Table V. Absorption Results and Proposed Assignments for the Solution Spectra of the $Pd(CN)_4^{-2}$ Ion

exptl *E*, cm^{-1}	calcd *E*, cm^{-1}	assignt
40 000[a]	38 100	$d \rightarrow a_{2u}$ ($^1A_{1g} \rightarrow {}^3A_{2u}$)
	39 800	($^1A_{1g} \rightarrow {}^3E_u$)
43 000[b]	42 800	($^1A_{1g} \rightarrow {}^3B_{1u}$)
45 500[a]	45 200	($^1A_{1g} \rightarrow {}^1E_u, {}^1A_{2u}$)
42 000[a]	42 000	$d \rightarrow e_u$ ($^1A_{1g} \rightarrow {}^3E_u$)
43 000[b]	43 100	($^1A_{1g} \rightarrow {}^3A_{1u}, {}^3A_{2u}, {}^3B_{1u}, {}^3B_{2u}$)
45 500[a]	45 400	($^1A_{1g} \rightarrow {}^3B_{1u}$)
47 500[a]	47 400	($^1A_{1g} \rightarrow {}^1E_u, {}^1A_{2u}$)
49 500[a]		$d \rightarrow b_{1u}$ ($^1A_{1g} \rightarrow {}^1E_u, {}^1A_{2u}$)

[a] These experimental energies are from Figure 8 of this paper. [b] Schatz et al. reported shoulders in their absorption spectra at 43 000 and 46 500 cm^{-1}, and this is the basis of the 43 000-cm^{-1} peak.

e_u transitions should occur at about 42 000, 43 100, 45 400, and 47 400 cm^{-1}. The Figure 2 $Pd(CN)_4^{2-}$ solution spectrum of Schatz et al.[11] shows absorption maxima at 42 000, 45 500, and 47 500 cm^{-1} with shoulders at 43 000 and 46 500 cm^{-1}. At about 40 000 cm^{-1}, the lowest energy observed absorption occurs. We conclude there is reasonable agreement between the experimental solution absorption data of Schatz et al. and the absorption patterns for $Pd(CN)_4^{2-}$ in KCl for the $d \rightarrow a_{2u}$ and $d \rightarrow e_u$ type transitions.

A summary of the absorption results and assignments for $Pd(CN)_4^{2-}$ in solution is given in Table V.

Summary

We have measured the luminescence and absorption spectra of tetracyanopalladate(II) ions doped into NaCl, KCl, NaCN, and KCN crystals and find evidence for the presence of both monomer and cluster species of $Pd(CN)_4^{2-}$. The luminescence spectra of the palladium-doped alkali halide and alkali cyanide crystals have lifetimes and energies very similar to the luminescence we have reported for pure $BaPd(CN)_4$ crystals; thus, we conclude palladium cluster species are responsible for the luminescence.

The absorption spectra of $Pd(CN)_4^{2-}$ in KCl are assigned on the basis of EPR measurements by Viswanath and Rogers[16] to a $Pd(CN)_4^{2-}$ monomer ion in C_{4v} site symmetry. Simple extended Hückel molecular orbital calculations for such a defect structure suggest that $d \rightarrow a_{2u}$ and $d \rightarrow e_u$ type transitions are separated in energy unlike in solution where they occur at the same energies. In contrast, KCN-doped palladium crystals have a yellow color and have a large percentage of cluster species unlike in KCl where the concentration is very small.

Acknowledgment. This research was supported by NSF, Department of Materials Research (Grant DMR 77-07140).

Registry No. $Pd(CN)_4^{2-}$, 15004-87-2; NaCl, 7647-14-5; NaCN, 143-33-9; KCN, 151-50-8; KCl, 7447-40-7; $BaPd(CN)_4$, 14038-83-6; $K_2Pd(CN)_4$, 14516-46-2; KBr, 7758-02-3.

Contribution from the Department of Chemistry,
University of California at San Diego, La Jolla, California 92093

Stereochemistry of the Photoaquation of Optically Active Tris(ethylenediamine)chromium(III) as a Probe of Excited-State Pathway

MARC C. CIMOLINO and R. G. LINCK*

Received September 26, 1980

The photoaquation of Λ-$Cr(en)_3^{3+}$ in acidic aqueous solution under ligand field excitation produces three isomers of $Cr(en)_2(enH)(H_2O)^{4+}$, the Λ-cis, Δ-cis, and trans isomers. Their quantum yields are 0.10, 0.03, and 0.24, independent of wavelength of irradiation from 365 to 685 nm. These data strongly imply reactivity only from the lowest lying quartet state with back intersystem crossing from the lowest doublet state to that quartet accounting for delayed reaction. The results are also analyzed in terms of a model predicting the stereochemical result of photoaquation of Cr(III) complexes.

