but complications due to ox-

Table I. Positional Parameters in *trans*-[$Ru(bpy)_2(OH)(OH_2)](ClO_4)_2$

atom	*x*	*y*	*z*
RU	0	0.0577(1)	0.6667(1)
CL	0.1821(1)	−0.2561(1)	0.8042(1)
O1	0.2904(4)	−0.2905(5)	0.8199(2)
O2	0.0805(4)	−0.3596(4)	0.7528(2)
O3	0.1166(5)	−0.2561(5)	0.8770(2)
O4	0.2421(5)	−0.1199(4)	0.7692(2)
O5	0.0688(3)	0.0896(3)	0.7779(2)
N1	0.1670(3)	0.2630(4)	0.6466(2)
C2	0.2846(4)	0.2735(4)	0.6136(2)
C3	0.4057(5)	0.4040(5)	0.6026(3)
C4	0.4082(6)	0.5246(5)	0.6281(3)
C5	0.2902(6)	0.5131(5)	0.6642(3)
C6	0.1735(6)	0.3820(5)	0.6736(3)
N1′	0.1584(3)	0.0213(3)	0.6221(2)
C2′	0.2758(4)	0.1393(4)	0.5946(2)
C3′	0.3789(5)	0.1296(6)	0.5524(3)
C4′	0.3634(6)	−0.0018(7)	0.5374(3)
C5′	0.2452(6)	−0.1204(6)	0.5638(3)
C6′	0.1448(6)	−0.1047(6)	0.6056(2)
HC3	0.494(5)	0.416(5)	0.574(3)
HC4	0.489(5)	0.613(5)	0.618(3)
HC5	0.285(5)	0.588(5)	0.678(2)
HC6	0.101(4)	0.372(4)	0.697(2)
HC3′	0.462(5)	0.217(5)	0.531(3)
HC4′	0.424(5)	−0.008(5)	0.512(3)
HC5′	0.238(4)	−0.211(5)	0.563(2)
HC6′	0.065(6)	−0.185(5)	0.626(3)
H1O5	0.144(5)	0.124(6)	0.779(3)
H2O5	0.012(9)	0	0.833(1)

Table II. Quantum Yields for Isomerization of $Ru(bpy)_2(OH_2)_2{}^{2+}$ at Various Wavelengths[a]

λ, nm	$\Phi_{cis \rightarrow trans}$	$\Phi_{trans \rightarrow cis}$
450	0.045	0.023
436	0.045	0.023
334	0.041	0.027
297	0.041	0.028

[a] Reactions carried out in 1 N H_2SO_4 at 25 °C.

idation of Ru(II) were encountered in 1.0 N $HClO_4$ and 1.0 N HNO_3.

Since both *cis*- and *trans*-$Ru(bpy)_2(OH_2)_2{}^{2+}$ are photoactive, a photostationary state is reached during photolysis. The equilibrium state is maintained for several hours after photolysis but over longer periods complete conversion of the trans to the cis isomer occurs thermally. The equilibrium state can be driven toward the trans isomer for synthetic purposes by using concentrated solutions of a counterion in which the salt of the trans isomer is only sparingly soluble. This approach was the basis for the high-yield preparation of the trans isomer described in the Experimental Section.

The "equilibrium constant" for the photostationary state under the conditions of our photolysis is 1.5 at 480 nm (K_{TC} = [trans]/[cis]). The variations in the position of the photostationary state with wavelength of irradiation are consistent with differences in extinction coefficients for the two species. The same photoequilibrium position is obtained by starting from either pure *cis*- or pure *trans*-$Ru(bpy)_2(OH_2)_2{}^{2+}$.

Both the Ru(II) and Ru(III) trans isomers are converted thermally from trans to cis. The Ru(III) complex is obtained by either Ce^{4+} or O_2 oxidation of *trans*-$Ru(bpy)_2(OH_2)_2{}^{2+}$, and its dominant form in solution appears to be the hydroxy complex $Ru(bpy)_2(OH_2)(OH)^{2+}$ except in strongly acidic solution. A few hours of moderate heating in acidic solution are sufficient to convert *trans*-$Ru(bpy)_2(OH_2)(OH)^{2+}$ completely to the cis isomer. Slightly longer times are required for the *trans*-$Ru(bpy)_2(OH_2)_2{}^{2+}$ to cis conversion and the reaction is complicated by the sensitivity of *trans*-$Ru(bpy)_2(OH_2)_2{}^{2+}$ to molecular oxygen. Heating of an air-saturated solution for 20 min, for example, results in nearly quantitative conversion to *trans*-$Ru(bpy)_2(OH_2)(OH)^{2+}$. Under the same conditions the cis isomer is not oxygen sensitive. The difference in air sensitivity between isomers may be due partly to the fact that the trans isomer is a stronger reducing agent. Reduction potentials for the couples [*cis*-$Ru(bpy)_2(OH_2)_2]^{3+/2+}$ and [*trans*-$Ru(bpy)_2(OH_2)_2]^{3+/2+}$ are 0.63 and 0.46 V vs. SCE in 1.0 N CF_3COOH as measured by cyclic voltammetry using a Pt bead electrode.

In contrast to the thermal trans → cis conversion, the reverse reaction cis → trans has not been observed. For example, *cis*-$Ru(bpy)_2(OH_2)_2{}^{2+}$ can be heated at reflux in 1 N H_2SO_4 for several hours under N_2 in the dark with no noticeable spectral changes.

