Inorg. Chem. **1992**, *31*, 656-661

Table IV. Equilibrium Constants[a] for 1:1 Complexes of Metal Ions with Free-Base Porphyrins

	TMPyP(2) pK_3 –0.9	TMPyP(4) pK_3 1.4	TAPP pK_3 3.6	TPPS pK_3 4.8
Zn(II)[b]	1.9×10^2	4.4	1.1	1.3×10^{-1}
$Hg(OH)_2$[c]	3.5×10^{-5}	2.3×10^{-6}	5.0×10^{-9}	4.0×10^{-9}
Cd(II)[d]	7.9×10^{-7}	6.1×10^{-9}	1.7×10^{-10}	8.3×10^{-11}
Pb(II)[e]	9.5×10^{-8}	2.0×10^{-8}	3.0×10^{-10}	3.4×10^{-10}

[a] Equilibrium constant (eq 1) units are M, at 25 °C. [b] TMPyP(2, 4), ref 1; TAPP, ref 21b; TPPS, ref 11. [c] TMPyP(2, 4), this work; TAPP and TPPS, ref 9a. [d] TPPS, ref 5, other porphyrins, ref 2. [e] TPPS, ref 3b; other porphyrins, ref 3a.

> Pb(II). This is because $(HO)_2Hg–P^{2-}$ forms orders of magnitude faster than the Pb or Cd(II)–P intermediates. Once formed, the rate constants for the reactions of any of these intermediates with a given entering ion are not vastly different. For example, the specific rate constants for Zn^{2+} incorporation into $(OH)_2$–Hg, Cd(II), and Pb(II)–TMPyP(4) are ~56, 79, and 14 M^{-1} s^{-1}, respectively.[3]

The Zn^{2+}/H_4-$TPPS^{2+}$ reactions come to equilibrium very slowly at pH 3.5, and Tabata and Tanaka demonstrated that the addition of 2.1×10^{-5} M Hg(II) leads to a more rapid determination of K_{IV} for this system, presumably via the formation of reactive mercury–porphyrin intermediates.[26] We noted with H_4-$TPPS^{2+}$ at this pH, however, that Hg(II) levels above ~10^{-4} M lead to rapid decomposition of this porphyrin into unknown species. These products could involve the substitution of the TPPS β-pyrrole protons by Hg atoms, a process found by Smith and co-workers[27] to occur in the highly basic deuteroporphyrin type series. The experiments reported in this paper were done with positively charged porphyrins which are substantially less basic than TPPS, and no changes in porphyrin spectra that could be attributed to the alteration in the β-pyrrole positions were ever found at any Hg(II) levels studied over the several hours that it took to collect our results. However, with micromolar levels of Cu(II)–TMPyP(4) in ~0.4 M HNO_3 and 0.1–0.5 M Hg(II), both the visible and Soret bands gradually shift over a period of days to higher wavelengths, consistent with the slow substitution of several β-pyrrole protons by Hg(II).

Table IV shows a comparison of the formation equilibrium constants that have been measured for 1:1 metal/porphyrin complexation. In general, the order is Zn(II) ≫ Hg(II) > Cd(II) ~ Pb(II). For a given metal ion, less basic porphyrins have larger formation constants. As noted previously,[2] this is due to the fact that the reverse $[H^+/M(II)–P]$ rate constants depend more strongly on porphyrin basicity than do the magnitudes of the forward $[M^{2+}/H_2$-P] specific rates.

In conclusion, equilibrium constants have been measured below pH 1 for Hg^{2+} and various H_2-P, H_3-P^+, and H_4-P^{2+} porphyrins which all produce the homodinuclear $[Hg_2–P]^{2+}$ as a product. The reactant in each case is probably the free base, since most metal ions in aqueous solution are less reactive with the protonated mono- or dication porphyrins.[17,24] Near neutral pH, $Hg(OH)_2$ and H_2-P form $(OH)_2Hg–P^{2-}$ (or O–Hg–P^{2-}) mononuclear adducts. The overall pattern is similar to that observed by Hudson and Smith[28] in their spectral study of Hg(II)–TPP. In methylene chloride Hg(II)–TPP is stable, and added traces of acid convert 2 Hg(II)–P into H_2-P and Hg_2–P^{2+}. Hg_2–P^{2+} then reacts with additional protons to form H_2-P and Hg^{2+}. This is in agreement with our results indicating that Hg_2–P^{2+} is more stable than Hg(II)–P under acidic conditions.

Registry No. TMPyP(4), 38673-65-3; TMPyP(2), 59728-89-1; TMQP(4), 85254-98-4; Hg, 7439-97-6; Cu, 7440-50-8; Zn, 7440-66-6.

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(26) At 0.70 M H^+, $I = 0.86$, with 5.0×10^{-4} M added Hg^{2+}, we found a formation constant for Zn(II)–TMPyP(2) of $(2.4 \pm 0.1) \times 10^2$ M, as compared to the uncatalyzed value of 1.9×10^2 M measured earlier[1] under slightly different conditions.

