Steady State and Transient Stereoretentive Photoaquation of [*trans*-Cr(1,9-diamino-3,7-diazanonane)$(CN)_2$]ClO_4

A. D. Kirk* and S. R. L. Fernando

Department of Chemistry, University of Victoria, P.O. Box 3055, Victoria, BC, Canada V8W 3P6

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In order to study the stereochemistry of equatorial photosubstitution in Cr(III) complexes, [*trans*-Cr(2,3,2-tet)-$(CN)_2$]ClO_4 (2,3,2-tet = 1,9-diamino-3,7-diazanonane) has been synthesized and characterized. Its photoaquation has been studied by proton uptake and cyanide release measurements. The molecule photoaquates one end of the 2,3,2-tet ligand with a quantum yield of 0.09 ± 0.01, while any photochemical cyanide loss has a quantum yield of ≤ 0.02. That the photoproduct has the cyanide ligands in the *trans* configuration is strongly indicated by its thermal recoordination at pH 6 to the starting complex, as well as by the UV–vis spectrum of the photoproduct. These results show that photosubstitution of the equatorial ligand in this complex is stereoretentive, in contrast to the stereochemical change that accompanies loss of the equatorial ligand in other Cr(III) complexes. Nanosecond laser flash photolysis experiments with conductivity detection showed that 100% of the reaction occurs as a single-exponential growth with a lifetime of 26 ± 1 μs, in good agreement with the observed doublet state emission lifetime at 21 °C of 28 ± 1 μs. The results are discussed in the context of data on analogous cyano complexes, the angular overlap theory of chromium(III) photochemistry including the Jahn–Teller distortions of the intermediates, and the behavior of photoinert cyclam complexes.

Introduction

A feature of the photoaquation reactions of Cr(III) complexes that has interested several research groups[1–4] is the stereochemical change that accompanies the processes. This feature contrasts markedly with the stereoretention that characterizes the corresponding thermal reactions in aqueous media. For most tetragonal complexes, the ligand preferentially photoaquated can be predicted using the simple rules proposed decades ago in the development of this area. The ligand aquated lies on the axis of weakest average ligand field strength in the complex and, if the two ligands on this axis differ, is the stronger field ligand.[5] This photoaquation mode is referred to as "axial labilization". For such axial labilizations, general occurrence of extensive or complete stereochemical change has been established[1,3] by a series of studies of tetram(m)ine and pentam(m)ine type complexes. Beyond this, a series of studies[6,7] of *trans*-cyclamL_2 complexes have strongly indicated that this stereochemical change is a requirement for photochemical aquation. That is, in these materials, stereochemical change is frustrated by the steric constraints imposed by the cyclam ligand and this leads to photoinert materials. There is some ambiguity, however, as there are reported instances[8,9] where steric constraints instead lead to an unanticipated reaction mode rather than photoinertness.

All the data discussed above refer to the stereochemistry of photoaquation, but recently the analogous behavior was demonstrated[10] for the photoanation reaction of a Cr(III) complex. The data accrued so far therefore indicate stereochemical change to be a required feature of Cr(III) photosubstitution processes involving an axial ligand. There are one or two known exceptions, but these can be rationalized in terms of the angular overlap theory, currently the most successful model for Cr(III) photosubstitution processes, lending credence to the general rule.

This theoretical treatment[11] of the phenomenon of stereochemical change in Cr(III) photosubstitution considers the symmetry restrictions on collapse of putative five-coordinate intermediates to trigonal-bipyramidal (tbp) species and their subsequent formation of final product by coordination of a nucleophile. In the most recent versions of this model,[12] Jahn–Teller distortions of these tbp intermediates were invoked to rationalize details of wavelength dependence of product, and differences in product geometry distributions seen for the same intermediate generated by different routes, and this extended model rationalizes the exceptions referred to above. Pathways involving five-coordinate intermediates are at odds with evidence[13,14] that Cr(III) photoprocesses have the negative activation volumes expected for associative transition states. The argument has been made[15] qualitatively, however, that analogous symmetry restrictions could operate in a mechanism involving distorted pentagonal-bipyramidal intermediates. Such a mechanism would satisfy both the stereochemical evidence and the photophysical data, and it differs from the earlier versions of the published model mainly in the relative timing of the ligand entry and loss; this timing may not be too crucial.

Only a few *trans*-diacido complexes show significant loss of an equatorial ligand, but where the ligands on the symmetry axis have the higher σ donor strength, for example those containing fluoride[16] or cyanide ligands,[4] this can become the dominant reaction mode. This situation is more difficult to explore. First, the stereochemical relationships between reactants and products

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are now poorly defined; substitution in the weak-field plane leads to the same product via either mechanistically retentive or nonretentive pathways. In addition, equatorial ligand loss could arise from either ^4E_g or $^4B_{2g}$ states, and these will have different predicted stereochemical outcomes.

This work attempted an unambiguous study of the stereochemistry of equatorial labilization. Given a simple model of Cr(III) photochemistry based on reaction from the lowest quartet excited state with required stereochemical change, [*trans*-Cr(tet)$(CN)_2$]ClO_4 should be photoinert. We have therefore synthesized and characterized this molecule and have studied its photoproperties.

Experimental Section

Synthesis. *Caution! Perchlorate salts of metal complexes containing organic ligands can be dangerously explosive when shocked or heated; prepare only small quantities.*

[*cis*-Cr(2,3,2-tet)Cl_2]ClO_4 and [*trans*-Cr(2,3,2-tet)Cl_2]ClO_4. These were made by the literature method[17] except that the 2,3,2-tet ligand was added slowly over 10 min at 125 °C rather than at 100 °C. Also, the solution was not heated after adding the ligand. If the ligand was added at low temperature (80 °C), only [*cis*-Cr(2,3,2-tet)Cl_2]Cl was formed rather than a mixture of *cis* and *trans* isomers.