Several attempts were made to grow crystals of *trans*-[$Ru^{II}(bpy)_2(OH_2)_2](ClO_4)_2$ to confirm the trans geometry of the photoisomer. Although crystalline products were obtainable, we have been unable to grow crystals suitable for X-ray analysis. Very good crystals of the salt *trans*-[$Ru^{III}(bpy)_2(OH_2)(OH)](ClO_4)_2$, however, could be grown with little difficulty.

The fact that the hydroxo complex $Ru^{III}(bpy)_2(OH_2)(OH)^{2+}$ was obtained rather than $Ru(bpy)_2(OH_2)_2{}^{3+}$ as the crystalline product is not surprising given the expected acid-base behavior of the Ru(III) ion. For example, the pK_{a_1} of $Ru^{III}(bpy)_2(py)(OH_2)^{3+}$ is 0.85, whereas the pK_{a_1} for the Ru(II) ion, $Ru(bpy)_2(py)(OH_2)^{2+}$, is 10.8.[31] Although we have not carried out pK_a measurements, it seems clear that $Ru(bpy)_2(OH_2)_2{}^{3+}$ is as strongly acidic as both the cis and trans isomers.

Description of the Structure. The crystal of [$Ru(bpy)_2(OH_2)(OH)](ClO_4)_2$ is composed of infinite chains of *trans*-$Ru(bpy)_2(OH_2)(OH)^{2+}$ cations linked by symmetrical hydrogen bonds. The cations interact with the $ClO_4{}^-$ anions through a number of hydrogen bonds and van der Waals contacts. The ruthenium atom and the hydrogen atom which links the cations through O-H···O hydrogen bonds (vide infra) both lie on crystallographic twofold axes. The details of the trans coordination environment of a single Ru(III) atom are shown in Figure 1. Figure 2 shows a view of the crystal packing and Figure 3 illustrates the hydrogen bonding and van der Waals interactions.

The inner coordination sphere of the Ru(III) ion is nearly octahedral despite the trans geometry, with trans bond angles ranging from 168.2 to 178.4°. The chelate bite of 2.632 (4) Å causes a N-Ru-N′ angle of only 77.5 (1)°, which is responsible for distortion in the equatorial plane. The angles formed by the axial oxygen atom and the equatorial nitrogen atoms range from 83.0 to 96.0°. The bond distances and angles are given in Table III. The axial Ru-O bond length of 2.007 (3) Å indicates very little multiple bonding, based on Pauling's radii[32] and the observation of much smaller values [e.g., 1.890 (7) Å][33] in systems suspected of containing multiple Ru-O bonding. The two Ru-N bond distances of 2.090 (3) and 2.099 (3) Å are very similar to those of 2.104 Å in [$Ru(NH_3)_6]^{3+}$.[34] The absence of any significant shortening of the Ru-N bonds relative to those in $Ru(NH_3)_6{}^{3+}$ again suggests an absence of structurally significant, multiple metal-ligand bonding in the complex.

The bipyridyl ligand is not abnormally distorted. Its configuration compares favorably with those reported for a number of cases where 2,2′-bipyridine is bound to a variety of metal centers. The average ring C-C and C-N bond lengths presented in Table III can be compared, for example, to those of the free ligand,[35] where values of 1.40 and 1.36 Å are found, or to the distances 1.383 and 1.352 Å found for [*cis*-(Me_3Si-

Table III. Selected Internuclear Distances (Å) and Angles (deg) in [*trans*-Ru(bpy)$_2$(OH)(OH$_2$)](ClO$_4$)$_2$

Perchlorate Anion

atoms	distance	atoms	distance
C1–O1	1.432(4)	C1–O3	1.433(4)
C1–O2	1.422(4)	C1–O4	1.422(4)

atoms	angles	atoms	angles
O1–C1–O2	109.0(2)	O2–C1–O3	110.2(3)
O1–C1–O3	108.3(2)	O2–C1–O4	109.8(2)
O1–C1–O4	110.1(3)	O3–C1–O4	109.5(3)

Hydrogen Bonds and van der Waals Contacts

atoms A–B···C	distance A···C	distance B···C	angle A–B···C
O5–H205···O5$^{\mathrm{I}a}$	2.538(6)	1.28(1)	169(9)
O5–H105···O3$^{\mathrm{I}}$	2.881(5)	2.18(5)	172(6)
C3–HC3···O1$^{\mathrm{II}}$	3.575(6)	2.56(5)	172(4)
C3′–HC3′···O1$^{\mathrm{II}}$	3.467(6)	2.51(5)	161(4)
C4′–HC4′···O2$^{\mathrm{III}}$	3.350(6)	2.55(5)	166(4)
C6′–HC6′···O2$^{\mathrm{IV}}$	3.256(7)	2.54(5)	134(4)

