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# Photochemistry of *trans*-Diisothiocyanatobis(ethylenediamine)chromium(III). Nature and Stereochemistry of the Reaction

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*Received July 30, 1973*

The photolysis of *trans*-$Cr(en)_2(NCS)_2^+$ in dilute acidic media has been studied at four wavelengths between 4000 and 5200 Å and at both 23 and 5°. There are two products of photolysis, *cis*-$Cr(en)_2H_2ONCS^{2+}$ and a molecule of stoichiometry $Cr(en)(enH)H_2O(NCS)_2^{2+}$ that is assigned a structure with thiocyanate groups trans to each other. The quantum yield at 5200 Å and 23° for the former ion is 0.23 and for the latter 0.13. The implications of these products on the question of stereomobility and models of photochemical behavior are discussed. It is concluded that stereomobility is not a requisite for photoaquation of chromium(III)-amine complexes.

## Introduction

The proliferation of models[1-4] to account for experimental results, and, perhaps, even to predict the results of experiments yet undone, is a welcome addition to the area of inorganic photochemistry.[5-7] We have been concerned with designing experiments that offer critical tests of some of those models[8,9] and with developing aspects of a model consistent with as many experimental results as possible.[8,9] Perhaps the key focus of all means of rationalization of the results of photolyses of Cr(III) complexes is the axis of labilization. Adamson[1] originally specified that the weakest ligand field axis would be labilized; Pyke and Linck[8] argued that $\sigma$ bonding was a more important parameter in specifying the labilized axis. More recently, both Zink[2] and Wrighton, Gray, and Hammond[3] have argued that MO calculations (at the geometry of the ground-state molecule) suggest that axial designation is only partially significant in determining the identity of the leaving group; in addition the ability of the ligands in the coordination sphere to be stabilized by $\pi$-bonding effects must be considered. Thus these two sets of authors argue that in *trans*-$Cr(en)_2Cl_2^+$, the lowest lying excited quartet state, $^4E_g$, is dominantly $d_{z^2}$ in character (87%)[10] and that the $\sigma^*$ effects of population of this state outweigh the favorable stabilization caused by depopulation of the $\pi^*$ ($t_{2g}\ \pi$) orbital in this state. Thus *trans*-$Cr(en)_2Cl_2^+$ exhibits photosubstitution of $Cl^-$, in agreement with experiment.[11] On the other hand, in *trans*-$Cr(en)_2F_2^+$, the $^4E_g$ state has less $d_{z^2}$ character (66%),[10] it is "octahedral-like",[3] and nonselective $\sigma$ weakening occurs: both Cr–F and Cr–N bonds are weakened in a $\sigma$ sense. However, $F^-$ undergoes strong $\pi$ bonding with Cr(III), and depopulation of the $t_{2g}\ \pi$ orbitals—an antibonding $\pi$ orbital—in $^4E_g$ stabilizes the $\pi$ bond between $F^-$ and Cr(III); hence, in a $\pi$ sense, fluoride is stabilized relative to the Cr–N bond. The latter should photosubstitute, as experiment has shown.[8]

It is to be noted that these MO models stress the importance of $\pi$-bonding stabilization at the expense of any differentiation between, for instance, Cr–N and Cr–F $\sigma$ bonds in "octahedral-like" molecules. In this paper we report our first exploration of a means of gaining an experimental test of these MO rationalizations. We report here a study of the photolysis of *trans*-$Cr(en)_2(NCS)_2^+$, a substance chosen to probe the question of the influence of $\pi$ stabilization in "octahedral-like"[3] molecules. Our experimental results in this study also suggest that the concepts[4,12,13] concerning stereochemical rearrangements during photolysis of Cr(III) complexes need to be enlarged. We comment below on the question of the validity of an axis of labilization as well as the requirement for stereochemical rearrangement in photolysis of Cr(III) complexes.

## Experimental Section

**Materials.** Crude *trans*-$[Cr(en)_2(NCS)_2]NCS$ was prepared from $Cr(en)_3(NCS)_3$ according to the procedure of Rollinson and Bailar.[14] This material was recrystallized as the perchlorate salt, but repeated recrystallizations yielded materials for which the extinction coefficient varied. A sample of doubly recrystallized material was, therefore, dissolved in water and passed down a Dowex 50W-X2 column in the $H^+$ form. Three bands were observed: the *trans*-$Cr(en)_2(NCS)_2^+$, first to be eluted by 0.5 *N* HCl, was precipitated with $HClO_4$; the second band was a reddish material; and the third was $Cr(en)_3^{3+}$. The purified solid exhibited spectral characteristics in rough agreement with Holba's[15] values, but those characteristics agree poorly with most other values in the literature.[16] We have repeatedly obtained the values listed in Table I on different preparations and on samples after ion exchange. *Anal.* Calcd for *trans*-$[Cr(en)_2(NCS)_2]ClO_4$: Cr, 13.43; NCS, 29.95. Found: Cr, 13.40; NCS, 29.80.