[*trans*-Cr(2,3,2-tet)$(CN)_2$]ClO_4. During this synthesis, as a precaution, the neck of the flask was kept closed whenever possible to minimize exposure to atmospheric moisture. A 1.0-g (2.8-mmol) sample of [*trans*-Cr(2,3,2-tet)Cl_2]ClO_4 (ash green) was dissolved in 15 mL of dmso (dried over 4A molecular sieves) by heating at 70 °C for 30 min in a RB flask under efficient magnetic stirring to give a reddish purple solution. Then 1.0 g (20 mmol) of finely ground NaCN (vacuum dried) was slowly added over 10 min. The solution became yellow-orange. Heating was continued at 70 °C for 1 h. The solution gradually turned yellow, and a yellow solid precipitated. This hot slurry was filtered through a medium-porosity sintered-glass funnel, and the crude product was washed on the filter with 25-mL portions of 2-propanol and ether to yield 0.9 g.

The crude product was dissolved in a minimum amount of water (~20 mL), a few drops of 8 M $NaClO_4$ was slowly added until crystallization just started, and then the mixture was allowed to stand in a refrigerator for several hours. Bright yellow crystalline material was collected by filtration through a medium-porosity sintered-glass funnel, washed with 25-mL portions of 2-propanol and ether, and vacuum-dried to yield 600 mg (63% overall) of the product.

Anal. Found (Canadian Microanalytical Service) (calcd): C, 29.7 (29.7); H, 5.5 (5.5); N, 22.8 (23.1); Cr, 13.9 (14.3).

The compound is readily soluble in water, slightly so in dmso and dmf, but insoluble in ethanol, methanol, acetonitrile, ethyl acetate, and acetone.

Subsequent attempts, described next, to prepare [*cis*-Cr(2,3,2-tet)$(CN)_2$]ClO_4 by the analogous reaction of [*cis*-Cr(2,3,2-tet)Cl_2]Cl with cyanide in dmso revealed efficient *cis* to *trans* isomerization. Consequently, in later syntheses of [*trans*-Cr(2,3,2-tet)$(CN)_2$]ClO_4, the crude mixture of [*cis*/*trans*-Cr(2,3,2-tet)Cl_2]Cl was used as the starting material.

[*cis*-Cr(2,3,2-tet)$(CN)_2$]ClO_4. A 240-mg sample of NaCN (vacuum dried) was dissolved in 5 mL of dmso (dried over 4A molecular sieves) in a 25-mL RB flask at 60 °C, and then 160 mg of [*cis*-Cr(2,3,2-tet)Cl_2]Cl was added. Continued heating at 60 °C for 30 min gave a yellow solid precipitate of [*trans*-Cr(2,3,2-tet)$(CN)_2$]ClO_4, which was removed by filtration. The filtrate was predominantly *cis*-Cr(2,3,2-tet)$(CN)_2^+$ together with minor amounts of Cr(2,3,2-tet)Cl(CN)$^+$ and unprecipitated *trans*-Cr(2,3,2-tet)$(CN)_2^+$, as determined by HPLC analysis. This solution was loaded on to a 4 × 1 (o.d.) cm^2 SP-Sephadex C-25 cation exchange resin column and eluted with 0.015 M aqueous $NaClO_4$. A small fraction of pure [*cis*-Cr(2,3,2-tet)$(CN)_2$]ClO_4 was isolated in solution.

UV/Vis Spectra. A Philips PU-8740 or Unicam SP8-400 scanning spectrophotometer was used except when the spectral data were to be stored on computer disk, when a Cary 5 UV/vis/near-IR spectrophotometer was used. Spectral data were evaluated using the numerical analysis program Igor (WaveMetrics, Inc.) run on a Macintosh IIci computer. This program was used to convert the absorbance values of a spectrum to molar absorptivity (ϵ), for calculation of the spectrum of a photoproduct or photoproducts by subtracting the spectrum of the solution before photolysis from that after the photolysis and for analysis of a spectrum into its component Gaussians.

HPLC Analysis. A Varian system 5000 liquid chromatograph with a 25-cm octadecylsilane RP column was employed. Eluents consisted of 5–25 mM tetraethylammonium (chloride) as the competing ion and 25 mM (sodium) butanesulfonate as the ion-interaction reagent in methanol/water at pH 3. The percentage methanol, 0–30%, and the concentration of competing ion were varied to optimize serparations of samples from preparations of complexes or from photolyzed solutions of the *trans* isomer. Peaks were detected by their UV absorption in the range 220–230 nm. The technique gave rapid separations of all the peaks of interest.

Emission Spectra and Lifetimes. Emission spectral measurements were made with excitation by a Hanovia xenon lamp/Bausch and Lomb monochromator/infrared filter (Balzers) source, with detection by using a Jarrel-Ash 0.25-m monochromator preceded by a Corning 3-71 red filter and a 1-cm path of concentrated potassium dichromate solution to remove light of wavelength shorter than about 650 nm. The detector was an RCA 31034 photomultiplier with a modified Keithley 410 electrometer.

Emission lifetimes were measured by following the emission decay using a PTI PL 2300 nitrogen laser/Jarrel-Ash monochromator/Hamamatsu R928 photomultiplier/Tektronix 2230 oscilloscope system with GPIB interface to an ATARI 1040 computer. Lifetimes were evaluated by weighted linear regression[18] on log(intensity) versus time plots over 1024 channels of decay.

Quantum Yield Determinations. Radiation at 436 nm (Balzers interference filter) from a 1000-W mercury lamp was passed through a 10-cm water filter to remove the infrared components. Radiation at 458 nm was from a Spectraphysics 2000 argon ion laser. The light intensities were 3×10^{-8} and 2×10^{-7} einstein s^{-1} at 436 and 458 nm, respectively.