Coordination Sphere of the Ruthenium Atom

atoms	distance	atoms	distance
Ru–O	2.007(3)	N···N′	2.623(4)
Ru–N	2.090(3)	O5–H105	0.71(5)
Ru–N′	2.099(3)	O5–H205	1.28(1)

atoms	angle	atoms	angle
O5–Ru–O5$^{\mathrm{IV}}$	178.4(3)	N′–Ru–N′$^{\mathrm{IV}}$	106.2(2)
O5–Ru–N	85.4(1)	Ru–N–C2	116.2(3)
O5–Ru–N′	96.0(1)	N–C2–C2′	115.1(4)
O5–Ru–N$^{\mathrm{IV}}$	95.6(1)	C2–C2′–N′	115.5(3)
O5–Ru–N′$^{\mathrm{IV}}$	83.0(1)	C2′–N′–Ru	114.7(2)
N–Ru–N′	77.5(1)	Ru–O5–H105	110(4)
N–Ru–N$^{\mathrm{IV}}$	101.1(2)	Ru–O5–H205	125(2)
N–Ru–N′$^{\mathrm{IV}}$	168.2(1)	H105–O5–H205	113(6)
N′–Ru–N$^{\mathrm{IV}}$	168.2(1)		

2,2′-Bipyridine Ligand

atoms	distance	atoms	distance
N–C2	1.352(5)	C2–C2′	1.454(6)
C2–C3	1.387(6)	C–N	1.350(13)
C3–C4	1.371(7)	C–C	1.377(8)
C4–C5	1.376(8)	C3–HC3	1.02(5)
C5–C6	1.367(7)	C4–HC4	0.94(5)
C6–N	1.345(5)	C5–HC5	0.88(4)
N′–C2′	1.366(5)	C6–HC6	0.84(4)
C2′–C3′	1.383(6)	C3′–HC3′	1.00(5)
C3′–C4′	1.380(8)	C4′–HC4′	0.82(5)
C4′–C5′	1.367(8)	C5′–HC5′	0.95(4)
C5′–C6′	1.388(7)	C6′–HC6′	0.94(5)
C6′–N′	1.336(5)	HC3···HC3′	2.14(7)
		HC6···HC6$^{\mathrm{IV}}$	2.18(8)
		HC6′···HC6′$^{\mathrm{IV}}$	1.86(10)

atoms	angle	atoms	angle
C6–N–C2	118.1(4)	C2–C3–HC3	123.3
N–C2–C3	121.3(4)	HC3–C3–C4	117(3)
C2–C3–C4	119.5(5)	C3–C4–HC4	119(3)
C3–C4–C5	119.0(5)	HC4–C4–C5	121(3)
C4–C5–C6	119.1(5)	C4–C5–HC5	122(3)
C5–C6–N	122.8(5)	HC5–C5–C6	119(3)
C6–N–Ru	125.0(3)	C5–C6–HC6	121(3)
C6′–N′–C2′	117.8(4)	HC6–C6–N	117(3)
N′–C2′–C3′	121.4(4)	C2′–C3′–HC3′	120(3)
C2′–C3′–C4′	119.6(5)	HC3′–C3′–C4′	121(3)
C3′–C4′–C5′	119.3(5)	C3′–C4′–HC4′	120(4)
C4′–C5′–C6′	118.8(5)	HC4′–C4′–C5′	121(4)
C5′–C6′–N′	123.1(5)	C4′–C5′–HC5′	122(3)
C6′–N′–Ru	126.3(3)	HC5′–C5′–C6′	118(3)
C2′–C2–C3	123.5(4)	C5′–C6′–HC6′	120(3)
C2–C2′–C3′	123.1(4)	HC6′–C6′–N′	117(3)

Table IV. Selected Least-Squares Planes and Dihedral Angles (deg) in [*trans*-Ru(bpy)$_2$(OH)(OH$_2$)]$^{2+}$

plane	atoms in plane	distance[a]	other atoms	distance[a]
1	N	−0.215	O5	2.006
	N′	0.206	HC6	−0.82
	N$^{\mathrm{IV}\,b}$		HC6′	0.44
	N′$^{\mathrm{IV}}$			
2	Ru	0.0	C2	0.063
	N	0.0	C2′	0.165
	N′	0.0	HC6	−0.34
			HC6′	−0.04
3	Ru	0.0		
	N$^{\mathrm{IV}}$	0.0		
	N′$^{\mathrm{IV}}$	0.0		
4	Ru	0.033	HC6	−0.30
	N	−0.017	HC6′	−0.09
	C2	−0.017		
	C2′	0.061		
	N′	−0.060		
5	N	0.022	Ru	0.152
	C2	−0.039	HC6	−0.22
	C2′	−0.039	HC6′	−0.01
	N′	−0.022		
6	N	0.024	Ru	−0.158
	C2	−0.016	N′	−0.380
	C3	0.000	C2′	−0.139
	C4	0.009	C3′	−0.036
	C5	−0.001	C4′	−0.176
	C6	−0.016	C5′	−0.400
			C6′	−0.490
			HC6	−0.05
7	N′	−0.008	Ru	0.338
	C2′	0.003	N	0.168
	C3′	0.004	C2	−0.001
	C4′	−0.006	C3	−0.219
	C5′	0.001	C4	−0.314
	C6′	0.006	C5	−0.192
			C6	0.024
			HC6′	−0.03

Dihedral Angles

planes	angle	planes	angle
1–2	9.23	2–7	23.85
1–4	19.93	4–6	27.35
1–5	10.42	4–7	31.76
1–6	18.09	5–6	8.13
1–7	15.79	5–7	7.17
2–3	18.46	6–7	9.74
2–6	27.31		

[a] Distance out of calculated plane in Å. [b] Raman superscripts refer to atoms in the following positions: (I) $x-y, -y, 5/3-z$; (II) $1-x, 1-x+y, 4/3-z$; (III) $1-x+y, -x, z-1/3$; (IV) $-x, y-x, 4/3-z$.