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Thermo- and Photoaquation of *trans*-$[Cr(1,3\text{-diaminopropane})_2(CN)_2]ClO_4$. Quenching of Photochemistry by Photoproducts

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The compound *trans*-$[Cr(tn)_2(CN)_2]ClO_4$, where tn = 1,3-diaminopropane, has been prepared and characterized. It undergoes an acid-catalyzed thermal aquation of the cyanide ligand to yield *trans*-$Cr(tn)_2(H_2O)(CN)^{2+}$ with a pseudo-first-order rate constant of 8×10^{-6} s^{-1} at 5×10^{-4} M H^+ and 15 °C. The further aquation to yield *trans*-$Cr(tn)_2(H_2O)_2{}^{3+}$ is significantly slower, so that solutions of relatively pure *trans*-$Cr(tn)_2(H_2O)(CN)^{2+}$ can be prepared by this route. Under these conditions, no aquation of the Cr–tn bond is observed. Photoaquation of *trans*-$[Cr(tn)_2(CN)_2]ClO_4$ was examined by difference spectroscopy, reversed-phase liquid chromatography, and direct proton uptake and cyanide release measurements. Both cyanide and tn are aquated. The proton uptake measurements showed that the photolysis behavior is nonlinear owing to quenching of the photoreactant doublet state by photoproducts. The total product quantum yields were therefore based on the zero-time slopes of the proton uptake data. $\phi(CN^-)$, $\phi(tnH^+)$ (irradiation wavelength): 0.035 ± 0.004, 0.048 ± 0.005 (436 nm); 0.023 ± 0.004, 0.052 ± 0.004 (458 nm). Loss of cyanide is not predicted by photochemical theory, and its occurrence is attributed to the role of ligand interactions in directing photoaquation modes.

Introduction

Zinato, Riccieri, and co-workers have reported[1-9] the thermal aquation and photoaquation behavior of an interesting series of cyano ammine complexes. Some of these molecules have long-lived doublet states which emit from room-temperature aqueous solutions, offering a favorable circumstance for the study of photophysical behavior of the excited states under photochemical conditions.

The dynamics of Cr(III) photochemistry has been elucidated by studies on the wavelength and temperature dependence of

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quantum yields, by picosecond flash photolysis studies, and by related studies of quenching and energy transfer. In several instances it has been observed that 1,3-diaminopropane (tn) complexes may behave differently from their ammine and diaminoethane (en) analogues.[10,11] Specifically, tn seems to be a much poorer leaving than other comparable amines with similar LF strengths, a trait which promotes preferential loss of the other ligands in the molecule.

Consistent with this, the title compound might be expected to show a larger extent of cyanide photoaquation than has been previously observed for its analogues. If so, it would be an interesting candidate molecule for wavelength dependence studies of product stereochemistry similar to that done[12] recently for $Cr(tn)_3^{3+}$. It might also offer the additional feature of two roughly equal reaction modes with potential for wavelength and temperature dependence of the ratio of their products. We therefore undertook to synthesize and characterize the molecule and to study its photoaquation behavior.

We report these results and their significance here. We also report our observation of an unusual quenching of the precursor photoactive doublet state by the photoproducts.

Experimental Section

Synthesis. ***trans*-Cr[$(tn)_2F_2$]Cl.** This was synthesized by the literature[13] method, but with 1,3-diaminopropane and with reaction overnight rather than for 2 h.

***trans*-Cr[$(tn)_2Br_2$]Br** was prepared from *trans*-Cr[$(tn)_2F_2$]Cl using a procedure analogous to that reported for the synthesis of *trans*-Cr-[$(en)_2Br_2$]Br.[14]

***cis*- and *trans*-Cr[$(tn)_2(H_2O)_2$]$(NO_3)_3$** were prepared as described in the literature.[15]

***trans*-[$Cr(tn)_2(CN)_2$]ClO_4.** *Warning!* Perchlorate salts of metal complexes containing organic ligands can be dangerously explosive when shocked or heated, which we have carefully avoided. For the synthesis, 1.8 g (37 mmol) of finely ground NaCN was dissolved in 20 mL of dimethyl sulfoxide (dmso) (Aldrich, dried over 4A molecular sieves) by heating to 60–62 °C in a 100-mL round-bottom flask. Then 2 g (4.5 mmol) of *trans*-Cr[$(tn)_2Br_2$]Br (green) was added to the solution, which immediately turned dark red. As a precaution, the neck of the flask was kept closed whenever possible to minimize exposure to atmospheric moisture. On heating at 60–62 °C with vigorous magnetic stirring for 140 min, the solution gradually turned orange and the UV/vis spectrum shifted to the blue, at which time the heating was stopped. The two ligand field band maxima of this solution were close to the expected wavelengths for the product. The cooled reaction mixture was then added to 400 mL of ice-cold 0.5 M $NaClO_4$ in dry ethanol. Allowing the mixture to stand on ice for 2 h resulted in the formation of a yellow precipitate, which was filtered off with the use of a sintered-glass funnel. The crude product yield was about 1 g (65% of theoretical).

The crude product (500 mg) was dissolved in 250 mL of distilled water, and the solution was placed on a 1.0 × 1.5 (o.d.) cm SP-Sephadex C25 cation-exchange-resin column, giving a yellow band, about 2 cm wide. At flow rates of about 20 mL min^{-1} the column was washed with 200 mL of distilled water and then eluted with 350 mL of 0.03 M aqueous $NaClO_4$. The initial and final pale yellow fractions, about 50 mL each, were discarded, while the middle yellow fraction was collected and rotary-evaporated to dryness. Then 15 mL of dry ethanol was added to obtain a concentration of $NaClO_4$ of about 0.5 M. The slurry was stirred thoroughly, allowed to stand for 1 h, and filtered using a medium-porosity sintered-glass funnel. The solid complex remaining was washed with 20-mL portions of dry ethanol and acetone and vacuum-dried to yield 400 mg of product, an overall yield of 50%. The compound was recrystallized from a minimum amount of room-temperature water by dropwise addition of 8 M $NaClO_4$ solution and cooling.