Perchloric acid solutions were prepared from G. F. Smith doubly distilled acid and doubly distilled water. All ion-exchange separations were accomplished with Dowex 50W-X2 resin of 200–400 mesh that had been partially screened by flotation after treatment with basic peroxide and reacidification.

**Techniques.** The photolyses were performed at four wavelengths using the xenon source and sample block previously described.[8] (Replacement of the General Electric bulb by an Osram bulb had no influence on quantum yields or product distribution.) The wavelengths were isolated with Oriel interference filters. The intensity of the source was measured by Reineckate actinometry;[17] the temperature was controlled by a water bath and measured continuously during the photolysis. The sample was mixed just prior to photolysis and was

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[1] A. W. Adamson, *J. Phys. Chem.*, 71, 798 (1967).

[2] J. I. Zink, *J. Amer. Chem. Soc.*, 94, 8039 (1972).

[3] M. Wrighton, H. B. Gray, and G. S. Hammond, *Mol. Photochem.*, 5, 165 (1973).

[4] (a) A. D. Kirk, Abstracts, 164th National Meeting of the American Chemical Society, New York, N. Y., 1972, No. INOR 22; (b) A. D. Kirk, *Mol. Photochem.*, 5, 127 (1973).

[5] V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, New York, N. Y., 1970.

[6] A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleishauer, and R. D. Lindholm, *Chem. Rev.*, 68, 541 (1968).

[7] R. B. Bucat and D. W. Watts, *MTP (Med. Tech. Publ. Co.) Int. Rev. Sci.: Inorg. Chem., Ser. One*, 9, 159 (1971).

[8] S. C. Pyke and R. G. Linck, *J. Amer. Chem. Soc.*, 93, 5281 (1971).

[9] G. Wirth and R. G. Linck, *J. Amer. Chem. Soc.*, 95, 5913 (1973).

[10] J. I. Zink, *Inorg. Chem.*, 12, 1957 (1973).

[11] A. D. Kirk, K. C. Moss, and J. G. Valentin, *Can. J. Chem.*, 49, 1524 (1971).

[12] A. D. Kirk, *J. Amer. Chem. Soc.*, 93, 283 (1971).

[13] E. Zinato and P. Riccieri, *Inorg. Chem.*, 12, 1451 (1973).

[14] C. L. Rollinson and J. C. Bailar, Jr., *Inorg. Syn.*, 2, 20 (1946).

[15] V. Holba, *Chem. Zvesti*, 19, 441 (1965); *Chem. Abstr.*, 63, 15621*d* (1965).

[16] C. S. Garner and D. A. House, *Transition Metal Chem.*, 6, 200 (1970).

[17] E. E. Wegner and A. W. Adamson, *J. Amer. Chem. Soc.*, 88, 394 (1966).

placed on an ion-exchange column held between 0 and 5° immediately after photolysis was complete.

Analysis for Cr content of various ion-exchange fractions was by spectrophotometry after basic peroxide oxidation to $CrO_4^{2-}$.[18] The concentration of $NCS^-$ was determined by measurement of the absorptivity of a $Fe(NCS)^{2+}$ solution at 4500 Å ($\epsilon$ 4210). For determination of coordinated $NCS^-$, a sample of the chromium complex was decomposed photolytically in an acetate buffer; the sample was then warmed with a slight excess of EDTA and finally treated with an excess of a Fe(III) solution to yield the $Fe(NCS)^{2+}$ complex whose absorptivity was monitored; the blank was a solution of the chromium complex in the absence of Fe(III).

## Results

**Thermal Aquation.** The thermal aquation of *trans*-$Cr(en)_2(NCS)_2^+$ has been studied previously by Holba;[15,19] we have repeated these experiments in order to ascertain the value of the rate constant and the nature of the product(s) under the conditions of our photolytic experiments.

Ion-exchange separation of a solution of *trans*-$Cr(en)_2(NCS)_2^+$ in dilute ($1.0 \times 10^{-3}$ *M*) $HClO_4$ that has been allowed to aquate partially (24 hr at 25°) shows three components. The first, the most minor component, is eluted with 0.5 *N* HCl, the second, starting material, with 0.75 *N*, and the third with 1.0 *N* HCl. The spectral characteristics of these species are given in Table I.[20] The first band corresponds spectrally to the complex observed by Thomas and Holba[21] and assigned by them to the complex $Cr(en)(H_2O)_2(NCS)_2^+$. Our data are consistent with this assignment. We find an $NCS^-$ to Cr ratio of 2.05; ion-exchange behavior is consistent with a unipositive ion. The third band off the ion-exchange column has an $NCS^-$ to Cr ratio of 2.00 ± 0.03 and elutes in a fashion characteristic of the "one-ended" ions $Cr(en)(enH)H_2OF_2^{2+}$ [8] and $Cr(en)(enH)H_2OFCl^{2+}$ [9,22]—more slowly than the parent chelated species and more rapidly than the corresponding *cis*-$Cr(en)_2H_2OX^{2+}$ species. These products fit the aquation scheme