CH$_2$)$_2$(bpy)$_2$Cr]I.[36] The C2–C2′ bond length is likewise very similar to the values reported in these other systems. It should be noted that the two separate pyridine groups show a twisting of 9.74° about the C2–C2′ axis. A survey of known structures shows that this angle ranges from 0 to 31° with an average value of 8°.[14-17,36-70] It is noteworthy that the biphenyl moiety has a similar twisted conformation in the gas phase which corresponds to a calculated energy minimum.[71] In addition to the twist, the entire ligand is slightly bowed about the C$_2$–C$_2$′ axis.

The five-membered chelate ring made up of the Ru, N, C2, C2′, and N′ atoms forms an envelope conformation where the Ru atom lies 0.152 Å away from the plane formed by the other four atoms. The dihedral angle (2θ) between the plane defined by Ru, N, N′ and that defined by Ru and the symmetry-related nitrogen atoms (N*, N′*) of the other bpy ligand (planes 2 and 3, Table IV) is 18.46°. This distortion is presumably due to the

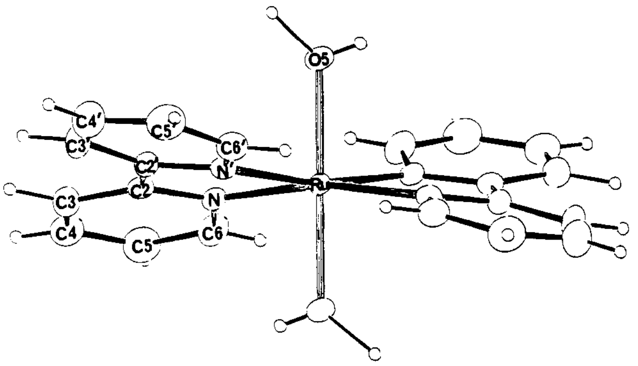


Figure 1. View of the coordination sphere around the ruthenium atom.

steric crowding experienced by the α hydrogen atoms. The resulting contact distances between hydrogen atoms are 2.18 (8) Å for HC6-HC6* and 1.86 (10) Å for HC6'-HC6'* (where the asterisk denotes an atom on the other bpy ligand). The difference between these two contacts is just greater than 3σ and may be ascribed to the stabilization offered HC6' through a van der Waals contact with oxygen atom O2 of the perchlorate anion. HC6 has no appropriate van der Waals contact less than 2.6 Å.

As suggested by McKenzie,[11] the steric strain imposed upon the *trans*-M(bpy)$_2$ group may be relieved by distortion of the coordination polyhedron and/or distortion of the chelate. In [Pt(bpy)$_2$][(TCNQ)$_2$][15] and [Pt(bpy)$_2$][(TCNQ)$_3$][16] this relief is accomplished through gross distortion of the ligand. In the remaining examples, including the present case, the ligand itself shows moderate distortion and the coordination polyhedron about the metal distorts, presumably to accommodate the α hydrogens. For the latter complexes, McKenzie's model[11] provides at least a qualitative correlation between the average M-N bond length and the dihedral angle, 2θ: Cu-N, 1.99 Å, $2\theta = 37°$;[17] Pd-N, 2.034 Å,[14] $2\theta = 24.3$; Ru-N, 2.094 Å, $2\theta = 18.46°$. The model cannot be expected to predict repulsion energies accurately, since the basis for the prediction is the αH-αH contact distance, which is strongly dependent on ligand distortions as well as polyhedral distortions about the metal center.[11,14] Since it seems that the major ligand distortion affecting the αH-αH contact distance is a twisting around the C2-C2' axis, addition of this parameter to the model might bring about some improvement. However, until we can reasonably describe the effect of conformational changes on the potential energy of the metal center, it will remain difficult to predict accessible configurations on the basis of this model.

The crystal packing in the lattice is stabilized by two important hydrogen bonds and to a lesser extent by a number of van der Waals contacts. The stronger of the two hydrogen bonds is constrained to be symmetrical and links the cation units into a chain along the crystallographic *c* axis. The O-H internuclear distance is 1.28 (1) Å, the O-H-O angle is 169 (9)°, and the O-O distance is 2.538 (6) Å. The weaker of the two hydrogen bonds forms a link perpendicular to the *c* axis between the cation chain and a perchlorate oxygen atom (O3). In this interaction, the heavy atom (O-O) separation is 2.881 (5) Å. The O3-H105 separation is 2.18 (5) Å, and the hydrogen bond angle is 172 (6)°.

The van der Waals radii for hydrogen and oxygen are reported as 1.2 and 1.4 Å, respectively,[32] giving a contact sum of 2.6 Å. There are a number of contacts less than 2.6 Å between the remaining perchlorate oxygen atoms and the aromatic hydrogen atoms on neighboring cation chains, i.e., chains other than the one to which oxygen O3 is hydrogen bonded. All of these interactions, as shown in Figure 3, are primarily directed in the *a,b* plane. Two of the Cl-O bonds, namely, Cl-O2 and Cl-O4, are just significantly shorter (3σ) than the others. This may be the result of their making weaker contributions to the contacts stabilizing the crystal packing. The three-dimensional network described probably contributes to the stability of this particular crystal form but not significantly to the configuration about the metal atom.

