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Cr(III) Photosubstitution without stereochemical change? Photoaquation of *trans*-dicyanotetram(m)ine complexes.

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ABSTRACT

Trans-[Cr(tet)(CN)$_2$](ClO$_4$) (tet = N,N'-bis(2-aminoethyl)-1,3-diaminopropane) has been synthesized and characterized and its photoaquation studied by proton uptake and cyanide release measurements. The molecule photoaquates one end of the tet ligand with a quantum yield of 0.09 ± 0.01. The geometric configuration of the photo-product was explored via its UV-vis spectrum and by observations of its re-coordination to the starting complex. The results indicate that the stereoretained photoproduct is formed, and therefore the photoreaction occurs in a stereoretentive manner.

INTRODUCTION

A notable feature of the photoaquations of Cr(III) complexes[1, 2, 3] is the accompanying stereochemical change, which contrasts with the stereoretentive thermal aquations. Most systems studied have been of tetragonal symmetry, and the ligand preferentially photoaquated often lies on the axis of weakest average ligand field[4]. For such "axial labilizations", stereochemical change appears general. Moreover, the photoinertness of trans-cyclam complexes[5, 6, 7] suggests that stereochemical change can be a requirement for such photoreaction. This is somewhat ambiguous, however, as steric constraints[8] can alternatively lead to an unusual reaction mode. Stereochemical change also accompanies the photoanation reaction of at least one Cr(III) complex[9]

The phenomenon of photostereochemical change in d^3 complexes has been rationalized[10] in terms of the symmetry restrictions on reactions via trigonal-bipyramidal intermediates, recently[11] including the effects of their Jahn-Teller distortions. Although such pathways are at odds with the negative activation volumes observed[12] , it has been argued[13] that parallel symmetry restrictions could apply to distorted pentagonal-bipyramidal intermediates.

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A few tetragonal complexes lose an equatorial ligand, and for some fluoro[14, 15, 16] or cyano complexes[17, 18], this can become the dominant reaction mode. This situation is more difficult to explore. First, the stereochemical relationships between reactants and products are now poorly defined and substitution in the weak field plane leads to the same product either via mechanistically retentive or non-retentive pathways. In addition, equatorial ligand loss can be from ^4E or $^4B_2$ states, with different predicted stereochemical outcomes.

This work attempted an unambiguous study of the stereochemistry of equatorial labilization. We have synthesized and characterized *trans*-$[Cr(tet)(CN)_2](ClO_4)$. Assuming reaction only from the lowest quartet excited state with required stereochemical change, this compound should be photoinert.

EXPERIMENTAL

Syntheses and characterization of *trans*-$[Cr(tet)(CN)_2](ClO_4)$.

Trans-$[Cr(tet)(Cl)_2]ClO_4$ (ash green)[19] was heated at 70°C for 30 min until reddish purple then reacted with NaCN at 70°C for 1 h. The yellow product precipitated out and was purified by reprecipitation from water using 8M $HClO_4$. Analysis, %found (calculated) : C 29.7 (29.7), H 5.5 (5.5), N 22.8 (23.1). The supernatant of the reaction mixture contained the isomers of the dicyano and cyanochloro species; *cis*-$Cr(tet)(CN)_2^+$ was separated and obtained in small amounts in solution by ion exchange chromatography.

RESULTS

UV-Vis spectra in solution and proof of configuration

The compound has UV-vis band maxima and molar absorptivities, emission spectrum and long emission lifetime in aqueous media that are comparable with those of analogues, Table1.

Unfortunately the UV-vis spectra of *trans* and *cis* isomers are usually closely similar, and so can not be used reliably to distinguish them. The infra-red spectra in the cyanide region are also of little help as these bands are very weak in Cr(III) dicyanotetram(m)ines. We therefore reacted the complex with 6M HCl for 30 min at 60 ^{o}C to convert it to $Cr(tet)(Cl)_2^+$. Chromatographic analysis and spectral comparison to authentic samples of *trans*- and *cis*-$Cr(tet)(Cl)_2^+$ showed that the resulting dichloro species was >90% *trans*. Since Cr(III) aquation and anation processes are typically stereoretentive in aqueous media, this indicates that our complex was the *trans* isomer. Ion-pair HPLC on the original dicyano complex, comparing with *cis*-Cr(tet)$(CN)_2^+$ solution, then showed that only the *trans* isomer was present.

Table 1. Spectral data for Cr(III) dicyanotetram(m)ine complexes.

Compound	L_2 nm (ε)	L_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	[21, 22]
c-$Cr(en)_2(CN)_2^+$	339(63.1)	433(70.8)	705	2	[21, 22]
t-$Cr(tn)_2(CN)_2^+$	344(47.5)	441(52.5)	703	185	[23]
t-Cr(tet)$(CN)_2^+$	338(46.0)	432(52.4)	705	30	-

Thermal chemistry of *trans*-[Cr(tet)$(CN)_2$](ClO_4).