Introduction

In this, the third decade of investigation of chromium(III)-amine photochemistry,[1,2] there lurks a question that was asked before:[3-5] Does reactivity occur from the lowest excited state, a doublet state, ^2X, and/or from the lowest excited quartet state, ^4Y?[6] In fact, this question was predominant in several studies published in the late 1950s. Plane and co-workers[3,7] and Schläfer argued the long-lived ^2X state could account for all photoreactivity because a plausible model for associative attack on this excited t_{2g}^3 species could be formulated[9] (and ϕ was reported as independent of excitation wavelength). Some years later Adamson[5] suggested that the excited quartet could be reactive, even with a short lifetime. This model became attractive to a number of investigators, has been the basis of several models[10-12] of photoaquation, and is now generally accepted as the conventional wisdom. Especially important experiments establishing that the ^4Y state was reactive (even though perhaps not the exclusive reactive state) are those of Chen and Porter[13] and Wasgestian.[14] However, several studies have appeared recently that have been interpreted to implicate partial reactivity from the ^2X state. This has been suggested especially in the case of *trans*-Cr-

---

* To whom correspondence should be addressed at the Department of Chemistry, Smith College, Northampton, MA 01063.

(1) Zinato, E. In "Concepts of Inorganic Chemistry"; Adamson, A. W., Fleischauer, P. D., Eds.; Wiley: New York, 1975; pp 143-201.
(2) Balzani, V.; Carassiti, V. "Photochemistry of Coordination Compounds"; Academic Press: New York, 1970.
(3) Edelson, M. R.; Plane, R. A. *Inorg. Chem.* **1964**, *3*, 231.
(4) Schläfer, H. L. *J. Phys. Chem.* **1965**, *69*, 2201.
(5) Adamson, A. W. *J. Phys. Chem.* **1967**, *71*, 798.
(6) The states are labeled ^4Y and ^2X to avoid specific comment on the symmetry of states that *must* be Jahn-Teller distorted in their equilibrium geometry.
(7) Plane, R. A.; Hunt, J. P. *J. Am. Chem. Soc.* **1957**, *79*, 3343.
(8) Schläfer, H. L. *Z. Phys. Chem.* (*Wiesbaden*) **1957**, *11*, 65.
(9) Taube, H. *Chem. Rev.* **1952**, *50*, 69.
(10) Zink, J. I. *J. Am. Chem. Soc.* **1972**, *94*, 8039.
(11) Wrighton, M.; Gray, H. B.; Hammond, G. S. *Mol. Photochem.* **1973**, *5*, 165.
(12) Vanquickenborne, L. G.; Ceulemans, A. *J. Am. Chem. Soc.* **1977**, *99*, 2208.
(13) Chen, S. N.; Porter, G. B. *Chem. Phys. Lett.* **1970**, *6*, 41. See also: Porter, G. B.; Chen, S. N.; Schläfer, H. L.; Gausmann, H. *Theor. Chim. Acta* **1971**, *20*, 81.
(14) Wasgestian, H. F. *J. Phys. Chem.* **1972**, *76*, 1947.

0020-1669/81/1320-3499$01.25/0

$(NH_3)_2(NCS)_4^{-}$ [15,16] and $Cr(en)_3^{3+}$ [17] although disputed in each case.[18,19]

The photochemistry of the latter molecule has been studied extensively. An early investigation[20] established that photoaquation produced $Cr(en)_2(NH_2CH_2CH_2NH_3)(H_2O)^{4+}$ with a wavelength-independent quantum yield of 0.37, a result verified recently.[21] The sensitized photoaquation has also been measured, and the quenching of the ^2X state by OH^- [22] and by Fe^{II} and Co^{II} has been reported.[23] What more can be learned by photolysis of this species?

What has not been recognized explicitly is the rich stereochemistry that is offered in the photoaquation of $Cr(en)_3^{3+}$ *if* one of the enantiomers of this material is the object of study. There are three possible products under these conditions, the Λ and Δ isomers of *cis*-$Cr(en)_2(enH)(H_2O)^{4+}$ and *trans*-$Cr(en)_2(enH)(H_2O)^{4+}$. This being true, the stereochemistry of the reaction products of, for instance, Λ-$Cr(en)_3^{3+}$, for different methods of populating the excited state offers the classic means of probing reaction pathways; one pathway between reactants and products will give a unique stereochemical result, and multiple pathways will yield a result that depends on the fraction of the molecules pursuing each path. This report establishes the stereochemical isomer distribution for photoaquation of Λ-$Cr(en)_3^{3+}$ and examines the consequences for the possibility of multiple reaction paths, namely, whether reactivity can occur from both ^2X and ^4Y. In addition, the results are used to examine the model[24] for the "stereoinversion"[1] of Cr(III) photoaquation.

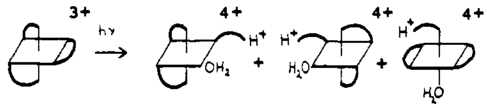
Experimental Section

Materials. $[Cr(en)_3]Cl_3 \cdot nH_2O$ was prepared as described by Pedersen[25] and resolved into both enantiomers according to the literature procedure.[26] All other reagents were of reagent grade and were used without further purification. Cation-exchange separations were carried out on Sephadex SP-C25 resin.