$$trans\text{-}Cr(en)_2(NCS)_2^+ \xrightarrow{k_1} Cr(en)(enH)H_2O(NCS)_2^{2+}$$

$$Cr(en)(enH)H_2O(NCS)_2^{2+} \xrightarrow{k_2} Cr(en)(H_2O)_2(NCS)_2^+$$

The first-order rate constant for thermal aquation was measured by ion-exchange separation of a partially aquated sample or by the change in $[H^+]$ resulting from the protonation of the one-ended ethylenediamine ligand. At 25.2° we find $k_1 = (2.7 \pm 0.2) \times 10^{-6}$ sec$^{-1}$ in $1 \times 10^{-3}$ *M* $HClO_4$ and estimate $k_2$ to be about $1 \times 10^{-6}$ sec$^{-1}$. At 40.1° we find $k_1 = 2.4 \times 10^{-5}$ sec$^{-1}$ and $k_2$ about $7.5 \times 10^{-5}$ sec$^{-1}$. The activation parameters derived from the temperature dependence of $k_1$ are $\Delta H^{\ddagger} \cong 28$ kcal mol$^{-1}$ and $\Delta S^{\ddagger} \cong 8$ cal mol$^{-1}$ deg$^{-1}$.

Table I. Spectral Characteristics of Complexes Studied

| | Exptl | | Lit. | | |
|---|---|---|---|---|---|
| Complex | λ, Å | $\epsilon$, $M^{-1}$ cm$^{-1}$ | λ, Å | $\epsilon$, $M^{-1}$ cm$^{-1}$ | Ref |
| *trans*-$Cr(en)_2(NCS)_2^+$ | 4870 | 87.1 | 4860 | 86 | 15 |
| | 4140 (min) | 25.2 | 4150 | 26 | |
| | 3650 | 62.1 | | | |
| $Cr(en)(enH)(H_2O)(NCS)_2^{2+}$ | 5080 | 117.5 | | | |
| | 3850 | 79.0 | | | |
| $Cr(en)(H_2O)_2(NCS)_2^+$ | 5220 | 123 | 5200 | ≃120 | 16 |
| | 3900 | 66 | 3700 | ≃60 | |
| *cis*-$Cr(en)_2NCS(H_2O)^{2+}$ | 4880 | 104.0 | 4880 | 102 | 20 |
| | 3800 | 59.1 | 3710 | 58 | |

**Photochemistry.** Under the influence of light in the visible region of the spectrum, *trans*-$Cr(en)_2(NCS)_2^+$ undergoes photolysis to produce two products. These are observed after separation by ion-exchange chromatography of a photolyzed solution of *trans*-$Cr(en)_2(NCS)_2^+$. Such an experiment reveals three different complexes on the column: the first is the starting material, the second is the same as the previously identified product of thermal aquation, $Cr(en)(enH)H_2O(NCS)_2^{2+}$, and the third complex, a salmon-colored species eluted with more difficulty than the other two, is identified by its spectral properties as *cis*-$Cr(en)_2H_2ONCS^{2+}$. Table I compares our values for λ ($\epsilon$) of this photoproduct with the values reported in the literature.[20] In addition, we have determined that this complex contains 1.12 $NCS^-$ per Cr(III).

Further evidence that these two complexes are the photoproducts can be obtained by measurement of the changes in $[H^+]$ in the solvent and the changes in $[NCS^-]$. In the absence of light, the $[H^+]$ in a solution $4 \times 10^{-3}$ *M* in *trans*-$Cr(en)_2(NCS)_2^+$ and $1 \times 10^{-3}$ *M* in $HClO_4$ remains essentially constant for 15 min at 23° (the calculated value after this time on the basis of the rate constant $k_1$ is $0.99 \times 10^{-3}$ *M*); when the same solution is photolyzed for about this length of time the $[H^+]$ changes rapidly and the amount of $H^+$ consumed is equal within experimental error to the amount of $Cr(en)(enH)H_2O(NCS)_2^{2+}$ found. In two experiments at 5200 Å in which the amount of secondary photolysis was negligible we found the amount of $H^+$ consumed to be 9.1 and 13.5 μmol; the corresponding quantities of $Cr(en)(enH)H_2O(NCS)_2^{2+}$ isolated from ion exchange of these solutions were 11.1, and 13.4 μmol, within experimental error of the values for the decrease in $[H^+]$. This agreement establishes that the third ion-exchange-resolvable complex has the same proton content as does *trans*-$Cr(en)_2(NCS)_2^+$ and cannot therefore be one of the isomers of $Cr(en)(enH)(H_2O)NCS^{3+}$. A similar result is obtained if a solution of *trans*-$Cr(en)_2(NCS)_2^+$ that has been photolyzed is placed on an ion-exchange column and that column is washed thoroughly with water to elute uncoordinated $NCS^-$; the quantity thus obtained is equal to the moles of *cis*-$Cr(en)_2H_2O(NCS)^{2+}$ if the photolysis is stopped before secondary photolysis is significant. In three experiments at 5200 Å and one at 4800 Å, the amounts of $NCS^-$ found were respectively 20, 28, 7.1, and 7.1 μmol whereas the corresponding quantities of *cis*-$Cr(en)_2H_2O(NCS)^{2+}$ were respectively 20, 27, 7.0, and 6.8 μmol.