The material is bright yellow and has a solubility of about 60 mg mL^{-1} in water at room temperature, decreasing to 5 mg mL^{-1} in 2 M $NaClO_4$. It is readily soluble in dmso but insoluble in methanol, ethanol, acetone, ether, ethyl acetate, chloroform, and methylene chloride.

Elemental analysis was performed by Canadian Micro Analytical Services. Anal. Found (calcd): C, 27.40 (27.32); H, 5.62 (5.73); N, 23.56 (23.89).

UV/Vis and IR Spectra. A Phillips PU 8740 scanning spectrophotometer was used for UV/vis spectral measurements, while a Perkin-Elmer 283 spectrophotometer with KBr disks was used for IR measurements.

Chromatographic Analysis. A Varian system 5000 liquid chromatograph with a 30-cm octadecylsilane RP column was employed. Eluents consisted of tetraethylammonium as the competing ion and butanesulfonate as the interaction agent in methanol/water at pH values of 2 and 3. Further details are given later where relevant. Peaks were detected by their UV/vis absorptions at 240 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 wavelengths 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 nitrogen laser[16]/Jarrel-Ash monochromator/Hamamatsu R928 photomultiplier/Tektronix 2230 oscilloscope system with a GPIB interface to an ATARI 1040 computer. Lifetimes were evaluated by weighted linear regression[17] on log (intensity) versus time plots over 1024 channels of decay.

Quantum Yield Determinations. Radiation at 436 nm (Balzers interference filter) and 365 nm (Corning CS 7-60 colored glass filter) from a 1000-W mercury lamp was passed through a 10-cm water filter to remove the infrared components. Radiation at 458 and 488 nm was generated by a Spectraphysics 2000 argon ion laser. The approximate light intensities were 3×10^{-8}, 8×10^{-8}, 6×10^{-8}, and 6×10^{-8} einstein s^{-1} at 436, 365, 458, and 488 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-μL stepping motor buret, to maintain the pH of the solution constant with recording of acid added. The pK_a values for the aquo-substituted photoproducts of tn 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 $Cr(tn)_3^{3+}$ [18] and $Cr(NH_3)_4(CN)_2^+$.[4] Solvent pH values were set between 2.9 and 3.3, which avoided errors arising from partial dissociation of photoproducts to their conjugate base forms.

An ionic strength buffer of 0.1 or 0.05 M $KClO_4$ was used throughout, and the extent of photolysis was kept below 12% to reduce secondary photolysis. The light intensity from the mercury lamp was computer-monitored continuously using the analogue 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 × 1 (o.d.) cm QAE-Sephadex A-25 anion-exchange column to remove free cyanide. 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 a few microliters of 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 evaluation, since tests showed that the complex did not affect the electrode readings.

Results

Characterization. The compound, which analyzed correctly for [$Cr(tn)_2(CN)_2$]ClO_4, shows two LF bands at 441 and 344 nm (Figure 1). As shown in Table I, the wavelengths of the peak maxima and their absorbance ratio are close to those for the analogous compound *trans*-[$Cr(NH_3)_4(CN)_2$]ClO_4.[4] The molar

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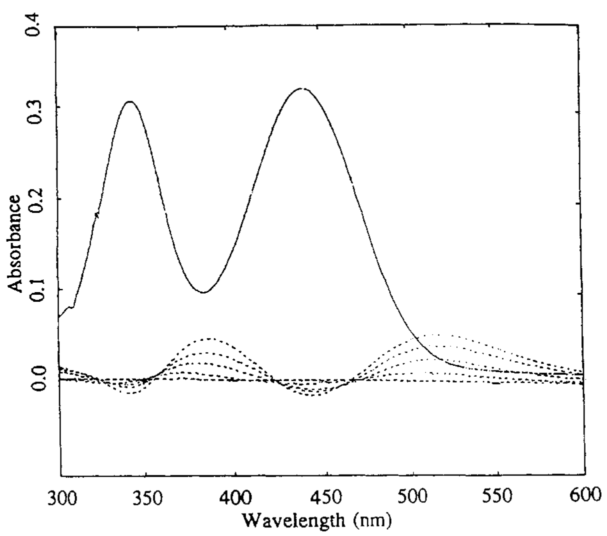

Figure 1. UV/vis absorption spectrum and photolysis difference spectrum for *trans*-$[Cr(tn)_2(CN)_2]ClO_4$. Conditions for difference spectrum: 1.0×10^{-2} M complex in 1×10^{-3} M $HClO_4$. Dotted lines correspond to room-temperature exposure to 50 mW of 458-nm radiation for 0, 2, 5, 7, and 10 min.

Table I. UV/Vis Absorption Data[a]

	λ_{max}, nm (ϵ, M^{-1} cm^{-1})		$\epsilon(L_1)$/ $\epsilon(L_2)$	ref
obsd	344 (47.5)	441 (52.5)	1.08	this work
trans-$Cr(NH_3)_4(CN)_2^+$	344 (41.5)	440 (42.6)	1.03	4
cis-$Cr(NH_3)_4(CN)_2^+$	342 (37.6)	436 (49.0)	1.30	4
trans-$Cr(en)_2(CN)_2^+$	337 (42.7)	432 (49.0)	1.15	31
	337 (42.7)	432 (50.1)	1.17	29
cis-$Cr(en)_2(CN)_2^+$	339 (63.1)	433 (71)	1.13	31
	339 (62.3)	434 (70)	1.12	32
	339 (62.2)	434 (69.5)	1.12	29

[a] L_1 and L_2 are the lowest and next highest energy UV/vis absorption bands.

absorptivities for our compound are higher than those for the tetraammine, as is usual for chelated compounds. Also included are the data for the analogous en derivatives. These do not parallel the data for the ammine analogues, and we believe this has its origin in the angular distortion present at Cr in the en compounds and absent in the tn analogues. The comparison of band positions and molar absorptivity ratios for the ammine and tn systems supports a trans geometry for our product, which we require to confirm our expectations for the nature of its photochemistry and stereochemistry.