Efficiently stirred solutions were irradiated in 1-cm rectangular cuvettes at 15 °C, and the pH was monitored by an Ingold LOT combination electrode interfaced to a PDP-11 computer. Standard acid (0.0730 M $HClO_4$) was added from a 200-mL stepping motor buret, to maintain the pH of the solution constant with recording of acid added, the pHstat method. The pK_a values for the aqua-substituted photoproducts of 2,3,2-tet or cyanide loss can be estimated to be in the range 4.5–5.5, on the basis of reported values for similar products of $Cr(tn)_3^{3+}$ [19] and $Cr(NH_3)_4(CN)_2^+$.[20] Solvent pH values were set between 2.9 and 3.3, which avoids errors arising from partial dissociation of photoproducts to their conjugate base forms but is not suficiently low to cause problems from competing acid-catalyzed aquation of cyanide.

An ionic strength buffer of 0.1 or 0.05 M $KClO_4$ was used throughout. The light intensity from the mercury lamp was computer monitored continuously using the analog output from an Alphametrics 1200 photometer and silicon photodetector. This signal was periodically calibrated in terms of the ferrioxalate actinometer so that the integrated computer reading during photolysis could be converted to integrated intensity falling on the front surface of the photolysis solution. Photolysis time was controlled with high precision by the computer using an electromechanical shutter.

For measurements of cyanide yield, a 2×10^{-2} M solution of complex in water was passed through a 3 × 0.8 (i.d.) cm^2 QAE-Sephadex A-25 anion exchange column to remove any free cyanide impurity. The eluate was mixed with an equal volume of 1.5×10^{-3} M $HClO_4$/0.1 M $KClO_4$ solvent. One portion was photolyzed, while a second was kept in the dark at the same temperature as a thermal blank.

After photolysis, the two solutions were adjusted to pH 12 with 1 M NaOH. The free cyanide in the samples was then measured using an Orion 94-06 cyanide/Ag/AgCl reference electrode combination with a Fisher Accumet digital pH meter. Using freshly made KCN solution, standardization plots were constructed in parallel with each analysis. These could be used directly for cyanide determination since tests showed that the complex did not affect the electrode readings.

Thermal Rate Constants. Pseudo-first-order thermal rate constants were determined either by the pHstat method or by following the depletion (or increment) in absolute peak areas in chromatograms (HPLC).

Flash Photolysis Measurements by Conductivity Change. About 60 mL of 1×10^{-3} M complex in 1×10^{-3} M $HClO_4$ solutions was flowed at 15 mL min^{-1} through a quartz cell (1 × 1 × 3 cm^3) fitted with three parallel platinum wire electrodes (0.05 (d) × 1 cm^2) spaced at 1.1-cm separation. A Spectra Physics Quanta-Ray GCR-11 neodymium-yag

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Table 1. UV–Visible Absorption and Emission Data for Chromium(III) Dicyano Tetram(m)ine Complexes

complex	λ_2, nm (ϵ)	λ_1 nm (ϵ)	λ_{em}, nm	τ, μs (20 °C)	ref
t-Cr(NH$_3$)$_4$(CN)$_2^+$	344 (41.5)	440 (42.6)	700	44	20
c-Cr(NH$_3$)$_4$(CN)$_2^+$	342 (37.6)	436 (49.0)	701	26	20
t-Cr(en)$_2$(CN)$_2^+$	337 (42.7)	432 (49.0)	703	1	33
c-Cr(en)$_2$(CN)$_2^+$	339 (63.1)	433 (70.8)	705	2	33
t-Cr(tn)$_2$(CN)$_2^+$	344 (47.5)	441 (52.5)	703	185	22
t-Cr(cyclam)(CN)$_2^+$	328 (62.5)	414 (62.5)	720	335	7
t-Cr(2,3,2-tet)(CN)$_2^+$	338 (46.0)	432 (52.4)	705	29	this work
c-Cr(2,3,2-tet)(CN)$_2^+$	337 (70 ± 10)	435 (70 ± 5)			this work

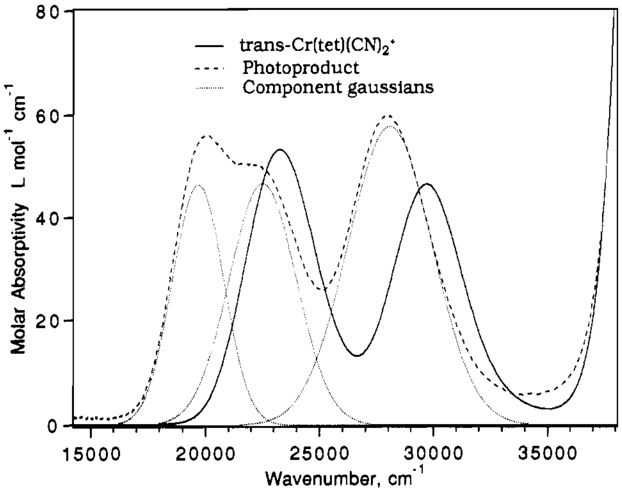

Figure 1. UV/visible spectra of [*trans*-Cr(2,3,2-tet)(CN)$_2$]ClO$_4$ and its photoproduct and the photoproduct component Gaussians.

laser provided 30 mJ (Molectron J 50 thermal detector/Tektronix 2445 oscilloscope), 5 ns pulses at 355 nm which irradiated a spot of ~0.6 cm diameter centered between the upper pair of electrodes. A 135-V square pulse of 4-ms duration was applied to the outside electrodes 1 ms prior to the laser pulse, and the conductivity change in solution induced by the laser pulse was measured on a Tektronix TDS-520 digital scope. The user interface to the extensive control and data acquisition system uses a Macintosh IIci computer with GPIB and I/O boards (National Instruments) with software developed here using Labview 2.2. The conductivity data were evaluated by a nonlinear least-squares fitting program based on the Levenberg–Marquardt algorithm[21] written in Pascal as a Labview code interface node (available from A.D.K.).