We have carried out quantitative photolyses of *trans*-$Cr(en)_2(NCS)_2^+$ at four wavelengths, three centered around the position of the lowest energy spectral band and one for which irradiation is into the higher energy band. Because the solubility of *trans*-$Cr(en)_2(NCS)_2^+$ is low (and slow in our hands) in $ClO_4^-$ media, photolyses converting enough material to products to be readily observable also deplete the starting concentration by a significant fraction, 0.05–0.25; since products have extinction coefficients of the same magnitude as those of *trans*-$Cr(en)_2(NCS)_2^+$, the fraction of light absorbed by *trans*-$Cr(en)_2(NCS)_2^+$ decreases with time. In addition, when photolyses were carried out long enough to consume about 12% of starting material, secondary products were apparent upon ion-exchange separation. Given these circumstances, an idealized scheme for the important processes can be constructed—see Scheme I where A is *trans*-$Cr(en)_2(NCS)_2^+$, B is $Cr(en)(enH)H_2O(NCS)_2^{2+}$, C is *cis*-$Cr(en)_2H_2ONCS^{2+}$, and D (probably more than one compound) is secondary products. In this scheme $k_1$ is the thermal path

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(18) G. Haupt, *J. Res. Nat. Bur. Stand.*, 48, 414 (1952).

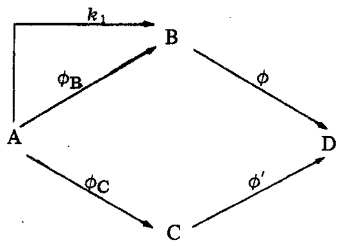
(19) V. Holba, *Z. Phys. Chem. (Leipzig)*, 226, 408 (1964).

(20) J. M. Veigl and C. S. Garner, *Inorg. Chem.*, 4, 1569 (1965).

(21) G. Thomas and V. Holba, *J. Inorg. Nucl. Chem.*, 31, 1749 (1969).

(22) See also J. M. DeJovine, W. R. Mason, and J. W. Vaughn, *Inorg. Chem.*, 13, 66 (1974).

Scheme I



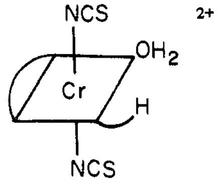
for production of $Cr(en)(enH)H_2O(NCS)_2^{2+}$. In order to analyze this situation we have been forced to make some limiting assumptions. First, the amount of thermally produced $Cr(en)(enH)H_2O(NCS)_2^{2+}$ is small (usually less than 0.7% of the *trans*-[$Cr(en)_2(NCS)_2^+$]) and most of this arises during dissolution of the complex rather than during photolysis. Thus we can correct for thermally produced $Cr(en)(enH)H_2O(NCS)_2^{2+}$ by simple subtraction of the calculated thermally produced quantity from the amount isolated by ion exchange of a photolyzed solution. Second, the yield of D is small (never greater than 20% of products and usually less than 5%); we have chosen to distribute the quantity of D observed to B and C in proportion to the relative extinction coefficients of B and C at the wavelength of photolysis—that is, to assume $\phi = \phi'$. This procedure is an approximation that tends to keep the B:C ratio independent of the quantity of D, thereby justifying the procedure. With these two corrections to the amounts of $Cr(en)(enH)H_2O(NCS)_2^{2+}$ and *cis*-$Cr(en)_2H_2ONCS^{2+}$ we can plot the apparent quantum yield

$$\phi_C(\text{app}) = [cis\text{-}Cr(en)_2H_2ONCS^{2+}]/I_0t$$

where $I_0$ is the absorbed light intensity in einsteins $l.^{-1}$ $sec^{-1}$ and $t$ is the time in sec *vs.* $f$, where $f$ is the fraction of the starting concentration of *trans*-$Cr(en)_2(NCS)_2^+$ left after photolysis, and extrapolate to $f = 1.0$.[23] Such a procedure has been used to obtain values of $\phi_B$, the quantum yield for $Cr(en)(enH)H_2O(NCS)_2^{2+}$, and $\phi_C$, the quantum yield for *cis*-$Cr(en)_2H_2ONCS^{2+}$. Figure 1 shows these plots for λ 5200 Å. Our values of $\phi$ at this and other wavelengths are given in Table II.