Procedures. Two separate kinds of photolytic experiments were utilized. In order to obtain large quantities of products quickly, we carried out photolyses with one of two broad-band filter systems: (1) a chromate solution filter allowing only $\lambda > 400$ nm at the 1% transmission level; (2) an (ethylenediamine)copper(II) solution filter, which transmitted light centered at 425 nm (about 75 nm half-width). Photolyses into selected wavelength regions were also undertaken. An 80-W medium-pressure mercury arc lamp and a Corning 5860 filter were used to isolate 365-nm light. For all other wavelengths, a focused xenon arc lamp was the source; interference filters were used at 400 and 457 nm, and Corning glass filters were employed to isolate the 520–580-nm region (Nos. 3486 and 9782) and 635–685-nm region (No. 2403). Photolyses were carried out at 15 °C or below unless otherwise noted.

So that the nature of the products might be determined, they were separated from excess reactant and then subjected to ion-exchange chromatography. In most of the experiments, separation was achieved by precipitation of the starting material from an ice-cold solution of about 15 mL (about 0.02 M in Cr(III)) by adding 0.25 mL of a solution prepared by dissolving 7 g of NaBr in about 10 mL of water, adding 16 g of $HgBr_2$ and 10 mL of concentrated HBr, and making up to 25 mL with water. The resulting solid ($[Cr(en)_3]_2[HgBr_4]_3$ by analysis for chromium content) was removed by filtration before column loading. This solid after dissolution with dilute HCl gave a spectrum consistent with pure reactant; further, $HgBr_4^{2-}$ will not precipitate a solution of the $Cr(en)_2(enH)(H_2O)^{4+}$ isomers under the mentioned conditions. After the filtrate was loaded on the column (it was rinsed with water or dilute sodium chloride to remove excess Hg(II) before any basic elutions), it was eluted with either $NaClO_4$ or NaCl eluants at pH 2.5 adjusted with the corresponding acid. In some earlier experiments, the preciptation step was not used. This made separation more difficult as the predominant $Cr(en)_3^{3+}$ band tailed sufficiently to overlap with the band of tetrapositive isomers unless elution was slow. However, the results were independent of whether or not $Cr(en)_3^{3+}$ was precipitated before ion-exchange chromatography. All ion-exchange separations were performed in a cold room at 2–3 °C.

Scheme I



Λ-$Cr(en)_3^{3+}$ *cis*-Λ-**1** *cis*-Δ-**1** *trans*-**2**

Measurements of absorbance were done on a Cary Model 14 recording spectrophotometer; those of optical rotation were done on a Perkin-Elmer Model 141 polarimeter at 25 °C.

Results

The primary photoproduct, $Cr(en)_2(enH)(H_2O)^{4+}$, can exist in a form where water is trans to the pendant amine (**2**) or as either enantiomer of the form with these two groups cis (Λ-**1** and Δ-**1**). We will establish below that photolysis of Λ-$Cr(en)_3^{3+}$ leads to all three products as illustrated in Scheme I. All results reported hold equally well if photolysis is carried out upon Δ-$Cr(en)_3^{3+}$, but the yields of Λ-**1** and Δ-**1** are reversed.

Thermal Aquation and Properties of 1. So that the true amount of inversion of configuration in the cis products might be determined, the molar rotation (expressed here as the rotation in degrees that would be observed for a 1 M solution in a 1-dm cell) of a pure enantiomer of **1** must be determined. A solution of Δ-$(+)_{436}$-$Cr(en)_3^{3+}$ was aquated for 2 min in dilute acid at 80 °C, quenched in ice, and subjected to ion-exchange separation with $NaClO_4$ at pH 2.5. After elution of the remaining starting material (and some *cis*-$Cr(en)_2(H_2O)_2^{3+}$) one band was observed on the column. This band was fractionated, but neither the extinction coefficient nor the molar rotation was a function of fractionation. This implies a single material is present in this band. The physical properties of this band averaged over about eight preparations are as follows for λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 474 (64.9); 362 (49.0). These values are in agreement with those reported by Mønsted and Mønsted,[27] 474 (60.8) and 361 (45.7). In addition, the molar rotation is +110° M^{-1} dm^{-1} at 436 nm (25 °C). The failure to see any deviation in extinction coefficient or molar rotation as a function of fractionation of the band suggests this thermal aquation product is pure **1**, uncontaminated by **2**. There remains the question of the optical purity of the product of thermal aquation. To probe this, we took advantage of the report[27] that **1** chelates *on* a Sephadex ion-exchange column in basic solution to form $Cr(en)_3^{3+}$. A solution of **1** produced thermally from Λ-$Cr(en)_3^{3+}$ was separated from the starting material and analyzed by spectral and optical rotation measurements. This solution was diluted to about 0.1 M ionic strength, with pH 2.5 HCl solution, and loaded onto a Sephadex column at 3 °C. The column was warmed to room temperature and then flushed with a buffer made from 2-amino-2-(hydroxymethyl)-1,3-propanediol at pH 7.8. After standing for 1 h, the column was ice-cooled and then eluted with 0.5 M NH_3/NH_4^+ at pH 9.8. The $Cr(en)_3^{3+}$ formed and

---

[15] Gutierrez, A. R.; Adamson, A. W. *J. Phys. Chem.* **1978**, *82*, 902.