In the infrared spectrum, a band occurs near 2130 cm^{-1} which can be attributed to the CN stretch. This band is weak, as might be expected for the trans isomer, but this cannot be relied on as proof of geometry or as an indicator of isomeric purity.

In past work, it has been found[19,20] that an IR criterion to distinguish cis and trans isomers of the analogous bis(diaminoethane) complexes is the band pattern between 395 and 550 cm^{-1}. All cis complexes show a pattern of at least four bands in this region whereas the trans complexes usually show only three strong bands, although anion effects can increase this number.[20] Our complex has three strong bands at 410, 455, and 510 cm^{-1}, consistent with trans geometry.

Thermal Reactions. Cr(III) cyano complexes undergo stereoretentive acid-catalyzed aquation in acidic aqueous medium. Here the reaction can be expected[4] to occur in two distinct steps:

$$Cr(tn)_2(CN)_2^+ + H_3O^+ \rightarrow Cr(tn)_2(H_2O)(CN)^{2+} + HCN \quad (1)$$

$$Cr(tn)_2(H_2O)(CN)^{2+} + H_3O^+ \rightarrow Cr(tn)_2(H_2O)_2^{3+} + HCN \quad (2)$$

UV/vis spectrophotometric monitoring of 6×10^{-3} M room-temperature solutions of *trans*-$[Cr(tn)_2(CN)_2]ClO_4$ at various concentrations of $HClO_4$ demonstrated cyanide aquation whose rate increased with acid concentration. At 3×10^{-3} M $HClO_4$, aquation occurred with three isosbestic points to give a stable product after 100 min. Comparison of our data to those for the tetraammine system (Table II) shows that this reaction corresponds to loss of the first cyanide to form *trans*-$(Cr(tn)_2(H_2O)(CN)^{2+}$ (reaction 1). The same reaction occurs immediately in 0.3 M $HClO_4$, and the monocyano monoaquo product is again stable for at least 12 h.

At 2 M $HClO_4$, however, the *trans*-$Cr(tn)_2(H_2O)(CN)^{2+}$ ion formed reacts further. This reaction also shows three isosbestic points (Table II) which parallel those for formation of *trans*-$Cr(NH_3)_4(H_2O)_2^{3+}$ from *trans*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$. After 8 h a stable compound remains, whose spectrum matches reasonably well that[10] for *trans*-$Cr(tn)_2(H_2O)_2^{3+}$.

The first aquation step of *trans*-$Cr(NH_3)_4(CN)_2^+$ has been shown[7] to have a strongly nonlinear hydrogen ion dependence arising from participation of protonated and unprotonated forms. We did not investigate this aspect, but measured, by the pH-stat method, the pseudo-first-order rate constant at 15 °C in 5×10^{-4} M $HClO_4$/0.050 M $KClO_4$. The rate constant obtained, 8.0×10^{-6} s^{-1}, is about an order of magnitude smaller than we estimate for *trans*-$Cr(NH_3)_4(CN)_2^+$ under our conditions by combining the published[7] rate data for low acid concentrations at 35 °C with the reported activation enthalpy of 17 kcal mol^{-1}. The rate constant for step 2 of the thermal reaction was not measured, although our results show it also is much smaller than that for aquation of *trans*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$.

The aquation reaction therefore proceeds as shown, in two separable steps. The isosbestic behavior and the product spectra are consistent not only with this pathway but also with the trans configuration for all these species. A small amount of cis impurity, however, would be missed.

HPLC Analysis of Thermal Products. Reversed-phase HPLC[21] allowed us to separate authentic samples of *cis*- and *trans*-$Cr(tn)_2(H_2O)_2^{3+}$ ions into baseline-resolved peaks. Using an eluent of 25 mM sodium butanesulfonate/25 mM triethylamine in 10% methanol/water at pH 2 and 2 mL min^{-1}, the trans isomer elutes after the cis with retention times of 7.3 and 6.5 min. The product mixture obtained from the second step of aquation in 2 M $HClO_4$ was injected under the same conditions. The major peak had a retention time of 7.3 min, confirming that the final thermal product is *trans*-$Cr(tn)_2(H_2O)_2^{3+}$. The chromatogram also showed a small peak for the cis isomer at 6.5 min, less than 5% of the major peak.

This cis product could have arisen from a small amount of isomerization before or during the aquation process. Cr(III) thermal reactions are known to be stereoretentive, however, so it may be revealing some cis impurity in our starting material. This leads us to a 95% lower limit on the isomeric purity of the *trans*-$[Cr(tn)_2(CN)_2]ClO_4$. A direct confirmation was not possible, as even had we had both isomers of $[Cr(tn)_2(CN)_2]ClO_4$ available, experience suggests that these would not be separable by our chromatographic technique.

Emission Properties. At room temperature in aerated solution, the complex shows an intense, structured emission with a maximum at 703 nm. For $Cr(NH_3)_4(CN)_2^+$, the emission band positions were 701 and 700 nm for the cis and trans isomers, respectively.[8]

The compound has the long emission lifetime, compared to many other Cr(III) complexes, of 185 ± 15 μs at 20 °C in aerated or deaerated water, obtained by extrapolation of solution τ/time data to zero time (see later). Quenching of the doublet excited state therefore tends to be efficient. Hydroxide, for example, gives a linear Stern–Volmer plot with a K_{SV} value of 9×10^5 M^{-1}, which corresponds to a collisional quenching rate constant of 5×10^9 L mol^{-1} s^{-1}, approaching a diffusion-controlled state.