## Discussion

The thermal and photolytic aquations of *trans*-$Cr(en)_2(NCS)_2^+$ yield a molecule in common, a molecule whose stoichiometry is $Cr(en)(enH)H_2O(NCS)_2^{2+}$. We believe that this species is assigned a trans structure with respect to $NCS^-$ groups



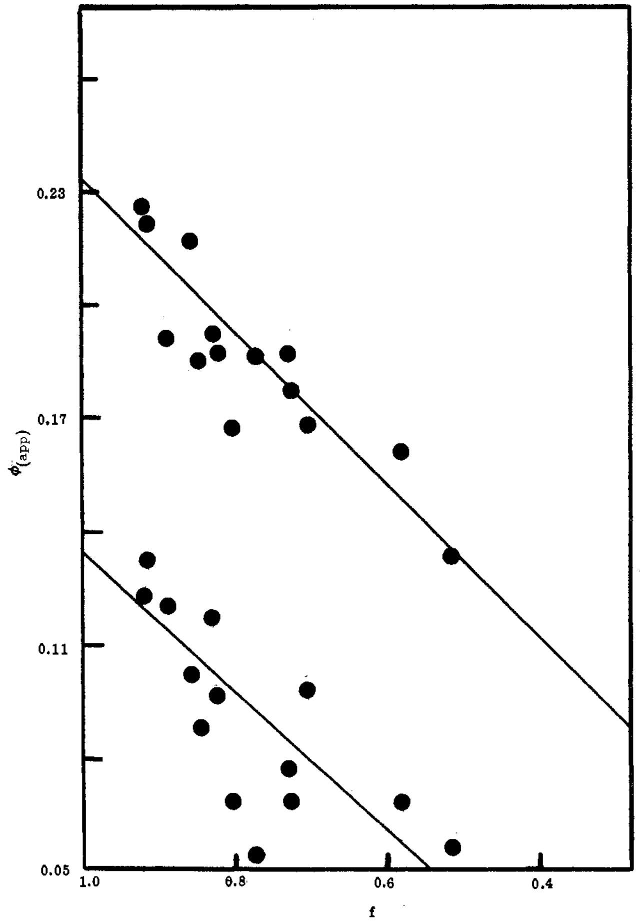


Figure 1. The apparent quantum yield of *cis*-$Cr(en)_2H_2ONCS^{2+}$ (upper line) and $Cr(en)(enH)H_2O(NCS)_2^{2+}$ (lower line) as a function of the fraction of *trans*-$Cr(en)_2(NCS)_2^+$ remaining after photolysis. Wavelength of irradiation is 5200 Å.

Table II. Quantum Yield Values for *trans*-$Cr(en)_2(NCS)_2^+$

| Wavelength, Å | No. of expts | T, °C | $\phi_B$ | $\phi_C$ |
|---|---|---|---|---|
| 5200 | 14 | 23 | 0.134 ± 0.02 | 0.233 ± 0.015 |
| 4800 | 4 | 23 | 0.109 ± 0.01 | 0.237 ± 0.01 |
|  | 2 | 5 | 0.095 | 0.175 |
| 4500 | 4 | 23 | 0.163 ± 0.02 | 0.265 ± 0.015 |
| 4000 | 4 | 23 | 0.08 ± 0.02 | 0.24 ± 0.01 |

The reasoning behind this decision is much the same as used previously in the case of the similar species $Cr(en)(enH)H_2OF_2^{2+}$:[8] chromium(III)-amine complexes thermally aquate, generally with retention of stereochemistry.[16,24] Since the original $NCS^-$ groups are trans, this would suggest that they remain so. In addition, the further aquation of $Cr(en)(enH)H_2O(NCS)_2^{2+}$ in dilute acidic solution yields $Cr(en)(H_2O)_2(NCS)_2^+$, a species that would be predicted by the rule of stereoretention also to have the $NCS^-$ groups trans to each other. This assignment is in agreement with that of Thomas and Holba,[21] who prepared this species from $Cr(en)(NCS)_4^-$. Further, the ion-exchange behavior of this latter species is that expected from $Cr(en)(H_2O)_2(NCS)_2^+$ with $NCS^-$ groups trans to each other: it is eluted much more readily than *trans*-$Cr(en)_2(NCS)_2^+$, a result that one would not expect if the $NCS^-$ groups were cis to one another. For these reasons we believe that the more rapidly eluted photoproduct (and the sole primary thermal product) of