Results

Characterization of [*trans*-Cr(2,3,2-tet)(CN)$_2$]ClO$_4$. The UV/vis spectrum of [*trans*-Cr(2,3,2-tet)(CN)$_2$]ClO$_4$ is shown in Figure 1; the compound has band maxima at 432 and 338 nm (Table 1), as is to be expected for a complex with four amine N and two cyanide ligands. Similarly, the 705 nm wavelength maximum of the emission spectrum and its 29 ± 1 μs lifetime at 20 °C in aqueous medium (Table 1) match well with those for analogous complexes. The molar absorptivity of the lowest energy quartet band, ϵ_{432} = 52.4 ± 0.9 M^{-1} cm^{-1} is comparable with those of other reported *trans* analogues (Table 1).

Unfortunately, the spectra of *trans* and *cis* isomers are usually closely similar, so that the UV/vis spectrum cannot be completely relied upon to distinguish them. Nevertheless, the molar absorptivity for the first ligand field quartet can be useful. For the tetrammine analogues, there is a 15% increase in molar absorbance in going from the *trans* to the *cis*. This is in the usual direction but is a smaller increment than is often observed. Among the analogues, Cr(en)$_2$(CN)$_2^+$ is more typical and is also likely the closest in structure to [*trans*-Cr(2,3,2-tet)(CN)$_2$]ClO$_4$. Both complexes have two en rings *trans* to one another, and this creates an angular distortion at the Cr center which is not present in the analogues with ammonia or tn ligands. This reduces the symmetry at the Cr center particularly in the *cis* isomer and can be expected to influence molar absorptivities. Thus although the wavelengths of the two peak maxima and their molar absorptivity ratio in [*trans*-Cr(2,3,2-tet)(CN)$_2$]ClO$_4$ are similar for both *cis*- and *trans*-Cr(en)$_2$(CN)$_2^+$, note that the absolute molar absorptivities of the two *trans* compounds are close to equal at 52.4 and 49.0 L mol^{-1} cm^{-1}, respectively. In contrast, the molar absorptivity for the first ligand field band of *cis*-Cr(2,3,2-tet)(CN)$_2^+$ obtained in solution was measured by means of Cr analysis and gave 70 ± 5 L mol^{-1} cm^{-1}, the same as the reported value for *cis*-Cr(en)$_2$(CN)$_2^+$. These results support our assignment of the configuration of the two isomers and their chromatographic retention times, used later.

There were no infrared bands observed in the cyanide region, but these bands are typically very weak in both *trans* and *cis* dicyano tetram(m)ines.[20,22] Two other procedures were therefore adopted to confirm the geometry of the compound. First, the complex was reacted with 6 M HCl for 30 min at 60 °C to convert it to Cr(2,3,2-tet)Cl$_2^+$. Chromatographic analysis and comparison to authentic samples of *trans*- and *cis*-Cr(2,3,2-tet)Cl$_2^+$ showed that the dichloro product was >90% *trans* and had the correct *trans* UV/vis spectrum. Since Cr(III) aquation and anation thermal processes are typically stereoretentive in aqueous media, this supports the *trans* assignment. Second, ion-pair HPLC, comparing retention times with those of the product obtained by reacting *cis*-Cr(2,3,2-tet)Cl$_2$ with cyanide in dmso showed that the *trans* and *cis* dicyano isomers were separable by HPLC and established unequivocally the identity of the *trans* dicyano complex. Taken together, these results unequivocally establish the correct identification of the *trans* and *cis* isomers of Cr-(2,3,2-tet)(CN)$_2^+$. The chromatograms showed further that the *trans* compound was isomerically pure.

Thermal Chemistry of [*trans*-Cr(2,3,2-tet)(CN)$_2$]ClO$_4$. The compound was stable in aqueous solution but was subject to acid-catalyzed loss of cyanide at pH of 3 or less. The rate constant for this process at 28 °C was less than 1×10^{-5} s^{-1} at pH 3, slow enough not to interfere with the photochemical studies. Chromatographic analysis confirmed that amine aquation was negligible and, from the sole product peak observed, identified the HPLC retention time of *trans*-Cr(2,3,2-tet)(H$_2$O)CN^{2+}.

Photophysics of [*trans*-Cr(2,3,2-tet)(CN)$_2$]ClO$_4$. The compound emits at 705 nm in either water or dmso solution, and the lifetime of emission (τ) is 28 ± 1 μs in acidic aqueous solution at 21 °C. Many other Cr(III) cyano am(m)ine complexes show relatively long emission lifetimes (Table 1). A plot of ln τ vs $1/T$ was linear in the temperature range 10–40°C (Figure 2) and yielded an activation energy of 38 ± 1 kJ mol^{-1}.

A Stern–Volmer plot of $1/\tau$ vs [OH$^-$] shows that the emission is linearly quenched by OH$^-$ (Figure 3). The intercept corresponded to the sample lifetime of 26 μs (the long-lived doublet states of cyano am(m)ines are very prone to quenching by impurities and thermo- and photoproducts) and the slope to the corresponding collisional quenching rate constant (k_q) of 4×10^8 M^{-1} s^{-1} at 20 °C. Thus OH$^-$ ions efficiently quench the emission of *trans*-Cr(2,3,2-tet)(CN)$_2^+$ as they do many other Cr(III)

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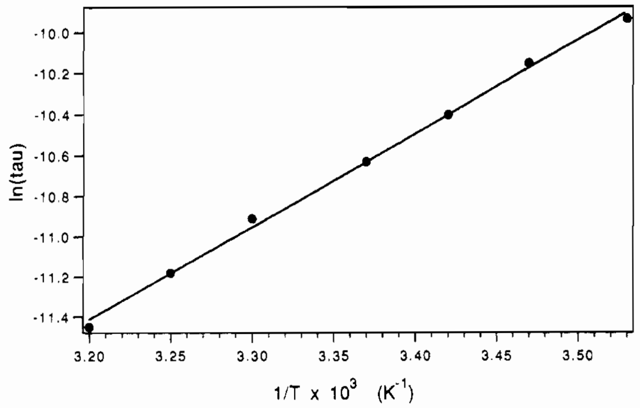

Figure 2. Temperature dependence of [*trans*-$Cr(2,3,2\text{-tet})(CN)_2]ClO_4$ emission lifetime in aqueous solution.