Photolysis Studies. Photolysis of the title compound in aqueous medium leads to proton uptake, shown by analysis to arise because

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Table II. Spectral Data for Thermal Acid-Catalyzed Reactions of *trans*-Cr(tn)$_2$(CN)$_2^+$

starting complex	λ, nm (ε(rel))											ref
	reaction 1					reaction 2						
	isosbestics			product spectra		isosbestics			product spectra			
trans-Cr(tn)$_2$(CN)$_2^+$	356 (1.0)	393 (0.4)	450 (1.2)	356 (1.0)	462 (1.3)	361 (2.0)	417 (1.0)	508 (1.0)	366 (1.5)	452 (1.0)	520[a] (0.72)	this work
trans-Cr(NH$_3$)$_4$(CN)$_2^+$	357 (1.0)	387 (0.4)	449 (1.3)	354 (1.0)	468 (1.5)	361 (2.6)	412 (1.0)	511 (1.8)	368 (1.4)	476 (1.0)	510[a] (0.92)	4
cis-Cr(NH$_3$)$_4$(CN)$_2^+$	*b*	*b*	*b*	355 (1.0)	468 (1.06)	367 (2.7)	405 (1.0)	479 (3.3)	366 (0.75)	495 (1.0)		4

[a] Spectral data match closely those for authentic[10] *trans*-Cr(tn)$_2$(H$_2$O)$_2^{3+}$, namely 368 (1.5), 452 (1.0), and 520 (0.68), whereas *cis*-Cr(tn)$_2$(H$_2$O)$_2^{3+}$ has 366 (0.89) and 490 (1.0). The 520-nm value is for a shoulder. [b] No isosbestics.

of aquation of CN$^-$ and one end of the tn ligand. For all runs for this compound, the pH-stat method gave H$^+$ uptake/time plots with downward curvature, a phenomenon we have never observed with other complexes, e.g., Cr(cyclam)(en)$^{3+}$, which gave linear plots as in Figure 2b. This plot also illustrates the nonfatal loss of tracking that can occur when mixing or electrode response is momentarily inadequate.

The curvature of the photochemical plots for this complex was present in all of ten runs to between 3 and 12% conversion. For a subset of four runs with conversion close to 5%, the slope of the plot at the end of photolysis was 71 ± 3% of the initial slope.

This decrease in the photochemical rate with extent of photolysis could have three possible causes: (a) decreasing absorption by the complex upon photolysis; (b) absorption by photoproducts, the inner-filter effect; (c) quenching of the doublet excited state of the starting complex by its photoproducts. The first of these is inconsistent with the combination of the starting absorbance of greater than 0.5 and the low extent of photolysis, not more than 5% in these runs. The second is excluded by our selection of 365, 458, and 436 nm as the photolysis wavelengths. These are close to minima in the photolysis difference spectrum (see Figure 1) where photoproducts absorb less strongly than the starting complex.

To investigate (c), the room-temperature doublet emission lifetime in the solution was measured immediately before, 136 ± 5 μs, and after, 84 ± 3 μs, photolysis to 5% conversion. Note that the emission lifetime of the thermal blank was also decreased to 119 ± 4 μs. The decreases in lifetime show that the doublet excited state is quenched by the thermo- and photoproducts and, by extension, that it is a reaction precursor.

This quenching can be explored semiquantitatively by using the above lifetime values and assuming that, as for the analogous complexes *trans*-Cr(NH$_3$)$_4$(CN)(NCS)$^+$ [9] and Cr(NH$_3$)$_5$(CN)$^{2+}$,[6] about 75% of the reaction goes via the doublet state. The estimated photochemical rate at the end of photolysis is then 73 ± 2% of the initial value,[22a] in agreement with the experimentally measured slope variation. The good agreement supports the claim that the observed curvature arises because of quenching of the doublet state of the complex by its own thermo- and photoproducts. Assuming further that all products quench equally efficiently leads to an estimated collisional quenching rate constant of 1 × 10^7 L mol^{-1} s^{-1}.[22b]