The compound was stable in aqueous solution but was subject to acid catalysed loss of cyanide at pH of 3 or less. The rate constant for this process was about 10^{-2} s^{-1} at pH 2 but at pH 3 was less than 10^{-5} s^{-1} at 28°C. Chromatographic analyisis confirmed that amine aquation was negligible.

Photochemistry of *trans*-[Cr(tet)$(CN)_2$](ClO_4).

On irradiation in the lowest energy quartet band, the compound photoaquated and good isosbestic points at 348, 400 and 450 nm were maintained up to a high extent of conversion (>50 %). Cyanide release and proton uptake for irradiation at 436 nm were measured using a cyanide electrode and the pHstat method at a fixed pH of 3.0. The quantum yield of proton uptake was 0.09 ± 0.01 at 15°C. The upper limit for cyanide photoaquation was $\Phi \leq 0.02$ based on the electrode detection limit.

The photoproducts were investigated using ion-pair HPLC. *Trans*-Cr(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 *cis* 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 ligand, Cr(tet-H)(H_2O)$(CN)_2^{2+}$. There are several such isomers possible. The small *trans*-Cr(tet)(H_2O)CN^{2+} peak observed was from concurrent thermolysis, and its *cis* isomer, the cyanide loss product expected photolytically, was less than 1% of photoproduct.

Separation of the components of a photolysed solution using cation exchange chromatography indicated that there was a single photoproduct. The evidence for this was that fractions collected throughout the band, which eluted after the starting material, all had the same UV-vis spectrum and gave the same, single peak in the HPLC.

The spectrum of the photoproduct, Figure 1, was obtained in two ways, which yielded essentially identical results. Direct measurement was made on a photoproduct solution obtained by photolysis to 20% conversion followed by ion exchange chromatography. Molar absorptivities were obtained via Cr analysis. The second method used difference spectra as a function of photolysis time combined with the corresponding proton uptakes to calculate the product spectrum. The absorption bands are shifted to the red relative to the starting material.

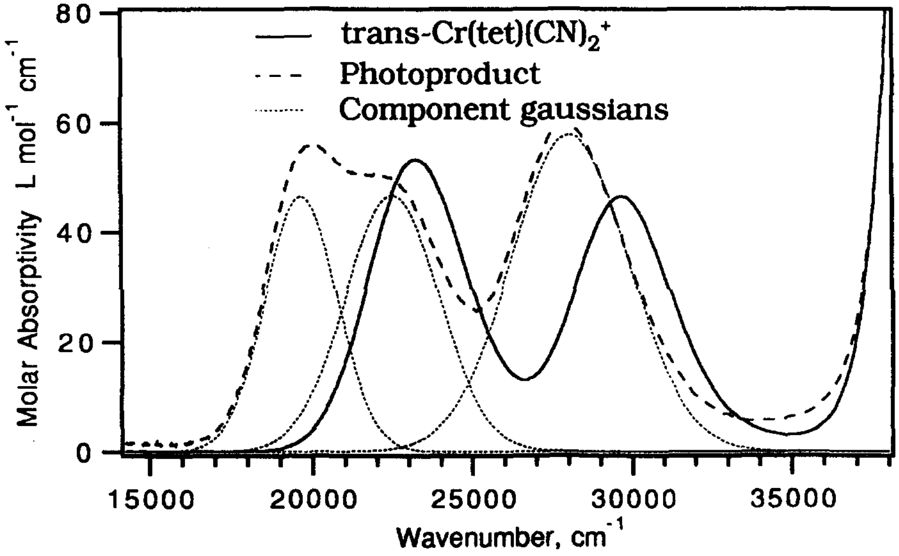

Figure 1. UV-visible spectra of *trans*-Cr(tet)$(CN)_2^+$ and its photoproduct.

Geometric configuration of the photoproduct.

Although fifteen isomers of $Cr(tet\text{-}H)(H_2O)(CN)_2^{2+}$ are possible, given the macrocyclic nature of the tet ligand and knowledge of typical photochemical pathways, we need consider only the meridional isomers with a protonated ethylenediamine arm. The question then reduces to a decision between those with *cis* and *trans* cyanides. To investigate this, two approaches were used.

First, since the UV-vis spectrum of the photoproduct was available, attempts were made to predict the spectra expected for the two meridional 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 a larger splitting in the first ligand field band in the isomer with *trans* cyanides. This is because the three components of this band correspond to 45° rotations of charge in the three orthogonal planes containing the ligands and the average ligand fields in the three planes differ more for the *trans*. 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 490, 435 and 415 nm and 460, 440, and 435 for *trans* and *cis*-dicyano products respectively. The lowest energy peak in the experimental photoproduct spectrum plotted on a wavenumber scale could be resolved into two gaussians with peaks at 508 and 444 nm. The large splitting and the long wavelength band present both imply that the product found has the cyanides *trans*.