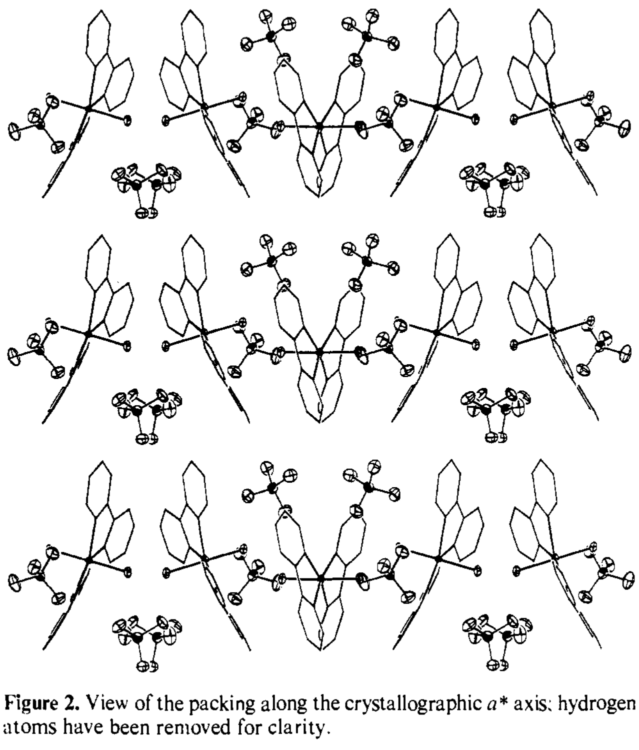


Figure 2. View of the packing along the crystallographic a^* axis; hydrogen atoms have been removed for clarity.

Discussion

Photochemistry. The electronic spectra of both *cis*- and *trans*-Ru(bpy)$_2$(OH$_2$)$_2{}^{2+}$ and a very large number[8] of complexes of the type Ru(bpy)$_2$L$_2{}^{2+}$ are similar except for some noticeable differences in the energies of the lowest energy absorption bands (Figures 4 and 5). It is by now well established that the low-energy bands can be assigned to metal to ligand charge transfer (MLCT) transitions, $(\bar{\text{bpy}})_2\text{Ru}^{\text{III}} \leftarrow (\text{bpy})_2\text{Ru}^{\text{II}}$. The remaining bands have been assigned to either charge transfer or ligand-centered transitions. The expected ligand field (LF) absorption bands are completely obscured by the presence of the high-intensity charge transfer and ligand-centered absorptions.[8]

The quantum yields for both the cis → trans and trans → cis conversions are independent of wavelength at least over the range 294-480 nm. The absence of a wavelength dependence has also been found for photosubstitution in complexes of the type Ru$^{\text{II}}$(bpy)$_2$L$_2$, for Ru(bpy)$_3{}^{2+}$,[4] and for Ru(NH$_3$)$_5$py^{2+}.[72] The results obtained suggest that following excitation a low-lying state is populated from which (1) photosubstitution can occur (this appears to be the case for complexes of the type Ru(NH$_3$)$_5$(py)$^{2+}$)[73] or (2) the lower state is in thermal equilibrium with a higher energy state which can undergo photosubstitution (a case which has been suggested for Ru(bpy)$_3{}^{2+}$).[4,74] The results obtained by Ford and co-workers[72,73] strongly suggest that the photoactive state in Ru(NH$_3$)$_5$(py)$^{2+}$ is a ligand field state (LF) and not a MLCT state. The absence of photolability in MLCT excited states of Ru(II) is not surprising given the known inertia to substitution usually found for complexes of Ru(III) and the large body of supporting experimental evidence, particularly from studies of Cr(III) and Co(III) complexes, which shows that simple substitution processes do not usually occur for CT excited states.[75]

We presume that the cis → trans photoisomerization ob-

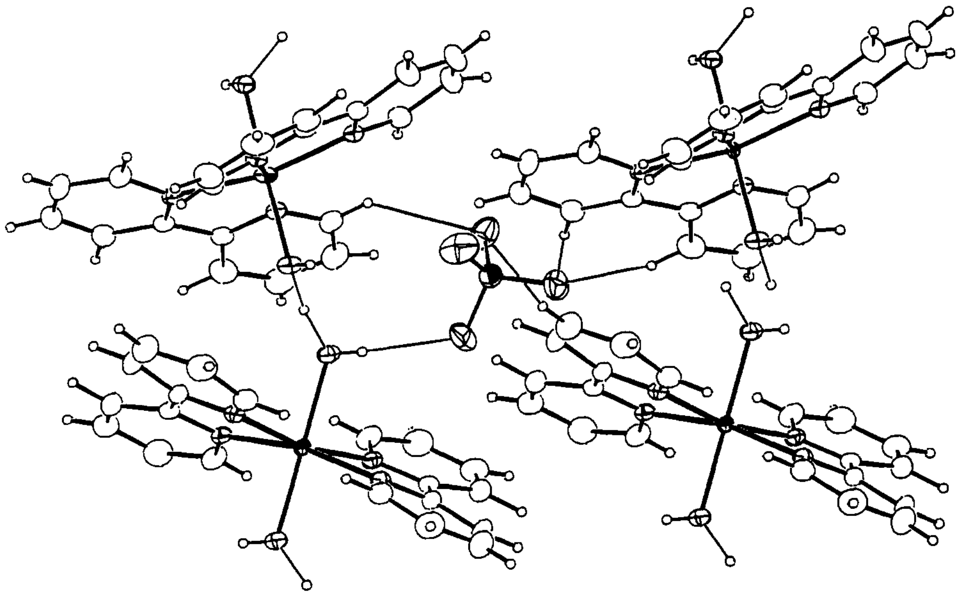


Figure 3. View of the hydrogen bonding and van der Waals contacts.