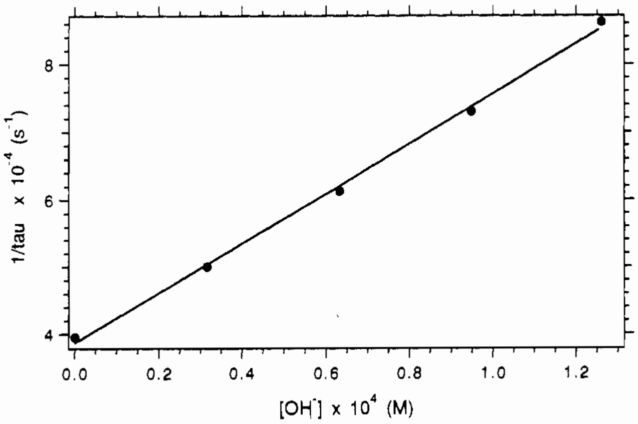

Figure 3. Stern–Volmer quenching of [*trans*-$Cr(2,3,2\text{-tet})(CN)_2]ClO_4$ by hydroxide ion in aqueous solution at 20 °C.

complexes. Chromatographic analysis showed that the quenching did not lead to any chemical reaction of the complex.

Photochemistry of [*trans*-Cr(2,3,2-tet)(CN)$_2$]ClO$_4$. The compound photoaquated on irradiation in the ligand field quartet bands. During photolysis, isosbestic points at 299, 341, 396, and 442 nm were maintained up to a high extent of conversion (>50%). These results showed also that 436 nm was a wavelength in the range where secondary photolysis is minimized as photoproducts absorb less strongly than the parent compound. The absence of secondary photolysis suggests that the primary products are fairly photoinert.

The photoproduct spectrum shown in Figure 1 was obtained in two ways. Direct measurement was based on photolysis to about 20% conversion followed by ion-exchange chromatographic separation of product and starting material. The molar absorptivities were estimated by Cr analysis of the resulting solution of photoproduct. The second method used difference spectra as a function of photolysis time combined with proton uptake measurements of the extent of photoaquation. Essentially identical spectra resulted via the two methods. Figure 1 shows that the bands are shifted to the red relative to the starting material by an amount that is consistent with replacement by water of an amine ligand, although more than reported for the analogous tetrammine.

The photobehavior was also studied by direct measurements of released cyanide and by measurements of the base released on photolysis at pH 3.0 using the pHstat method. The overall quantum yield of proton uptake was measured to be 0.09 ± 0.01 at 15 °C and conversion <10% for irradiation into either of the ligand field bands. The cyanide analysis showed that little or none of this total yield was owing to cyanide photoaquation; $\Phi_{CN^-} \leq 0.02$ based on the detection limit of the cyanide electrode.

HPLC Investigation of the Photoproducts. The photoproducts were also investigated using ion-interaction HPLC. *trans*-$Cr(2,3,2\text{-tet})(CN)_2^+$ gave a single peak at a retention time of 3.1 min, just following the peak for its *cis* isomer at 2.5 min. Under these eluent conditions, *trans*-$Cr(tet)(H_2O)CN^{2+}$ elutes at about 40 min and we expect the corresponding *cis* compound just prior to this. On photolysis a single peak grew in at 11 min. The photoproduct retention time is therefore intermediate between those for 1+ and 2+ ions; this is typical for a complex with a 2+ charge, but with one dangling protonated ethylenediamine-type ligand, $Cr(2,3,2\text{-tetH})(H_2O)(CN)_2^{2+}$. The small *trans*-$Cr(2,3,2\text{-tet})(H_2O)CN^{2+}$ peak observed was consistent with expectation for the small concurrent thermal reaction, and the amount of *cis* isomer to be expected from cyanide photoaquation (an axial photoreaction) was less than 1% of photoproduct. These data therefore also support amine aquation only.

Geometric Configuration of the Photoproduct. The evidence presented above shows that the title complex photolyzes an amine ligand to yield a single photoproduct. Although many isomers of $Cr(2,3,2\text{-tetH})(H_2O)(CN)_2^{2+}$ are possible in principle, given the polydentate nature of the 2,3,2-tet ligand and knowledge of typical photochemical pathways, which do not show aquation of an N ligand involved in more than one ring, we need consider as possible products only the isomers with a protonated ethylenediamine arm. The question then reduces to a decision between the *fac* isomer and the two *mer* species with *cis* and *trans* cyanides.

Since the UV/vis spectrum of the photoproduct was available, attempts were made to predict the spectra expected for these isomers on the basis of ligand field theory. Because of the low symmetry of the complexes, this is not easy, but one may expect that there would be the largest splitting and the lowest energy component in the first ligand field band of the *mer* isomer with *trans* cyanides. This is because the three components of this quartet band correspond to 45° rotations of charge in the three orthogonal planes containing the ligands. The average ligand fields in the three planes are predicted to be distributed over the largest range in the *trans-mer* isomer.