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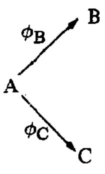
[23] The approximations made amount to simplifying Scheme I to the scheme

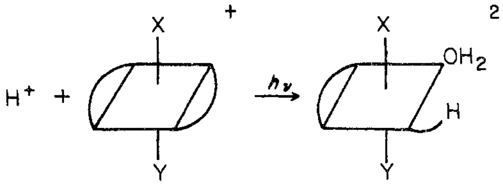


for which the appropriate differential equation can be integrated. That integrated form is a function of the parameters $\epsilon_A$, $\epsilon_B$, $\epsilon_C$, $\phi_B$, $\phi_C$, $I_0$, and $t_0$ and for values typical of our system it can be shown that a plot of $\phi_C$(app) *vs.* $f$ is linear within experimental error over the values of $f$ we encounter.

[24] M. C. Couldwell and D. A. House, *Inorg. Chem.*, 11, 2024 (1972), and references therein.

*trans*-$Cr(en)_2(NCS)_2^+$ is *trans*-$Cr(en)(enH)H_2O(NCS)_2^{2+}$. The other photoproduct is the cis isomer of $Cr(en)_2H_2ONCS^{2+}$ as determined by the Cr to NCS ratio and spectral properties in agreement with those in the literature.[20]

The two photoaquation products of *trans*-$Cr(en)_2(NCS)_2^+$ illustrate, in a single photolysis, phenomena that are becoming common in studies of the stereochemistry of Cr(III) photoaquation.[25-31] Table III summarizes the available data. Photolysis of $Cr(NH_3)_5X^{2+}$, where $X^-$ is $Cl^-$,[25,26] $Br^-$,[27] $NCS^-$,[30] and carboxylic acids,[28] yields as the *dominant*[31] photoproduct *cis*-$Cr(NH_3)_4H_2OX^{2+}$. In photolytic chloride aquation of *trans*-$Cr(en)_2Cl_2^+$,[11] *trans*-$Cr(en)_2NCSCl^+$,[32] and *trans*-$Cr(en)_2FCl^+$,[9] the dominant products are *cis*-$Cr(en)_2H_2OCl^{2+}$, *cis*-$Cr(en)_2NCSH_2O^{2+}$, and *cis*-$Cr(en)_2H_2OF^{2+}$, respectively. All of these data have been taken as illustrative of a stereospecific rearrangement in which the entering water molecule is found not in the position vacated by the group that leaves but rather in the position adjacent to the group that was trans to the leaving group. On the other hand, the information concerning molecules of the type $Cr(en)_2XY^+$ is now sufficient to convince us that photolytic aquation of ethylenediamine can lead to stereoretention of configuration. Thus in all three cases that have been examined, the evidence indicates that "in-plane" photolysis takes place according to the equation



for $X^-$, $Y^-$ being $F^-$, $F^-$,[8] $F^-$, $Cl^-$,[9] and, in our case, $NCS^-$, $NCS^-$; in all three cases the photoproduct is identical in composition with the thermal aquation product. This argument is based on indirect structural assignments of the thermal aquation products; but the likelihood that all three aquations violate the usual case of stereoretention in aquations of Cr(III) complexes and violate it to the extent of greater than 95% stereochemical change seems to us highly improbable. Since the "in-plane" photoproducts are identical with the thermal product, they are also stereoretentive. This analysis therefore strongly implies that the recently voiced necessary condition of stereomobility for photosubstitution is not correct.

Our data on the photoaquation of *trans*-$Cr(en)_2(NCS)_2^+$ should also be examined from the point of view of the axis of labilization and the role of π-bonding effects in determining the identity of the leaving group. We have observed the loss of both $NCS^-$ and an amine group in the photolysis of *trans*-$Cr(en)_2(NCS)_2^+$. If we accept that this system is "octahedral-like" in the terminology of Wrighton, Gray, and Hammond,[3] then any strong π donor should not leave: this model predicts loss of an amine group only if $NCS^-$ is a π donor. But is $NCS^-$ a π donor? This latter question can be addressed from four points of view.