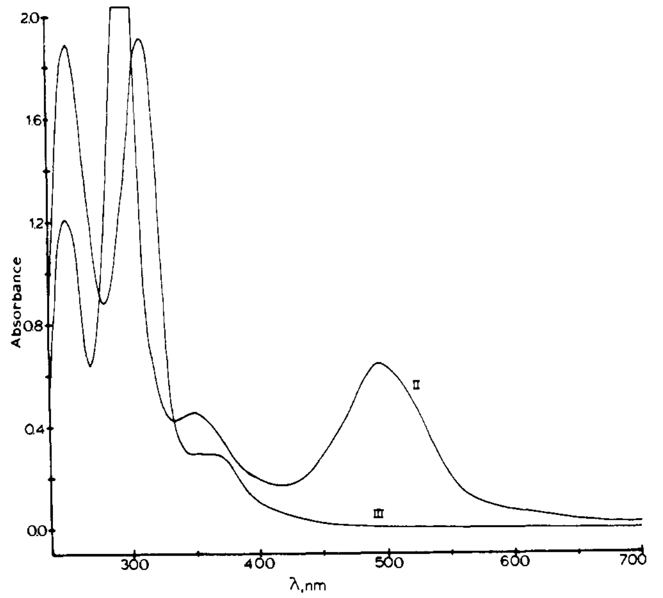


Figure 4. UV–visible spectra of *cis*-Ru(II) and Ru(III) diaquobis(2,2′-bipyridyl) complexes, 4.7 × 10^{-5} M in 0.5 M CF$_3$COOH, 1-cm cell.

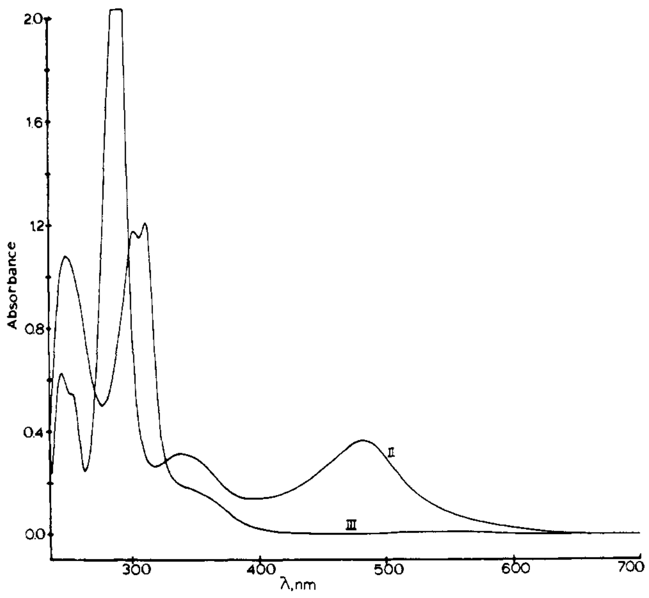


Figure 5. UV–visible spectra of *trans*-Ru(II) and Ru(III) diaquobis(2,2′-bipyridyl) complexes, 6.4 × 10^{-5} M in 0.5 M CF$_3$COOH, 1-cm cell.

served for the diaquo system also has its origin in processes based on LF excited states. Although we have no direct spectroscopic evidence for the intervention of LF states, given the results of earlier studies it would be surprising to find evidence to the contrary.

We also have no definitive evidence as to whether a photolabile LF state lies lowest in the excited-state manifold for Ru(bpy)$_2$(OH$_2$)$_2^{2+}$ or that instead the LF state is thermally populated from a lower lying MLCT state. This may appear to be a minor detail but it provides an important link between the two systems, Ru(bpy)$_3^{2+}$ and Ru(NH$_3$)$_5$(py)$^{2+}$, where complementary photochemical and photophysical information has been obtained.[4,5]

The results of one experiment do suggest that a MLCT state is lowest lying. For a large number of complexes of the type Ru^{II}(bpy)$_2$L$_2$, emissions from MLCT excited states are observed but frequently only at low temperatures.[8,10] For complexes like Ru(bpy)$_2$Cl$_2$ at room temperature in solution, emission bands are weak, if even observable, and photosubstitution reactions do occur. When taken together, the two observations suggest that there are lowest lying MLCT states from which luminescence is observed and at higher energies thermally populable LF states which are relatively short lived and lead to photosubstitution. Although nonluminescing in water at room temperature, both *cis*- and *trans*-Ru(bpy)$_2$(OH$_2$)$_2^{2+}$ exhibit weak emissions at 77 K in H$_2$O–methanol glasses (Figure 6). Luminescence from the cis isomer is much stronger than from the trans. The emission maxima are at 660 nm with strong tailing to lower energies for cis and 700 nm for trans. By comparing the shapes and energies of the observed emission bands with those of related complexes, it seems reasonable to assign these to LMCT transitions from what are probably the lowest electronic excited states in the molecule.