Using $10Dq$ values for cyanide, water, and amine of 2.66, 1.73, and 2.16 μm^{-1}, respectively, the average field strengths calculated for the three planes suggest transition components at 460 (doubly degenerate) and 415 nm for the *fac* isomer and at 490, 435, and 415 nm and 460, 440, and 435 nm for *trans* and *cis-mer* dicyano products, respectively. For the experimental photoproduct spectrum plotted on a wavenumber scale, the lowest energy peak could be resolved into two Gaussians with peaks at 508 and 444 nm (Figure 1). The large splitting and the presence of a long-wavelength band in the experimental spectrum both imply that the product found is the *mer* isomer with the cyanides in *trans* orientation.

The second approach took advantage of our observation that the isolated photoproduct recoordinates the dangling amine ligand on standing at a temperature of 25 °C. At first this was considered a major impediment as it frustrated all our attempts to obtain single crystals of the photoproduct suitable for X-ray structure determination. All the procedures tried, using several different counterions, with crystallization or freeze-drying, led only to starting material or decomposition products. The rate of the recoordination process was observed to depend on pH in a manner that suggested that the most active species was $Cr(2,3,2\text{-tetH})(OH)(CN)_2^+$; the recoordination half-life at 25 °C was only 8 min at pH 6 but increased[23] to 30 min at pH 9 and to more than 30 h at pH 3. HPLC analysis of solutions of isolated photoproduct that had been allowed to stand for various times showed a decrease in the peak for the photoproduct and a steady growth of a new peak with the same retention time as the starting material. This product of recoordination had the same spectrum, including molar absorptivity in the first quartet band (50 ± 5 M^{-1} cm^{-1}), as *trans*-$Cr(2,3,2\text{-tet})(CN)_2^+$. Assuming that recoordination is stereo-

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[23] Fernando, S. R. L. Doctoral Thesis, University of Victoria, 1993.

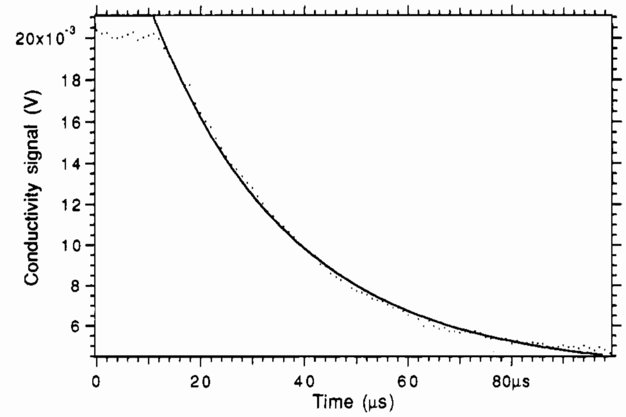

Figure 4. Time dependence of solution conductivity for [*trans*-Cr(2,3,2-tet)(CN)$_2$]ClO$_4$ in pH 3.00 solution after excitation by a 30 mJ, 5 ns pulse at 355 nm. The solid line is the nonlinear least-squares fit of the data points shown to an exponential decay.

retentive, this also demonstrates that the photoproduct is the *mer* isomer with *trans* cyanides.

Excited State Participation. To establish the identity of the excited states leading to reaction, the time dependence of photoproduct formation was investigated using nanosecond laser flash photolysis with dc conductivity detection. In these experiments a sample of complex with luminescence lifetime of 28 ± 1 µs at 21 °C was used and gave the result shown in Figure 4. It reveals that 100% of the photoreaction occurs in a single-exponential process with a lifetime of 26 ± 1 µs, within experimental error the same as that of the doublet state.

For comparison purposes, and for a check of the validity of our implementation of the techniques, an experiment for Cr(NH$_3$)$_6^{3+}$ was also performed. Seventy percent of the reaction occurred with the doublet lifetime of 1.9 µs at 21 °C, while the remaining 30% occurred as a second, nanosecond exponential process. This faster exponential process had a lifetime inversely proportional to the proton concentration, indicating that protonation of the released ammonia is the rate-limiting step being observed here. This "prompt" component is traditionally assigned to reaction from the quartet state before or after vibrational and solvent shell relaxation. These results agree well with published data.[24]

Discussion

The Nature of Equatorial Labilization. As explained in the Introduction, there is good evidence to show that the photosubstitutions of axial ligands in tetragonal Cr(III) complexes occur with required stereochemical change and are inhibited when this is not possible. The objective of this study was to search for parallel behavior in complexes showing equatorial labilization as their main reaction modes. There is an inherent ambiguity in the concept of equatorial ligand loss from complexes with tetragonal symmetry, however. This is because it can occur in principle by two routes, either as a result of excitation into the $^4B_2$ state with labilization solely in the equatorial plane or as one of the two reaction modes possible when excitation is into the two orthogonal planes corresponding to the ^4E state. The latter process has been analyzed stereochemically by means of a comparison between the photochemistries of Cr(NH$_3$)$_5$F^{2+} and *trans*-Cr(en)$_2$(NH$_3$)F^{2+}. The conclusion was that this latter type of equatorial reaction mode shows stereochemical change in parallel with the axial ligand loss mode from the same state.[25] The model presented there was recently elaborated[12] by Vanquickenborne and co-workers, as discussed later.

In this work the interest was to establish the stereochemistry of the first possibility, loss of an equatorial ligand as a result of excitation in the equatorial plane. If this photosubstitution process also involves required stereochemical change, then, because the polydentate ligand prevents entry of the water ligand *trans* to the departing amine ligand, *trans*-Cr(2,3,2-tet)(CN)$_2^+$ should be photoinert. Our results show clearly it is not. But why?