Table III. Dominant Photoaquation Products of Chromium(III)-Amine Complexes upon Irradiation into the Lowest Quartet State

| Complex | Product | $\phi$ | Ref |
|---|---|---|---|
| $Cr(NH_3)_5Cl^{2+}$ | *cis*-$Cr(NH_3)_4H_2OCl^{2+}$ | 0.36 | 25, 26 |
| $Cr(NH_3)_5Br^{2+}$ | *cis*-$Cr(NH_3)_4H_2OBr^{2+}$ | 0.35 | 27 |
| $Cr(NH_3)_5$-$CF_3COO^{2+}$ | *cis*-$Cr(NH_3)_4H_2O(CF_3COO)^{2+}$ | 0.36 | 28 |
| $Cr(NH_3)_5NCS^{2+}$ | *cis*-$Cr(NH_3)_4H_2ONCS^{2+}$ | 0.42 | 29, 30 |
| *trans*-$Cr(en)_2Cl_2^+$ | *cis*-$Cr(en)_2H_2OCl^{2+}$ | 0.31[a] | 11 |
| *trans*-$Cr(en)_2FCl^+$ | *cis*-$Cr(en)_2H_2OF^{2+}$ | 0.31 | 9 |
| | *trans*-$Cr(en)_2H_2OF^{2+}$ | 0.03 | 9 |
| | *trans*-$Cr(en)(enH)H_2OFCl^{2+}$ | 0.04 | 9 |
| *trans*-$Cr(en)_2(NCS)_2^+$ | *cis*-$Cr(en)_2H_2ONCS^{2+}$ | 0.24 | This work |
| | *trans*-$Cr(en)(enH)H_2O(NCS)_2^{2+}$ | 0.13 | This work |
| *trans*-$Cr(en)_2F_2^+$ | *trans*-$Cr(en)(enH)H_2OF_2^{2+}$ | 0.46 | 8 |
| *trans*-$Cr(en)_2NCSCl^+$ | *cis*-$Cr(en)_2H_2OCl^{2+}$ | 0.06[c] | 31 |
| | *cis*-$Cr(en)_2H_2ONCS^{2+}$ | 0.18[c] | 31 |
| | *b* | 0.01[d] | 31 |

[a] This value is for $Cl^-$ loss. Only >70% of the chloride deficient material has been established to be *cis*-$Cr(en)_2H_2OCl^{2+}$. [b] Uptake of $H^+$ was the only result recorded. [c] $T = 1°$; there is a temperature effect reported. [d] $T = 15°$.

First, $NCS^-$ is a somewhat weaker σ donor than is $NH_3$ on the basis of acidity, although the comparison between species of different charge types is not rigorous because of solvation phenomena. Arguments can be made that $NCS^-$ is about as effective in σ donation as is $NH_3$ in cobalt(III)-amine complexes in order to explain electron-transfer rates.[33] If this is true, $NCS^-$ must be a π donor in order to have a *Dq* value below that of $NH_3$. Second, the aquation of *trans*-$Co(en)_2NCSCl^+$ leads to substantial rearrangement, suggesting π-donor ability. Third, Dubicki and Martin[34] aruged that it is expected on the basis of the resonance structures that $NCS^-$ should be a π donor. This result, they argued, is consistent with the values of the tetragonal crystal field parameters, *Ds* and *Dt*, needed to fit the spectrum of *trans*-$Cr(NCS)_4(NH_3)_2$.[33] Fee and Harrowfield[35] have also made a spectral analysis of *trans*-$Cr(en)_2(NCS)_2^+$, as well as some *trans*-$Cr(en)_2NCSX^+$ complexes, and concluded, with reservations, that $NCS^-$ is a π donor, although as weak as one as $H_2O$. Fourth, we note that in order to explain the results on the photolysis of $Cr(NH_3)_5NCS^{2+}$, namely, that the principal photoproducts are $NH_4^+$ and *cis*-$Cr(NH_3)_4H_2ONCS^{2+}$, it is necessary in the MO schemes[2,3] to call $NCS^-$ a π donor.

All of the above arguments can be used with the MO rationalizations[2,3] to predict that the photolysis of *trans*-$Cr(en)_2(NCS)_2^+$ should yield loss of an amine group, with the quantum yield for $NCS^-$ loss significantly smaller. In fact, of course, the ratio of $\phi_C/\phi_B$ is not significantly less than unity but is, at least at low irradiation energies, greater than unity, having a value of about 2 (Table II) when irradiation is into

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(31) A discussion of the difference between the experimental rigor with which exclusive isomerization has been established and the conceptual rigor that has been utilized in discussions of these data is to be found in ref 9.

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the states derived from $^4T_{2g}$ in octahedral symmetry.[36] Further we note that for irradiation at 4800 Å the ratio is not highly sensitive to temperature even though the quantum yields appear to drop somewhat at lower temperatures.