The mechanism for the cis $\rightleftharpoons$ trans isomerization may involve photosubstitution steps but it is also necessary to consider possible intramolecular rearrangements. We have no direct

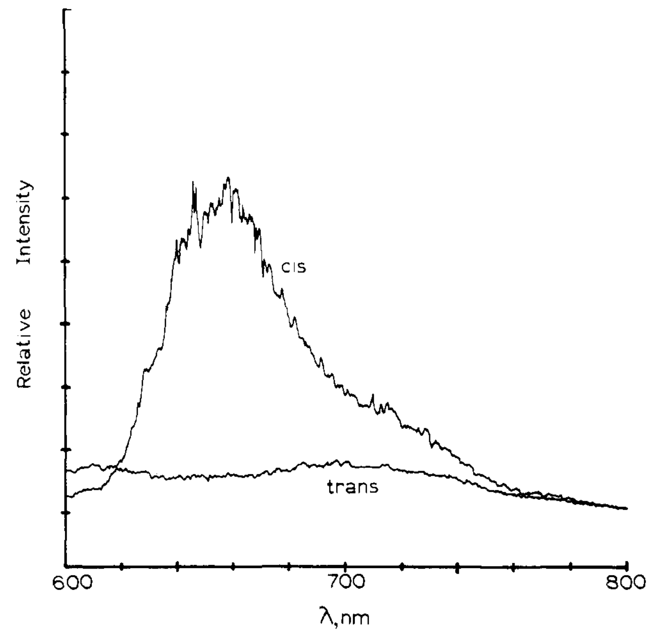


Figure 6. Emission spectra of *cis*- and *trans*-$Ru(bpy)_2(OH_2)_2^{2+}$ in 1 N H_2SO_4/methanol glass (1:1) at 77 K.

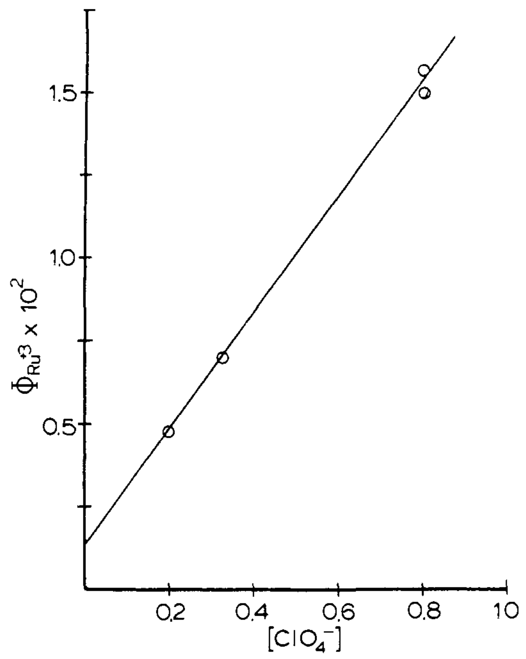


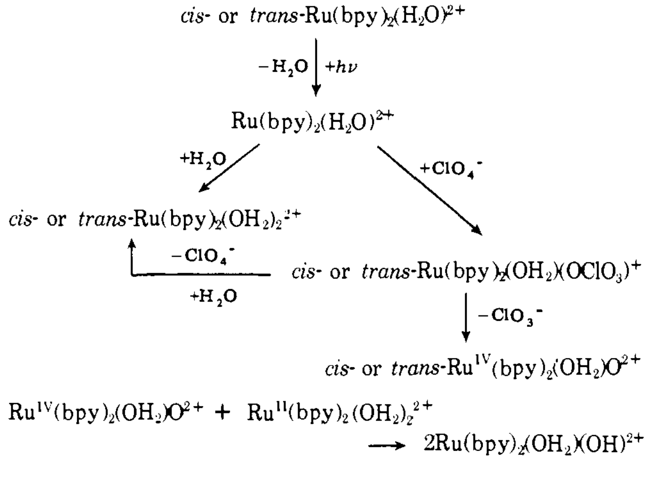
Figure 7. Plot of the quantum yield for the oxidation of $Ru(bpy)_2(OH_2)_2^{2+}$ at 334 nm vs. $[ClO_4^-]$ at pH 0.

evidence that the H_2O ligands are exchanged with the solvent during photolysis, which would be required if isomerization occurs by substitution. By way of indirect evidence we have observed very efficient photosubstitution of pyridine in $Ru(bpy)_2(py)_2^{2+}$ by a number of anions in nonaqueous solvents[7] and photoaquation in a series of complexes of the type $Ru^{II}(bpy)_2L_2^{2+}$ (L = py, CH_3CN, etc.).[76] The importance of these observations is that they show that photosubstitution does occur for related bis(2,2′-bipyridyl) complexes of Ru(II), suggesting that such pathways are available for the cis ⇌ trans isomerization observed in the diaquo system. In addition, most of the experimental evidence to date concerning photosubstitution reactions of metal complexes indicates that these processes are primarily dissociative in nature.[1,75]