Possible Reactive Excited States. The laser flash conductivity data presented in Figure 4 show that the photoreaction occurs entirely via the doublet state. Together with the observation that the photochemistry is stereoretentive in contrast to that of most other Cr(III) complexes studied, this photoreaction could easily be attributed to a direct reaction of the doublet state, activated by 38 kJ mol^{-1}. Because the doublet state has the same metal orbital populations as the ground state, it might reasonably be expected to parallel its stereoretentive reaction modes. However, such a facile explanation fails to place these results in the general context of Cr(III) photochemistry and specifically fails to relate them to the results for close analogues of this compound.

Much of Cr(III) photochemistry has been shown to occur via two pathways, one of which is attributed to reaction of the lowest quartet excited state. For many systems, *trans*-Cr(tn)$_2$(NH$_3$)$_2^{3+}$ is a good example;[26] this unquenchable component of photoreaction occurs with stereochemical change. Also, there exists the angular overlap theory which explains why stereochemical change should occur for reaction via the lowest excited quartet states.

The doublet state also participates in reaction, likely as a reservoir of excitation energy rather than as a primary reactive species. Two models of this photochemistry currently compete. One assigns it to reaction of a ground state intermediate;[27] the other, to the same intermediate as is derived from reaction of the lowest electronically excited quartet state. For these cyano tetram(m)ine complexes this is $^4B_{2g}$. The behavior is further complicated in reality, as details of quantum yield wavelength and temperature dependence often demand[28] that the higher excited quartet state, here ^4E, may also be a primary reactive species, in violation of Kasha's rule. These precursors seem to contribute[4,28,29] to photochemical yields in ratios that do not reflect the Boltzmann equilibria expected on the basis of their estimated energies. To account for this, and the frequent observation of constant product ratios for the two pathways, one of the authors has suggested that the reverse intersystem crossings required in one of these models are controlled by solution kinetic factors rather than by spectroscopic considerations.[15]

The above points can be illustrated by reviewing the behavior of the dicyano tetram(m)ine systems. The dicyano cyclam complex[30,31] is photoinert, has a long solution doublet emission lifetime of 335 µs (all values cited for 20 °C), and populates the doublet state with a unity intersystem crossing yield. The dicyano bis(1,3-diaminopropane) analogue[22] has a doublet lifetime of 185 µs and a total aquation quantum yield of 0.08, of which 40% is loss of cyanide (axial) with stereochemical change. The amine loss pathway leads to about equal amounts of the photoproduct with *cis* and *trans* cyanides, implying reaction from both $^4B_{2g}$ and ^4E states. The dicyano tetrammine has a doublet lifetime of 44 µs and loses ammonia with a quantum yield of 0.24 to give meridional products, 30% *cis*- and 70% *trans*-dicyano aquo triammine.[4] Behavior very parallel to this has been reported for Cr(NH$_3$)$_5$CN^{2+}, for which the further information is available that 73% of the reaction occurs via the doublet and that the quenchable and unquenchable pathways have the same apparent activation energy for ϕ_{NH_3}, product ratio, and stereochemistry.[4]

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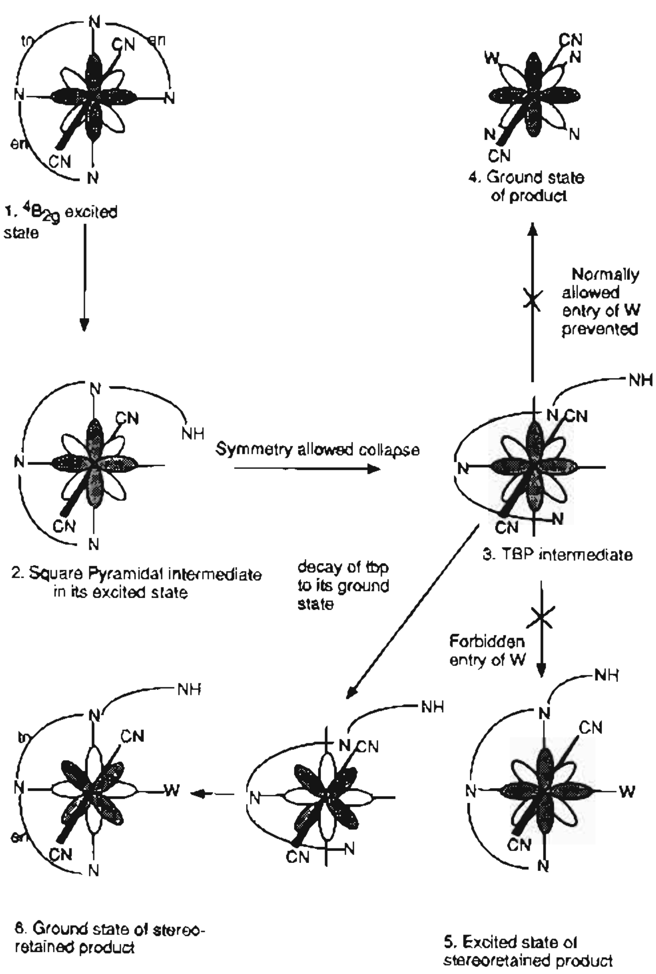

Figure 5. Pictorial representation of angular overlap theory of photostereochemistry for [*trans*-Cr(2,3,2-tet)$(CN)_2$]ClO_4. The normal pathway of photoaquation would be via the tbp intermediate to the stereochemically changed product shown at the upper left. The ligand constraints prevent this. The pathway to the stereoretained product at the lower right is symmetry forbidden. The complex therefore should be photoinert. Further details of the possible pathway of reaction also shown can be found in the Discussion.

Zinato and co-workers recognized that one possible explanation of these results was simultaneous reactions of the $^4B_2$ and ^4E states after reverse intersystem crossing.