[16] Kang, Y. S.; Castelli, F.; Forster, L. S. *J. Phys. Chem.* **1979**, *83*, 2368.

[17] Fukuda, R.; Walters, R. T.; Mäcke, H.; Adamson, A. W. *J. Phys. Chem.* **1979**, *83*, 2097.

[18] Shipley, N. J.; Linck, R. G. *J. Phys. Chem.* **1980**, *84*, 2490.

[19] Kirk, A. D., University of Victoria, personal communication, 1980.

[20] Geis, W.; Schläfer, H. L. *Z. Phys. Chem.* (*Wiesbaden*) **1969**, *65*, 107.

[21] Kirk, A. D.; Frederick, L. A.; Wong, C. F. C. *Inorg. Chem.* **1979**, *18*, 448.

[22] Kane-Maguire, N. A. P.; Phifer, J. E.; Toney, C. G. *Inorg. Chem.* **1976**, *15*, 593.

[23] Wasgestian, H. F.; Ballardini, R.; Varani, G.; Moggi, L.; Balzani, V. *J. Phys. Chem.* **1973**, *77*, 2614.

[24] Vanquickenborne, L. G.; Ceulemans, A. *J. Am. Chem. Soc.* **1978**, *100*, 475.

[25] Pedersen, E. *Acta Chem. Scand.* **1970**, *24*, 3362.

[26] Galsbol, F. *Inorg. Synth.* **1970**, *12*, 274.

[27] Mønsted, L.; Mønsted, O. *Acta Chem. Scand., Ser. A* **1975**, *A29*, 29.

the remaining **1** in the form $Cr(en)_2(en^*)(OH)^{2+}$ were isolated from each other and from a monopositive band of aquation products and then acidified and characterized by spectral and optical rotation measurements. Although an attempt was made to determine the kinetics of the chelation reaction, it was found to lack good reproducibility, perhaps because of the relatively slow change of $[H^+]$ from pH 2.5 to 7.8 as the buffer flowed through the region of the column on which **1** was adsorbed. In addition, these kinetic studies indicated the heterogeneity of the reaction (chelation occurs *much* more slowly in homogeneous solution)[28] may be affecting the kinetic scheme. What was demonstrated was the following: (1) Λ-**1** racemizes in basic media (*on* the column) with an apparent rate constant of 6×10^{-4} s^{-1} (25 °C, pH 10.8); (2) when the length of time that the band of Λ-**1** was subjected to basic conditions was decreased, the $Cr(en)_3^{3+}$ found had a higher molar rotation. In the experiment performed with minimal exposure time in base it was found that Λ-$Cr(en)_3^{3+}$ of molar rotation $-348 \pm 2°$ M^{-1} dm^{-1} aquated to **1** and then chelated in base produced $Cr(en)_3^{3+}$ of rotation $-306 \pm 7°$ M^{-1} dm^{-1}; the residual **1** had racemized in base from -110 ± 3 to $-84 \pm 1°$ M^{-1} dm^{-1} during the time of chelation. Thus during the cycle given in eq 1 the inversion in both steps can amount to

$$Cr(en)_3^{3+} \xrightarrow{H^+} \mathbf{1} \xrightarrow{OH^-} Cr(en)_3^{3+} \qquad (1)$$

no more than a total of six acts of inversion per hundred. Yet note that **1** has racemized to an extent of 12% during the time in base. This necessitates that at least some, and most likely all, of the racemized $Cr(en)_3^{3+}$ arises from chelation of racemized **1**.

Physical Properties of 2. Thermal aquation yields only **1** in the tetrapositive band after ion-exchange separation. However, if a solution of $Cr(en)_3^{3+}$ is photolyzed into the lowest energy spin-allowed transition, both geometrical isomers of $Cr(en)_2(enH)(H_2O)^{4+}$ are formed. A photolyzed solution of $Cr(en)_3^{3+}$ was separated, and the tetrapositive band was isolated and cut into two fractions by elution with $NaClO_4$ (note that NaCl gives a less efficient separation); there was no clear separation between the two components of this band, but two components were present because both the apparent extinction coefficient and the absolute magnitude of the apparent molar rotation were larger in the second fraction. So that the yields of **1** and **2** and the extinction coefficient of **2** might by determined, advantage is taken of the experimental fact that there is not even a partial resolution of **1** by elution on Sephadex with $NaClO_4$ as eluant; that is, the fractional excess of Λ-**1** over Δ-**1** is independent of cut. In eq 2 the

$$\chi = \frac{[\Lambda\text{-}\mathbf{1}]_i - [\Delta\text{-}\mathbf{1}]_i}{[\Lambda\text{-}\mathbf{1}]_i + [\Delta\text{-}\mathbf{1}]_i} \qquad (2)$$

enantiomeric purity, χ, measures this excess for any cut i. Equation 2 considered with the equations for the absorbances and observed rotations of the cuts, eq 3 and 4, and the