The quantum yield for the photochemical oxidation of $Ru^{II}(bpy)_2(OH_2)_2^{2+}$ to Ru(III) increases linearly with $[ClO_4^-]$ as shown in Figure 7. Both the cis and trans isomers undergo the reaction and during photolysis ClO_4^- oxidation and cis ⇌ trans isomerization occur simultaneously so that the quantum yields refer to total oxidation of Ru(II) to Ru(III). No attempt was made to determine the [cis]/[trans] ratio of the oxidized products quantitatively, although both cis and trans complexes of Ru(III) are formed as shown by spectral and electrochemical experiments. As discussed above, given the acidity of bis(2,2′-bipyridyl)aquo complexes of Ru(III), the product solution contains mixtures of the cis and trans hydroxo and aquo complexes, $Ru(bpy)_2(OH_2)_2^{3+}$ and $Ru(bpy)_2(OH_2)(OH)^{2+}$, with the relative amounts of each depending on the pH. The complex *trans*-$Ru(bpy)_2(OH_2)_2^{2+}$ does undergo a slow thermal oxidation by ClO_4^- in acidic solution but the reaction is noticeable only on a time scale of hours. The cis complex is stable under the same conditions for at least 1 day.

Both the cis ⇌ trans isomerization and ClO_4^- oxidation can be accounted for by assuming an initial dissociative photochemical step as shown in Scheme I. In Scheme I a five-coordinate intermediate is formed which when captured by water can give either *cis*- or *trans*-$Ru(bpy)_2(H_2O)_2^{2+}$. According to Scheme I, in the presence of sufficiently high concentrations of ClO_4^-, the intermediate can be captured by ClO_4^- to give the perchlorato complexes *cis*- or *trans*-$Ru^{II}(bpy)_2(OH_2)(OClO_3)^+$. Recent experiments[77,78] have shown that complexes of Ru(II) are capable of reducing oxy anions by reactions in which Ru(IV)-oxo complexes are formed as intermediates (eq 2 and 3).

Scheme I



$$Ru(bpy)_2(py)(OH_2)^{2+} + NO_3^- \xrightarrow[-H_2O]{} [Ru(bpy)_2(py)(ONO_2^+)] \xrightarrow[-NO_2^-]{} Ru(bpy)_2(py)O^{2+\ 77} \quad (2)$$

$$Ru(NH_3)_5(acetone)^{2+} + ClO_4^- \xrightarrow[-acetone]{} [Ru(NH_3)_5OClO_3^+] \xrightarrow[-ClO_3^-]{} Ru(NH_3)_5O^{2+} \quad (3)$$

$$Ru(NH_3)_5O^{2+} + Ru(NH_3)_5(acetone)^{2+} \xrightarrow[-acetone]{} (NH_3)_5RuORu(NH_3)_5^{4+\ 78}$$

The perchlorato complexes once formed may, in part, undergo simple aquation to give *cis*- or *trans*-$Ru(bpy)_2(H_2O)_2^{2+}$. To account for the observed oxidation to Ru(III) would require that they also undergo reactions like eq 2 and 3 to give *cis*- or *trans*-$Ru(bpy)_2(OH_2)O^{2+}$ followed by a comproportionation reaction between Ru^{IV} and Ru^{II} which is known to be rapid in the analogous aquo-pyridyl system.[77]

In the aquo-pyridyl system the Ru(IV) ion, $Ru(bpy)_2(py)O^{2+}$, has been prepared and isolated by the two-electron oxidation of $Ru^{II}(bpy)_2(OH_2)py^{2+}$ using Ce(IV) as oxidant.[31] A potentiometric titration using Ce(IV) shows that two-electron oxidation of *cis*-$Ru(bpy)_2(H_2O)_2{}^{2+}$ occurs, presumably to give $Ru(bpy)_2(OH_2)O^{2+}$, but the Ru(IV)-aquo ion has not yet been isolated and characterized.

If the cis $\rightleftharpoons$ trans photoisomerization occurs by a dissociative photosubstitution pathway, the results obtained here have important implications for the stereochemistry involved in related photochemical reactions. For example, photochemical substitutions in $Ru(NH_3)_5py^{2+}$ [72] and $Mo(CO)_5PPh_3$,[79] both of which are spin-paired $4d^6$ cases, give both cis and trans products. In the diaquo system the cis isomer is the thermodynamically stable isomer, and yet in the photostationary state the trans isomer is favored, at least slightly. It is interesting to note that trans → cis isomerizations are rare in ammine complexes of Co(III) and Ru(III) and this behavior has been rationalized by Vanquickenborne and Ceuleman[80] on the basis of the greater stability of square-pyramidal five-coordinate intermediates. A detailed rationale of our results is not possible because, as an example, the stereoselectivity that we observed may be the result of a higher photosensitivity in the cis isomer. The answer to the problem of stereoselectivity in bis(2,2′-bipyridyl)complexes of Ru(II) may be better answered in a study of the photochemistry of *cis*-$Ru(bpy)_2(py)_2{}^{2+}$, where yields for the loss of a ligand can be relatively easily measured.

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Supplementary Material Available: The atomic thermal parameters and a list of observed and calculated structure amplitudes (14 pages). Ordering information is given on any current masthead page.

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