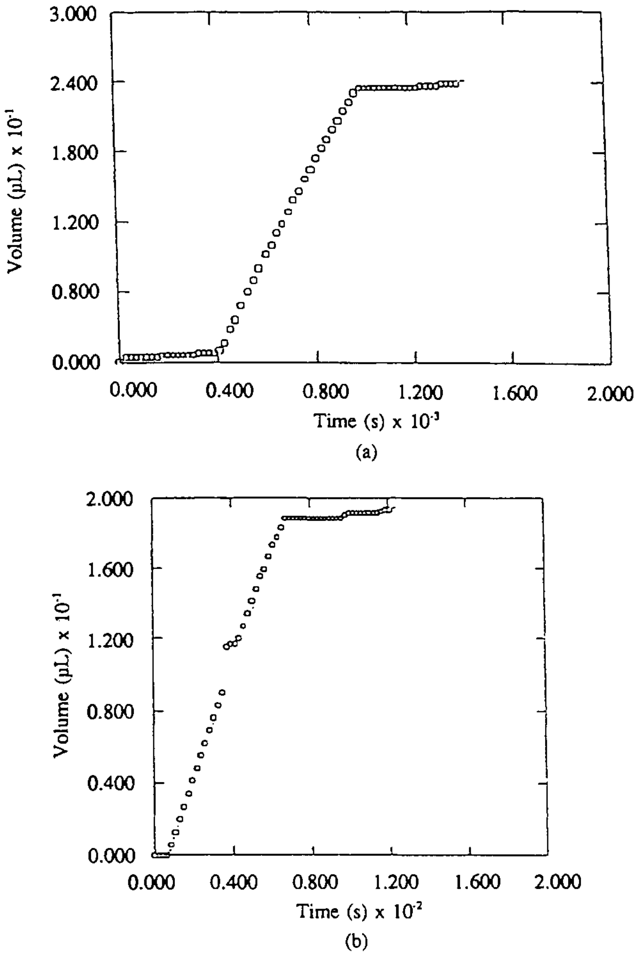

Figure 2. Acid uptake vs time plots during photolysis using the pH-stat method with 0.0730 M HClO$_4$ titrant of (a) *trans*-[Cr(tn)$_2$(CN)$_2$]ClO$_4$ and (b) [Cr(cyclam)(en)](ClO$_4$)$_3$.

Total quantum yield values ϕ_T were evaluated from the initial slopes of the rate plots (Figure 2) with correction for the thermal reaction as follows. The experimental proton uptake curve was fitted to a quadratic equation in time and the initial slope (at $t = 0$) obtained as the coefficient of the first-order term. The rate of thermal proton uptake either was estimated by linear regression on sections of the proton uptake plot before and after the photolysis or was calculated using the known thermal rate constant. This rate was then subtracted from the initial slope to obtain the total corrected initial proton uptake rate.

The direct cyanide measurement obviously leads to an average, incorrect quantum yield, $\phi_{CN,a}$, and here it was not possible to measure the time dependence of the rate. We have therefore assumed the two photoreaction modes are quenched to the same extent[9] and have calculated corrected cyanide quantum yields, ϕ_{CN}, from the simple proportion of the apparent ($\phi_{T,a}$) to the corrected total quantum yields: $\phi_{CN} = \phi_{CN,a}(\phi_T/\phi_{T,a})$. Finally,

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(22) (a) For quenching of the 75% reaction via the doublet, $\phi_0/\phi_t = \tau_0/\tau_t$, so for the total photolysis

$$\text{rate}_t/\text{rate}_0 = (0.25 + 0.75 \times 84/185)/(0.25 + 0.75 \times 136/185)$$

The actual extent of reaction quenching in base was not measured directly because of the difficulties and unreliability expected. Only the cyanide yield could be directly determined, and the tn yield would have to be estimated on the basis of assumptions about the pK_a values for the photoproducts. The above calculation should be considered illustrative; the ±3% uncertainty in the observed 71% decrease in rate is consistent with any percentage reaction via the doublet in the range 74–87%. Many other strong-field complexes have values in this range. (b) H$^+$ uptake was 17.7 μL of 0.0730 M acid; total product = 1.29 μmol in 3.1 mL, i.e. 4.2 × 10^{-4} M. This quencher concentration, the lifetime data, and the Stern–Volmer equation yield $k_q = 1.1 \times 10^7$ L mol^{-1} s^{-1}.

Table III. Quantum Yields[a] for Photolysis of *trans*-$[Cr(tn)_2(CN)_2]ClO_4$

λ, nm	ϕ_T	ϕ_{CN^-}	ϕ_{tn}
458	0.075 ± 0.004	0.023 ± 0.004	0.052 ± 0.004
436	0.083 ± 0.004	0.035 ± 0.004	0.048 ± 0.005
365	0.118 ± 0.002		

[a] In acidic aqueous solution at 15 °C. The means and standard deviations are for sets of three runs throughout.

$\phi_{tn} = \phi_T - \phi_{CN}$. Various extents of photolysis, 8–12%, show no systematic variation in ϕ_{tn}, supporting the assumptions, although our large experimental uncertainties would not allow us to detect small variations.

These quantum yields are given in Table III and show that the cyanide photoaquation mode is about 37 ± 6% of the total and may exhibit some wavelength dependence.

Chromatographic Analysis of Photoproducts. The original objective of this work required a precise, rapid, and convenient technique for the analysis of photoproducts. Conventional ion-exchange chromatography was attempted using several resins; it failed to separate all photoproducts, it was complicated by resin-catalyzed decomposition of the complexes, and the total time for a chromatogram was 2 h.

We therefore optimized the reversed-phase HPLC technique[21] for this analysis. A sample chromatogram showing the products of a single photolysis is displayed in Figure 3; conditions are given in the figure caption. All primary thermo- and photoproducts were resolved in less than 7 min.

In Cr(III) photoaquation, the product geometry can usually be predicted by an edge displacement mechanism.[23] Thus *trans*-$Cr(tn)_2(CN)_2^+$ could photoaquate to *cis*- and *trans*-$Cr(tn)(tnH)(H_2O)(CN)_2^{2+}$ (cis and trans denote the relationship of the cyanide ligands) and to *cis*-$Cr(tn)_2(H_2O)(CN)^{2+}$. The unavoidable thermal reaction will give *trans*-$Cr(tn)_2(H_2O)(CN)^{2+}$.

Experience with the chromatographic behavior of similar complexes suggests the following guidelines to aid in peak identification:

(a) Cations elute in order of increasing charge, and unit charge difference creates a larger separation than is seen between isomers.

(b) In the case of tn aquation, one end of the ligand remains coordinated and, at our pH, the free end protonates, resulting in a unit charge increase for the product. This "dangling" plus charge does not contribute fully to the charge seen by the chromatographic process, however. Here such species should elute with retention times between those for the 1+ (starting material) and the 2+ (cyanide loss) ions.