$$\bar{A}_i = \epsilon_1([\Lambda\text{-}\mathbf{1}]_i + [\Delta\text{-}\mathbf{1}]_i) + \epsilon_2[\mathbf{2}]_i \qquad (3)$$

$$\alpha_i = [R_0]([\Lambda\text{-}\mathbf{1}]_i - [\Delta\text{-}\mathbf{1}]_i) \qquad (4)$$

equations giving the total chromium in the cuts generate for two cuts a system of seven equations in seven unknowns—the six concentrations and the parameter of interest ϵ_2, the extinction coefficient of **2**. In eq 3, $\bar{A}_i$ is the absorbance of cut i and ϵ_1 is the known extinction coefficient of **1**, and in eq 4, α_i is the observed rotation in deg dm^{-1} where $[R_0]$ is the molar rotation of optically pure **1**. Use of this procedure produces ϵ_2 at any desired wavelength; the spectrum of **2** derived in this way is compared with the spectra of **1** and $Cr(en)_3^{3+}$ in Figure 1.

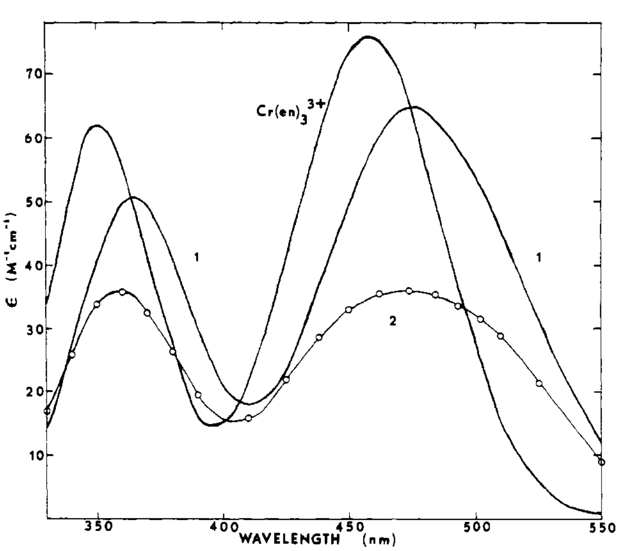
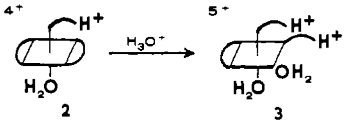


Figure 1. Absorption spectra of $Cr(en)_3^{3+}$, **1**, from thermal aquation and **2** calculated from photoproduct mixtures at the wavelengths indicated by open circles (see text). All solutions were 1 M in $NaClO_4$, pH 2.5 with $HClO_4$.

A second property of **2** was investigated briefly, that of its reactivity. Solutions of the tetrapositive ions **1** and **2** are orange. They underwent a fairly rapid change to pink. A comparison of this rate of change with that of pure **1** isolated from thermal aquation of $Cr(en)_3^{3+}$ indicated that **2** is considerably more labile. This is consistent with the known lability of *trans*-$Cr(en)_2XY^{n+}$ systems.[29] An estimated rate constant for aquation of **2** is 6.4×10^{-5} s^{-1} at 15 °C. In all experiments there is always evidence of a small amount of a pentapositive band on the column. The amount of this material can be increased by allowing the column to stand before separation, even at 2–3 °C; the amount of this material shows no relationship to extent of photolysis. The conclusion is that the lability of **2** is such that there is aquation of this material to form, as expected,[29] a pentapositive ion, **3**, in reaction 5.



(5)

Therefore a correct determination of the absolute yield of **2** upon photolysis requires knowledge of the amount of pentapositive ion. There are two places **3** occurs in the experiments reported herein: as a separate band, mentioned above, and as a contaminant in the tetrapositive band, a contaminant that grows with time. For the elimination of errors from this last source, all calculations of the fraction of the tetrapositive band that is **1** were made at 462 and 362 nm, isosbestic wavelengths for reaction 5.

Stereochemistry of Photoaquation. The availability of the extinction coefficients of both **1** and **2** and the molar rotation[30] of Λ-**1**, combined with the apparent extinction coefficient and apparent molar rotation of the tetrapositive ion-exchange band, allows a calculation of the three components of that band. This information, coupled with knowledge of the amount of pentapositive material (see discussion above) can be used to determine the fractional yields of the three products of photolysis of Λ-$Cr(en)_3^{3+}$. These have been measured at several wave-

---

[28] Andersen, P.; Berg, T.; Jacobsen, J. *Acta Chem. Scand., Ser. A* **1975**, *A29*, 381.

[29] Linck, R. G. *Inorg. Chem.* **1977**, *16*, 3143 and references therein.

[30] It should be noted that even if the value of $-110°$ dm^{-1} M^{-1} is incorrect, only the details of the arguments are changed, not the essential features.

lengths. The results are given in Table I. To establish that the irradiation at 635–685 nm populates the doublet, we performed a "blank" experiment in parallel with the experiments listed in Table I. In this run the Cr(en)$_3^{3+}$ was dissolved in 0.01 M OH$^-$; the observed yield of photoproducts was less than 4% of that found in the irradiation in acidic medium. Since OH$^-$ quenches the doublet of Cr(en)$_3^{3+}$,[22] this result establishes that photochemistry originating from doublet population is predominantly monitored by the 635–685-nm experiment.