In light of this background, we recognize the possibility that the unexpected photoactivity of *trans*-Cr(2,3,2-tet)$(CN)_2^+$ could arise as a result of photoreaction from the higher-lying ^4E state. In the ^4E state, the cyanide ligands and two equatorial amine sites would be labilized. Because of the strong bonding of cyanide to Cr(III), an amine ligand would be the predicted leaving group. There is experimental support[8,31,32] for suggesting that the secondary nitrogen atoms of the ligand, involved in more than one ring, are constrained from leaving but that the ethylenediamine arm can do so. Such a photoreaction, since it corresponds to the archetypal axial process, is expected to occur with *trans* entry of the water ligand and stereochemical change to give the meridional isomer with *cis* cyanides. Again, experimental results for the analogous dichloro complex support[6] the feasibility of the ligand rearrangements required. A parallel process attributed to the ^4E_g state has earlier been suggested to account for the analogous 30% of photoreaction[29] in *trans*-$Cr(NH_3)_4(CN)_2^+$. In all these examples, the photoproduct has been shown to have *cis* geometry for the diacido ligands. As the product we obtained has the cyanide ligands *trans*, our results strongly indicate that this is not the pathway of reaction. We conclude that this is a genuine, if somewhat inefficient, stereoretentive reaction. Placed in the context of the behavior of other *trans*-dicyano tetram(m)ine species, the photoaquation likely occurs via reverse intersystem crossing to the $^4B_{2g}$ state. This is supported by the 38 kJ mol^{-1} energy barrier we find for the major process depleting the doublet state, as this is a typical value found[4] for systems that apparently react via the reverse intersystem-crossing route.

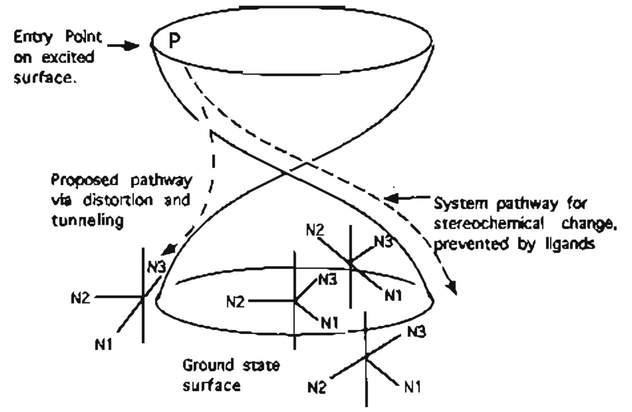

Figure 6. Jahn–Teller distorted excited and ground states of putative square pyramidal (sp) and trigonal bipyramid (tbp) intermediates in $CrA_4(CN)_2$ photoreactions. The diagram shows the tbp species at the center of the coordinate space, with, located at 120° intervals on the periphery, the three square pyramids into which it can evolve by Berry pseudorotations. On excitation, the complex can lose one of the terminal nitrogen ligands, here N4, to form an excited state square pyramid corresponding to the entry point P on the upper surface of the system. In the title complex, N1 and N2 comprise an en ring and N2 and N3 a tn ring, providing steric constraints that prevent access to the two sp forms on the right of the diagram, which would be the normal pathway for reaction. Indeed they likely limit access to the tbp form, which is the degenerate configuration of the complex if all N ligands were equal in ligand field strength. A possible stereoretentive pathway is shown and discussed further in the text.

The orbital symmetry theory for this photoreaction is shown pictorially in Figure 5. Loss of a terminal amine ligand is the first step toward photoaquation. The square pyramid (sp) intermediate formed in its $^4B_2$ excited state should rearrange to a trigonal bipyramid (tbp) as shown. The normally allowed entry of water ligands at the two tbp edges bearing a lobe of the vacant t_{2g} orbital is now prevented by the steric blocking by the in-plane ligand rings, the basis of our expectation of a photoinert complex. How can we then obtain a stereoretentive reaction? Two scenarios can be suggested, but in considering them, we must bear in mind the need to accommodate the observation that *trans*-Cr(cyclam)-$(CN)_2^+$ is photoinert.

The first recognizes that the amine nitrogens in this tbp do not all have the same ligand field strength; the secondary amines are stronger. This gives a small splitting of the lowest quartet states of the tbp intermediate, and the allowed motion for the sp → tbp conversion produces the tbp in its quartet excited state. It is this excited state that is predicted to show stereochemical change but which is sterically constrained from reaction. Since the excited state reaction is prevented, there is now time for internal conversion to populate the ground state tbp, which has the opposite stereochemical behavior. Now the vacant t_{2g} lobe is located on the free edge of the tbp and can coordinate a water ligand, leading to the stereoretained photoproduct, as found. If the same model is applied to the cyclam system, it is found that the tbp is produced in its ground state with a stereochemical change requirement, explaining its failure to react.

The second scenario recognizes the reality that the ligand constraints are such that it is impossible for this molecule to achieve the tbp configuration envisaged in the above theory, or probably even the seven-coordinate equivalent that has been suggested as a better alternative. It was recently proposed[12] that

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the stereochemistry of these photoprocesses is controlled by the motions of the system on a "Mexican hat" Jahn–Teller excited/ground state surface connecting the symmetric tbp configuration and the three sp intermediates reproduced in Figure 6. Our system would enter the excited state surface at point P and would attempt to relax to the symmetric degeneracy point but is prevented from doing so by the steric constraints. If, as shown, it can distort sufficiently that it can tunnel to the lower surface, this would lead to a stereoretentive reaction mode as found. The photoinertness of the cyclam analogues can then be rationalized in terms of the greater ligand stiffness. This would prevent the distortion necessary to approach the crossing point of the tbp intermediate and encourage internal conversion to the ground state without reaction.

It is clear that this work has raised and left partially unresolved some interesting issues concerning the mechanism of this unexpected photoreaction and the reality of stereochemical change associated with equatorial labilization of D_{4h} complexes. We intend to perform further experiments on model compounds to clarify further the processes occurring.

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