(c) For most geometric isomers of Cr(III) aquo complexes, the cis elutes before the trans at eluent pH's around 3, an order that can be reversed[10] in a higher pH range.

(d) Substitution of am(m)ine ligands by aquo ligands in otherwise similar complexes causes more rapid elution.

The peak corresponding to the starting complex, S, was easily identified by injection of the pure complex. When the complex was allowed to stand in an acidic medium, a peak developed at T showing this to be the elution time of *trans*-$Cr(tn)_2(H_2O)(CN)^{2+}$ ion. The peak C, which elutes just prior this, was therefore assigned to the expected cis isomer (c, above).

The tn loss species should elute before C and T, and in the sequence cis before trans, suggesting the assignment A = *cis*-$Cr(tn)(tnH)(H_2O)(CN)_2^{2+}$ and B = *trans*-$Cr(tn)(tnH)(H_2O)(CN)_2^{2+}$; note that the geometric relationship of the tnH and H_2O ligands in these compounds is not known.

To obtain more definitive evidence for the peak assignments, the thermal reactions of the photoproducts were studied. Generally, aquation of monoacido complexes is slower than that of corresponding diacido complexes,[24] and it has been found that,[4] in contrast to the usual sequence, *trans*-$Cr(NH_3)_4(CN)_2^+$ aquates faster than its cis isomer.

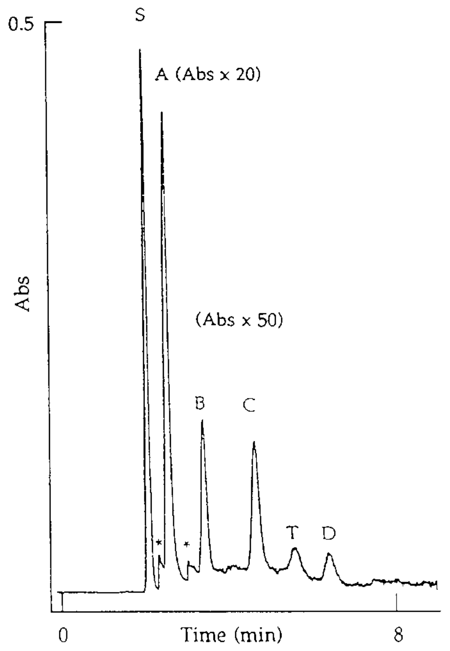

Figure 3. Chromatographic analysis of thermo- and photoproducts of *trans*-$[Cr(tn)_2(CN)_2]ClO_4$. Peak assignments (see text): A = *trans*-$Cr(tn)(tnH)(H_2O)(CN)_2^{2+}$, B = *cis*-$Cr(tn)(tnH)(H_2O)(CN)_2^{2+}$, C = *cis*-$Cr(tn)_2(H_2O)(CN)^{2+}$, S = *trans*-$Cr(tn)_2(CN)_2^+$ (starting complex), T = *trans*-$Cr(tn)_2(H_2O)(CN)^{2+}$ (thermal product), D = a secondary photoproduct, ✱ = scale changes. Conditions: eluent, 25 mM sodium butanesulfonate and 12.5 mM triethylamine in water at pH 3; flow rate, 2 mL min^{-1}; detection wavelength, 240 nm.

A photolyzed sample was acidified to make it about 1 M in $HClO_4$, and the reaction was followed chromatographically for over 1 h. Peaks S, A, B, and C decreased gradually, enhancing T greatly and generating new peaks at longer retention times than shown in Figure 3. The times for disappearance of A, B, and C were quite distinct, about 15, 50, and 80 min, respectively. These results indicate that A = *trans*-$Cr(tn)(tnH)(H_2O)(CN)_2^{2+}$, B = *cis*-$Cr(tn)(tnH)(H_2O)(CN)_2^{2+}$, and C = *cis*-$Cr(tn)_2(H_2O)(CN)^{2+}$. We consider the rate data for A and B more definitive than the conflicting sequence suggested by guideline c and adopt this last assignment in the following discussion.

Chromatography allows semiquantitative analysis of photoproducts. For 488- and 458-nm photolysis, the integrated relative peak areas, A:B:C, are (7.4 ± 0.5):1.0:(0.92 ± 0.13) and (4.7 ± 0.6):1.0:(1.22 ± 0.05), respectively (in four runs each). The C:(A + B) ratios are 0.11 and 0.21, respectively, consistent with the proportional increase in cyanide loss at shorter wavelength shown by the quantum yield data in Table III.

A and B have the same set of coordinating atoms and differ only in geometry. Since the detection wavelength is in the charge-transfer region, these two products are likely to have very similar molar absorptivities so that the peak area ratios closely reflect the true A:B ratio. Product C has a different set of coordinating atoms, however, so the proportion of cyanide reaction mode cannot be estimated reliably chromatographically. Indeed, our results indicate that product C has a lower molar absorptivity than the other products. At 458-nm, for example, the peak areas indicate that 17 ± 2% of the reaction is cyanide, compared with 31 ± 5% for a direct cyanide measurement. We observed also that the total product peak area was less than the peak area decrease of starting material, S, and that this deficit increased toward shorter irradiation, wavelengths where more C is produced.

Discussion

Thermal Aquation. Although it was not studied in detail, the thermal acid-catalyzed aquation of *trans*-$Cr(tn)_2(CN)_2^+$ appears to parallel the behavior of the analogous tetraammine.[4,7]

A small point of interest is the greater stability of both the starting complex and the monoaquo product. The latter particularly is quite stable, up to almost 2 M acid, while at this acid

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concentration, the tetraammine analogue readily aquates to form the diaquo product.