In addition to these experiments, several runs were also done in which photolysis was produced by biacetyl sensitization of photoaquation of Cr(en)$_3^{3+}$. In these experiments the results were corrected for direct production of products (which was less than 30% of total products for the 400-nm light used). The relative amounts found from four sensitized photoaquations are as follows: Λ-**1**, 0.27; Δ-**1**, 0.08; **2**, 0.65. While these values were highly reproducible, the observed quantum yields gave too high a scatter to allow a precise fixing of the sensitized quantum yield.

Discussion

The stereochemical consequences reported in Table I require the molar rotation of **1** obtained from pure Λ-Cr(en)$_3^{3+}$ by thermal aquation to be that of pure Λ-**1** and not a mixture of the two enantiomers. The chelation experiments reported above demonstrate that the opening *and* chelation of the Cr–N bond retained at least 94% of the enantiomer present in the original Cr(en)$_3^{3+}$. This result, coupled with the known fact that the racemization of Λ-**1** in base is competitive with chelation to form Cr(en)$_3^{3+}$, suggests that the ring opening process occurs with complete retention of configuration. Such a conclusion is in agreement with the careful studies of Jackson and co-workers,[31] who have shown the high degree of stereoretention in thermal aquation of chromium(III)–amine complexes. Thus the value of −110° M^{-1} dm^{-1} seems appropriate as the molar rotation of Λ-**1**. The other properties determined for **1** and for the corresponding trans isomer, **2**, are consistent with the assigned geometries. Figure 1 shows the spectral properties; as usual, the extinction coefficients of the trans isomer, **2**, are less than those of the cis isomer, **1**, because of greater symmetry in **2**.

Number of Reactive States. The stereochemistry upon photoaquation of Cr(en)$_3^{3+}$ allows an assessment of the probability of multiple pathways for reaction of this species. The argument is that if there are two paths to products, i.e., from the vibrationally relaxed lowest energy quartet state *and* from the vibrationally relaxed doublet state, the stereochemical consequences obtained from these different reactive states should differ. The results given in Table I show that there is no detectable difference in stereochemistry upon doublet irradiation, nor do the stereochemical consequences differ when higher vibrational or electronic states are irradiated. The simplest conclusion from these data is that there is only one reactive state for this molecule. Since Adamson and co-workers[17] have found prompt reaction occurs upon irradiation, reaction consistent with direct reaction from ^{4}Y,[32,33] the conclusion is that only the ^{4}Y state is photoreactive; in this model, the slow reaction found by the above-mentioned authors[17] occurs by back intersystem crossing of ^{2}X to ^{4}Y.

The conclusion drawn above is at variance with that made by Adamson and co-workers.[17] On the basis of the ratio of delayed to prompt formation of products, they concluded that both the ^{2}X and ^{4}Y states were reactive, with efficiencies of 0.88 and 0.15, respectively. This conclusion is consistent with our data *only* if both of these reactive states show identical stereochemistries. The electronic states of ^{2}X and ^{4}Y differ substantially, the former belonging to the configuration t_{2g}^3, as does the ground state, and the latter to the configuration $t_{2g}^2e_g$. The ^{2}X state (t_{2g}^3), as was observed long ago,[4,8] is of the correct configuration (at least part of the wave function describing this state can be written as $t_{2g}^a(\alpha)t_{2g}^b(\beta)t_{2g}^b(\alpha)$) for nucleophilic attack at the open t_{2g} orbital. If one believes that associative attack is dominant in the ground-state configuration,[34] the ^{2}X state should be more likely to undergo such reaction because of its excited nature. On the other hand, the ^{4}Y state with dominant $t_{2g}^2e_g$ configuration is likely to undergo dissociative activation because the antibonding nature of the configuration lengthens bonds. It is probable such diverse reactivity profiles would lead to some variations in stereochemical consequences. Of course, the possibility is extant that the mechanism of reaction of these two configurations is the same (be that dissociative or associative); nevertheless, if different electronic configurations yield products, the stereochemical consequences, barring the accidental coincidence of them, would differ. One final possibility exists: the lifetime of a common intermediate produced by *both* reactive states is long enough that its fate is independent of its source. This possibility also seems unlikely because experiments designed to generate such intermediates in induced aquations of Co(III) complexes have shown that the stereochemical patterns may differ when charge and solvation patterns differ[37,38]—the intermediate lives a very short time.

Figure 2. Isomerization pathways of the tetragonal-pyramid intermediate.