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. The rate of this process was observed to depend on pH in a manner that suggested the active species was $Cr(tet\text{-}H)(OH)(CN)_2^{+}$; the recoordination half-life at 25°C was only 10 min at pH 6, but much slower at higher or lower pH. Chromatography 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 was found to have the same spectrum, including molar absorptivity, as *trans*-$Cr(tet)(CN)_2^{+}$. Assuming that recoordination is stereoretentive, this demonstrates that the photoproduct is the meridional isomer with *trans* cyanides.

DISCUSSION

The nature of equatorial labilization.

Equatorial ligand loss from complexes with tetragonal symmetry can occur as a result either of labilization in the equatorial plane($^4B_2$) or in one of the two orthogonal planes(^4E). The stereochemistry of the latter has been studied through comparison of the photochemistry of $Cr(NH_3)_5F^{2+}$ and *trans*-$Cr(en)_2(NH_3)F^{2+}$. This showed that such equatorial reaction occurs with stereochemical change just as does the axial ligand loss from the same state[14].

Our concern here was to explore the stereochemistry of the alternate possibility, loss of an equatorial ligand as a result of excitation in the equatorial plane. If this also involves stereochemical change, and if it is a requirement of the photoaquation, then because the macrocyclic ligand prevents entry of the water ligand *trans* to the departing amine ligand, *trans*-$Cr(tet)(CN)_2^+$ should be photoinert. Our results show it is not, but why?

Possible reactive excited states

Much of Cr(III) photochemistry occurs via reaction out of the lowest quartet excited state. The doublet state also participates, probably as a reservoir of excitation energy rather than as a primary reactive species. Details of quantum yield wavelength and temperature dependence have indicated[24] that higher excited quartet states may also be primary reactive species, in violation of Kasha's rule. These precursors seem to contribute[17, 24] to photochemical yields in ratios that do not reflect the Boltzmann equilibria expected based on their estimated energies. This could be because their interconversions are controlled by solution kinetic factors rather than by spectroscopic considerations[13]. We therefore thought it necessary to eliminate the possibility that the unexpected photoactivity of the title compound arose as a result of photoreaction from the higher-lying ^4E state.

In the ^4E state, the cyanides and two amine sites would be labilized. Because of the strong bonding of cyanide to Cr(III), the amine ligands are the predicted leaving groups. There is experimental support[25] for suggesting that the secondary nitrogen atoms of the tet ligand are constrained from leaving, but the ethylenediamine arm can do so. Such a photoreaction, being the archetypal axial process, should occur with *trans* entry of the water ligand and stereochemical change to give the meridional isomer with *cis* cyanides. Again, experiment supports[26] the feasibility of the ligand rearrangements required. Also a parallel process attributed to the ^4E_g state has been suggested to account for 30% of the photoreaction[17] in the analogous *trans*-$Cr(NH_3)_4(CN)_2^+$. However our results show that it is not occuring here, since the product we obtained has the cyanides in the *trans* relationship.

We are left with an unusual stereoretentive reaction mode either from the $^4B_2$ state or from the doublet state.

Comparison to analogues

The dicyanotetram(m)ine systems exhibit a range of behaviours. The cyclam complex[6] is photoinert and has a long solution doublet emission lifetime of 385 μs (all values cited for 20 °C). The bis(1,3-diaminopropane) analogue[23] has a doublet lifetime of 185 μs and a total aquation quantum yield of 0.08, of which 40% is loss of cyanide with stereochemical change. The amine loss pathway leads to about equal amounts of the photoproduct with *cis* and *trans* cyanides. The tet complex has a doublet lifetime of 30 μs, a 0.09 amine loss mode to give the *trans* dicyano product only. The tetrammine has a doublet lifetime of 40 μs[27] and loses ammonia[17] with a yield of 0.24 to give meridional products, 30% cis and 70% trans dicyano. There is a crude relationship between doublet lifetime and reactivity but the relationships between ligand structure and the reaction modes and stereochemistries seem to be quite subtle.

Conclusions

This work has indicated that *trans*-$Cr(tet)(CN)_2^+$ exhibits a stereoretentive reaction mode likely via the $^4B_2$ excited state in defiance of theory. The reasons for this may lie in the difference in ligand field strength of secondary and primary amine nitrogen ligands, or in the stereochemical constraints imposed by the ligand on the possible reactive intermediates. Alternatively, this system may represent an example of a stereoretentive reaction of the doublet state. Further studies are being undertaken to clarify this latter point.

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