Photolysis. One of the more interesting results is that the photoproducts efficiently quench the photoreaction. We believe this is the first such observation in the photochemistry of inorganic systems, although the effect of thermal products was previously reported[6] and the possibility of a photochemical analogue recognized. It is reminiscent of observations made on the hexacyanocobaltate system, where in biacetyl-quenching and -sensitized reaction of the complex, the monaquo pentacyano product was a 10^3 times better quencher than the hexacyano.[25] For our system the long lifetime of the doublet state obviously is important, probably assisted by the low charges on the reactant and photoproduct molecules and the presence of ligands that favor efficient energy transfer.[26-28] In other systems there is often a greater Coulomb barrier to bimolecular quenching of reactant by product.

The estimated quenching rate constant is only 10^7 L mol^{-1} s^{-1}, which is almost 3 orders of magnitude lower than our measured value for OH$^-$ and considerably less than expectation for a diffusion-controlled process. This suggests the potential for such quenching in systems having shorter reactant excited-state lifetimes. A search might well reveal further examples or, failing that, illuminate the special circumstances that make it important in this system. Usually, the time course of photochemical rate is not observed with the precision required to reveal an effect of this magnitude. Where the reactive excited-state lifetime can be readily measured, however, the best check is the one we have applied here of lifetime measurement before and after photolysis.

We have not been able to determine how many of the three photoproducts are responsible for the quenching. The effect on the total quantum yield is easily eliminated from our data by taking the initial slope of the proton uptake curves, but it is more difficult to accommodate in the cyanide results, where the time evolution of product is not available.

One effect of these complications is to render this system unsuitable for the kind of wavelength dependence study that prompted our initial investigation. Such a study requires precise measurement of the small changes in product yields or product stereochemistry with wavelength and necessitates precise product analysis. The large thermal corrections to the cyanide mode, the nonlinearity of the time course of photolysis, and the need to assume that both modes are quenched to the same extent preclude such work using this system.

These problems lead to large uncertainties in our final quantum yields. Nevertheless, there is clearly a significant cyanide mode in this molecule, one that is much larger than has been found for the analogous ammine[3] and en[29] systems and one that increases to shorter wavelength on the basis of both direct and chromatographic measurements. This mode is not predicted by the angular overlap theory,[30] and in the following we will argue that it represents a further example of the competitive ligand loss phenomenon reported[10,11] for complexes with tn as the bidentate ligand.

Using published spectrochemical parameters (using NH$_3$ values for tn[10]) and theory,[30] the ^{4}E/^{4}B$_2$ energy gap in this molecule is 0.25 μm^{-1}, with the ^{4}B$_2$ state being lower. Photochemical predictions for this lowest state are exclusive loss of equatorial tn (calculated excited-state bond strengths: tn, 0.9 μm^{-1}; CN, 1.9 μm^{-1}), which should give[23] the sole product with trans cyanides (A). There should be no cyanide loss from this state, but its predicted reactivity accounts for the major product observed.

The cyanide mode and product B can be explained if one allows the possibility of reaction also from the higher lying ^{4}E state. This should again lose tn to give B, having cis cyanides, but now the calculated excited-state bond strengths are much closer (tn, 1.1 μm^{-1}; CN, 1.3 μm^{-1}) and the poor leaving ability of tn can assist loss of the cyanides present[10,11] on both possible planes of labilization.

The calculated ^{4}E/^{4}B$_2$ spacing argues against thermal population of ^{4}E from ^{4}B$_2$ (the room-temperature Boltzmann factor is 10^{-5}), although this could be altered by strong interactions with the nucleophilic solvent. More likely is direct population by branching from the Franck–Condon state, with rapid, irreversible relaxation and reaction of the generated ^{4}E precursor, in violation of Kasha's rule. Such a model is more consistent with the observed decrease in the tn mode and increase in the cyanide mode as the irradiation wavelength moves toward the higher energy quartet compartment. The nature and pathway of the reaction via the doublet are unclear.

The study shows that *trans*-Cr(tn)$_2$(CN)$_2^+$ is another example of a complex in which tn serves to promote photoaquation of a ligand that is not normally a leaving ligand. The molecule shows interesting wavelength dependence and offers the potential for study of quartet and doublet reaction modes, their temperature dependence, etc. Unfortunately, the precise work required is hampered by the thermal lability of the cyanides and the interesting but problematical self-quenching by products.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council and the University of Victoria for financial support. We are particularly grateful to the reviewer who alerted us to the abnormal sequence of dicyano tetraammine aquation rates.

Registry No. *trans*-[Cr(tn)$_2$F$_2$]Cl, 63231-42-5; *trans*-[Cr(tn)$_2$Br$_2$]Br, 30862-87-4; *trans*-[Cr(tn)$_2$(CN)$_2$]ClO$_4$, 137594-62-8; *trans*-Cr(tn)$_2$(H$_2$O)(CN)$^{2+}$, 137594-63-9; *trans*-Cr(tn)$_2$(H$_2$O)$_2^{3+}$, 38985-24-9; *trans*-Cr(tn)(tnH)(H$_2$O)(CN)$_2^{2+}$, 137594-64-0; *cis*-Cr(tn)(tnH)(H$_2$O)(CN)$_2^{2+}$, 137694-22-5; *cis*-Cr(tn)$_2$(H$_2$O)(CN)$^{2+}$, 137693-27-7.

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