It is to be recognized that since one expects the $\pi$-donor strength of $NCS^-$ to be small, subtle effects may be playing a role in determining the photolysis pathway in *trans*-$Cr(en)_2(NCS)_2^+$. But we beleive our data and other data in the literature can be illuminated as follows. We suggest that the dominant role in deciding the nature of the photoproduct is based on the $\sigma$-bonding contribution. Excitation of a chromium(III)-amine complex leads to population of $\sigma^*$ orbitals which produce a stretching of chromium-ligand bonds. In complexes of $D_{4h}$ or $C_{4v}$ symmetry, the $\sigma^*$ orbitals (comprised of metal ion orbitals $d_{z^2}$, $d_{x^2-y^2}$, s, and p) except s are such that ligands trans to each other are influenced in a similar fashion: population of a $\sigma^*$ orbital with metal ion composition of $d_{z^2}$ or $p_z$, for instance, will influence most dominantly the ligands on *both* the $+z$ and $-z$ axes. In response to this population, stretching of both ligands along the $z$ axis will occur. The question is, "Will the $z$ axis or the $xy$ plane ($d_{x^2-y^2}$ and the degenerate pair $p_x$, $p_y$) undergo the most violent stretching?"

One way to answer this question is to examine the composition of the multielectronic wave function in the state into which the photon places the Cr(III) complex and to use its composition to predict the "direction" of photoaquation—see Introduction. We prefer to consider the situation in the following simplified model. Excitation of the Cr(III) complex places it on an excited electronic energy surface but also in an excited vibration level of that surface. The minimum is as much as 10–15 kcal $mol^{-1}$ lower in energy.[37] There are, in this simplified model that neglects distortions necessary to remove the degeneracy of the state, two stretching motions that can occur and lead to minimum energies, along the $z$ axis or in the $xy$ plane. Which occurs should depend on the depth of the minima as well as the shape of the energy surface. We believe that the bonding interaction in the metal–ligand bond, determined, as usual, principally by $\sigma$ interactions, will be of prime importance in determining the direction of distortion. Once the molecule has reached the lower vibrational levels of this distorted state, substitution occurs, with leaving group abilities determined by effects common to ground-state chemistry (relative net bond strengths, solvation) as well as the degree of distortion of normal bonding that has occurred from depopulation of $\pi^*$ orbitals.

Our model thus is capable of rationalizing the results of photoaquation of *trans*-$Cr(en)_2F_2^+$ (Cr–en cleavage[8]), in which the strong Cr–F $\sigma$ bonds are reluctant to stretch, *trans*-$Cr(en)_2Cl_2^+$ (Cr–Cl cleavage[11]), in which the weaker Cr–Cl $\sigma$ bonds give way, and $Cr(NH_3)_5NCS^{2+}$ (principally Cr–$NH_3$ cleavage[29,30]), in which the $z$-axis activation is combined with $\pi$ stabilization of the Cr–NCS bond to lead to $NH_3$ loss,[38] as well as the more complicated systems *trans*-$Cr(en)_2FCl^+$ [9] (both Cr–en and Cr–Cl cleavage) and *trans*-$Cr(en)_2(NCS)_2^+$ (both Cr–NCS and Cr–en cleavage) in which the $\sigma$-bonding strengths along the $z$ axis and in the $xy$ plane are about equal.

These concepts are not too different from those of the MO rationalization[2,3] but differ in two aspects. (1) $\sigma$-Bonding interactions are of more importance than $\pi$ in determining the axis (or plane) labilized, even in "octahedral-like" molecules, whereas $\pi$ effects do come to play in determining the labilized group along the axis. (2) Our model tries to take into account the distortion from the ground-state geometry and tries to anticipate the nature of that distortion, a process that should retain the most favorable bonding situation. We do not believe that the detailed wave functions at ground-state geometry are of extreme importance in understanding the distorted state from which photoaquation presumably takes place, especially in view of the relatively large energetic differences between the vibrational level of the photoproduced species and the lowest vibrational level of that electronically excited species[37] and the large geometrical distortions attendant upon that energy difference.[39]

**Acknowledgments.** This work was supported by a grant from the Academic Senate, UCSD. We are grateful for that support and wish also to acknowledge support from Consejo Nacional de Investigaciones Cientificas y Tecnologicas, Caracas, Venezuela. We thank Professors H. B. Gray and J. I. Zink for preprints of their articles.

**Registry No.** *trans*-$[Cr(en)_2(NCS)_2]ClO_4$, 43176-07-4; $Cr(en)(enH)(H_2O)(NCS)_2^{2+}$, 43176-08-5; $Cr(en)(H_2O)_2(NCS)_2^+$, 43209-04-7; *cis*-$Cr(en)_2NCS(H_2O)^{2+}$, 25078-44-8.

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(36) It is especially interesting to note that this result is even more dramatic if the factor "$R$" of the Wrighton, *et al.*,[3] work is considered. Since the rate constant for ground state chromium-amine bond breakage is >70 times that of Cr–NCS bond breakage, the difference in the excited state between chromium–amine and Cr–NCS bond breakage is on this weighted scale greater than $10^2$.

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(38) The model predicts that in $Cr(NH_3)_5NCS^{2+}$ the $z$ axis and $xy$ plane will both be activated since the $\sigma$-bonding characteristics of $NH_3$ and $NCS^-$ are close. In either case $NH_3$ should be lost.

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