The common stereochemical pattern found under all conditions of irradiation suggests a single pathway for reaction, yet the flash photolysis data have been analyzed and were used to suggest both ^{2}X and ^{4}Y reactivity. The analysis of the flash photolysis data depends on the value of four parameters, and most of the data points can be fit by parameters other than those chosen by the authors.[17] The exception is the data point at a monitoring wavelength of 620 nm. This point has large errors associated with it because of small absorbance changes. For instance, under the assumption that the only decay path for ^{2}X is back intersystem crossing and that 70% of the excited molecules proceed through ^{2}X (obtained from quenching experiments with OH$^-$), a value for the ratio of the delayed absorbance change to the prompt one of 3.6 can be calculated for a ratio of extinction coefficient of photoproducts to Cr(en)$_3^{3+}$ of 8; this value is within the stated error limits of the data of Fukuda et al.[17] A similar analysis has been made by Kirk.[19] Therefore the stereochemical data presented above is more definitive in establishing that only one state, ^{4}Y, is dominant in producing the photoaquation products of Cr(en)$_3^{3+}$.

It has been reported[39] that biacetyl sensitization of Cr(en)$_3^{3+}$ photoaquation leads to photoproducts with a very high

---

(31) Jackson, W. G.; Vowles, P. D.; Fee, W. W. *Inorg. Chim. Acta* **1977**, *22*, 111.

(32) Kirk, A. D.; Hoggard, P. E.; Porter, G. B.; Rockley, M. G.; Windsor, M. W. *Chem. Phys. Lett.* **1976**, *37*, 199.

(33) Pyke, S. C.; Windsor, M. W. *J. Am. Chem. Soc.* **1978**, *100*, 6518.

(34) Swaddle, T. W. *Coord. Chem. Rev.* **1974**, *4*, 217; see also ref 35 and 36.

(35) Randolph, L.; Linck, R. G. *Inorg. Chem.* **1977**, *16*, 2653.

(36) Ferrer, M.; Sykes, A. G. *Inorg. Chem.* **1979**, *18*, 3345.

(37) Buckingham, D. A.; Olsen, I. I.; Sargeson, A. M.; Satrapa, H. *Inorg. Chem.* **1967**, *6*, 1027.

(38) Jackson, W. G.; Lawrance, G. A.; Sargeson, A. M. *Inorg. Chem.* **1980**, *19*, 1001.

(39) Balzani, V.; Ballardini, R.; Gandolfi, M. T.; Moggi, L. *J. Am. Chem. Soc.* **1971**, 93, 339.

Table I. Fractional Yields for Photoaquation of Λ-$\mathrm{Cr(en)_3}^{3+}$ [a]

λ_{irr} [b]	Λ-1 [c]	Δ-1 [c]	2 [d]
365 (2)	0.29	0.09	0.62
400 (1)	0.28	0.06	0.66
457 (3)	0.29	0.07	0.64
520–580 (2)	0.29	0.09	0.62
635–685 (2)	0.26	0.07	0.67
broad-band, $\lambda > 400$	0.26	0.07	0.67

[a] $[\mathrm{Cr^{III}}] = 0.02$ M in 0.03 N aqueous HCl with less than 15% reaction. [b] Wavelength in nm. The number in parentheses indicates the number of experiments under each condition. [c] Errors on these values, as defined by standard deviation, are ±0.02. [d] Errors on these values are ±0.03.

quantum yield, 0.8. This result demands a different source of reactivity than direct population of the excited state or a branching within the vibrational relaxation from the directly populated state that is absent in the sensitized process. It was found that the stereochemical consequences of biacetyl sensitization are identical with those of direct irradiation. This establishes that a new pathway is *not* opened by sensitization with biacetyl and calls into question the value of the sensitized quantum yield.

Modeling of the Stereochemistry. Recent theoretical work by Vanquickenborne and Ceulemans[24,40] focused on rationalizing the stereochemical pathway for aquation of Cr(III) complexes of less than octahedral geometry. The results reported herein are the first on the stereochemistry of photoaquation of a complex of octahedral microsymmetry, although the detection of stereochemical processes relies on the presence of the chelate rings. In the model of Vanquickenborne and Ceulemans[24] there are two rearrangement processes for the tetragonal-pyramid intermediate formed in its excited state by loss of a ligand; for a $\mathrm{Cr(N)_5}$ species, one path, which we call A, involves motion that holds one point in the basal plane stationary, point PV in Figure 2A. This reaction coordinate maintains C_s symmetry. The other path, B, maintains C_{2v} symmetry and is shown in Figure 2B. If we consider a $\mathrm{Cr(NN)_2N}$ species, there are several additional possibilities because of the lower symmetry of the original tetragonal pyramid; these are illustrated in Figure 3A,B. In Figure 3A, the results of path A are shown. If the pivot point is either of the atoms labeled 1 or 2, the tetragonal pyramid produced from Λ-$\mathrm{Cr(en)_3}^{3+}$ is converted to a trigonal bipyramid, Δ-4 (labeled "Δ" because aquation will lead to Δ-*cis*-$\mathrm{Cr(en)_2(enH)(H_2O)}^{4+}$ and 2); if the pivot point is 3, the racemic intermediate 5 is produced, and if it is 4, the motion cannot take place. Figure 3B shows the possibilities for path B; these yield Λ-4 (a material labeled Λ to specify the enantiomer of *cis*-$\mathrm{Cr(en)_2(enH)(H_2O)}^{4+}$ that it will produce upon collapse) and the racemic intermediate 5. Within this framework it is necessary to account for the production of substantial amounts of 2 and some, but not complete, racemization of the resulting 1.

The Vanquickenborne-Ceulemans theory[24] predicts that path A is electronically forbidden in the lowest quartet state in the $\mathrm{CrN_5}$ or $\mathrm{CrN_4X}$ systems because of an avoided crossing between two A′ states in C_s symmetry. For the $\mathrm{Cr(NN)_2N}$ structure, both paths A and B are forbidden in the C_1 reaction coordinate, although it is likely that the crossover in path B will not be strongly disallowed.[40] The pertinent question concerning the partial racemization of 1 is as follows: Does a small fraction of reaction take place by the strongly disallowed path, A, through Δ-4 or does partial racemization occur via the racemized intermediate, 5, produced in the slightly disallowed path, B, an intermediate that stretches an ethylenediamine 120°? Critical to a decision between these two possibilities is the question of how unstable a situation it is to have an ethylenediamine stretched 120° in intermediate 5. Our view[41] is that intermediate 5 is not unstable at all; in fact, motion from 5 in which the triangular base of the bipyramid is equilateral to one in which it is isosceles with the ethylenediamine bridging an angle of less than 120°, even a little less than 90°, is both sterically (from the small ethylenediamine "bite" size) and electronically allowed. The latter result can be appreciated if, in intermediate 5 in Figure 3A, the $d_{x^2-y^2}$ orbital is taken to be occupied, and the N labeled "2" defines the X axis. Motion of the nitrogens at positions 3 and 4 toward each other moves them from a position that is antibonding by virtue of partial overlap with $d_{x^2-y^2}$, to, at a 90° value for the $\mathrm{N_3}$–Cr–$\mathrm{N_4}$ angle, a nonbonding position on the nodal surface of $d_{x^2-y^2}$. These can also be seen in Figure 3A,B of ref 24 where the slope of the $^1a_1$ orbital and the $^4B_2$ state, respectively, are still negative at $\alpha = 30°$. Therefore, we take the intermediate 5 to be reasonably stable (compare footnote 16 of ref 40).

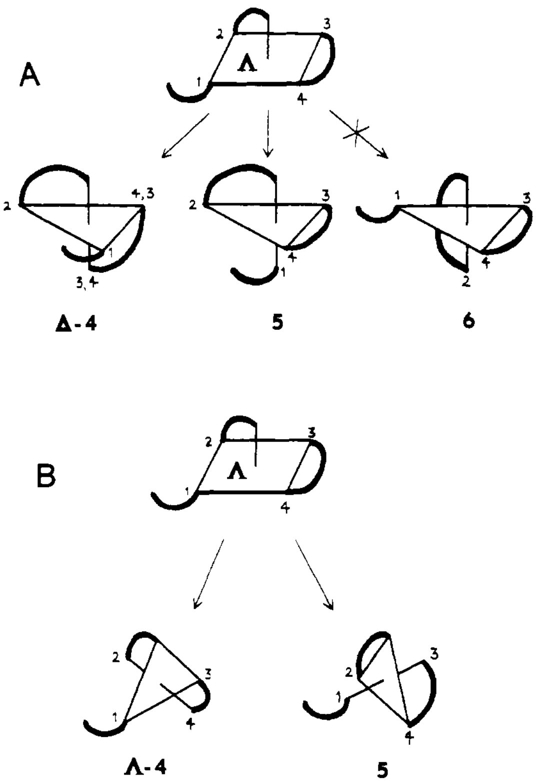


Figure 3. Trigonal-bipyramid intermediates formed from isomerization of the tetragonal pyramid with bidentate ligands: (A) path A; (B) path B.

An explanation for the observed partial racemization in *cis*-$\mathrm{Cr(en)_2(enH)(H_2O)}^{4+}$ then involves path B, consistent with only a small electronically forbidden character, and production of Λ-4 and 5 as intermediate, with 5 reacting to produce racemic *cis*-$\mathrm{Cr(en)_2(enH)(H_2O)}^{4+}$ and Λ-4 producing only the Λ isomer of the cis isomer. This explanation satisfactorily accounts for the nature of the cis product but fails completely to account for the large amount of trans product. Electronically, collapse of intermeidate Λ-4 can produce only 33% trans product. Clearly the theory[24] does not account for the data in the photoaquation of $\mathrm{Cr(en)_3}^{3+}$, which demands that Λ-4 produces 2 about 75% of the time. Whether this failure is due to steric features of the ethylenediamine groups, to a preferential "trans" collapse of the incipient intermediate as it is formed, to a complete failure of the theory, or to some other factor will require further experiments to decide.

Registry No. *cis*-Λ-1, 78306-76-0; *cis*-Δ-1, 78306-77-1; *trans*-2, 78306-78-2; Λ-$\mathrm{Cr(en)_3}^{3+}$, 41509-53-9.

---

(40) Vanquickenborne, L. G.; Ceulemans, A. *Inorg. Chem.* **1979**, *18*, 3475.

(41) We thank a reviewer for inspiration to consider aspects presented below.