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The Preparation and Photoaquation of *trans*-$[Cr(en)_2NH_3NCS]^{2+}$

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Reaction of *trans*-$[Cr(en)_2(NCS)Br]NCS$ in acidic liquid ammonia has been found to give a good yield of the cis and trans isomers of $[Cr(en)_2NH_3NCS]^{2+}$. These isomers can be separated by fractional crystallization of the thiocyanate salts. The purified trans isomer was characterized by analysis, by comparison of the ir and uv spectra of the cis and trans isomers, and by comparison of the X-ray powder photographs of the cis and trans isomers with authentic samples of the analogous cobalt complexes. Photolysis of *trans*-$[Cr(en)_2NH_3NCS]^{2+}$ at 479 nm, corresponding closely to the maximum of the first quartet absorption band, gives proton uptake as the main reaction mode, with a quantum yield of 0.5, consistent with that for isothiocyanatopentaamminechromium(III) ion. Comparison of the measured proton uptake with the directly determined free ammonia shows, however, that only about 40% of the released base is ammonia, while the remainder is presumably due to the formation of a protonated monodentate ethylenediamine species. Thus it has been generally incorrect to assume that observation of ammonia aquation in the photolysis of acidopentaammine complexes indicates loss of the strong-field ligand on the weak field axis. In the particular complex studied here the weak-field axis is favored only by a factor of 2 over purely statistical loss of amine ligands. The significance of this result for the concept of weak-field axis labilization is discussed.

Introduction

In 1967 Adamson[1] proposed that the data then existing on the photoaquation mode of chromium(III) complexes could be rationalized in terms of loss of the strong-field ligand on the weak-field axis. This proposal caused some dispute[2-4] which continues to this day. The present status has been recently reviewed,[5] but to summarize one can say that there are only three known exceptions to the rule, two involving fluoride[4,6] and one oxalate,[7] both apparently ligands with a strong affinity for Cr(III).[8]

A pillar of support for the proposal[1] has been the data on the photolysis of acidopentaammine complexes, where observation of ammonia photolysis was taken to imply, or at least be consistent with, loss of the ammonia on the weak-field axis. A problem existed here with the observation that the products of these photolyses were largely or exclusively the *cis*-aquoacidotetraammines, but this subsequently seemed understandable in view of the observations of stereochemical change in studies of diacidotetraammine complexes.[5] However a few dissidents, including the writers, continued to maintain that there is no definite evidence to show that the photoaquation of acidopentaammines can be used in support of such a photolysis rule. For this reason it was suggested earlier[3] that this point could be settled only by study of the photolysis of a complex with a unique amine ligand in the trans position, such as *trans*-$Cr(NH_3)_4(^{15}NH_3)X]^{2+}$. Because of the difficulties involved in preparing, separating, and assigning the stereochemistry of such a species, the writers undertook to prepare the analogous $[Cr(en)_2NH_3X]^{2+}$ complexes recognizing that the photolyses of $[Cr(en)_3]^{3+}$ and $[Cr(NH_3)_6]^{3+}$ are sufficiently similar in quantum yield[9] to suggest that there would be no large intrinsic difference in the tendency for the complex to lose ammonia or ethylenediamine, other things being equal.

This paper reports the preparation, isolation, and characterization of such a complex, *trans*-$[Cr(en)_2NH_3NCS](NCS)_2$. It has been found that photolysis of this complex does not result in the loss exclusively of ammonia, although the photolysis mode and quantum yield parallel those of $[Cr(NH_3)_5NCS]^{2+}$.[10,11]

Experimental Section

Preparation of Complexes. *trans*-$[Cr(en)_2F_2]ClO_4$ was prepared by the method of Vaughn, *et al.*[12]

trans-$[Cr(en)_2Br_2]Br$ was prepared from $[Cr(en)_2F_2]ClO_4$ by the method of Fee, *et al.*[13] It was observed that a reaction time of about 12 hr was required and that yields were improved by using the same sample of concentrated HBr with up to three successive batches of $[Cr(en)_2F_2]ClO_4$.

trans-$[Cr(en)_2NO_2Br]ClO_4$ and *trans*-$[Cr(en)_2H_2OBr]ClO_4$ were prepared by the method of Fee, *et al.*[13]

trans-$[Cr(en)_2(NCS)Br]ClO_4$ was prepared by method of Fee, *et al.*,[13] except that the perchloric acid concentration was raised to 0.3 *M* to prevent the reaction mixture from becoming too weakly acidic. The reaction occurred in 2-4 hr, rather than overnight. The compound was recrystallized as the thiocyanate or perchlorate, by addition of the appropriate sodium salt.

$[Cr(en)_2NH_3NCS]XY$ was prepared by reaction of *trans*-$[Cr(en)_2(NCS)Br]ClO_4$ or *trans*-$[Cr(en)_2(NCS)Br]NCS$ with slightly acidic (ammonium perchlorate or thiocyanate) anhydrous ammonia. The latter was obtained by distillation *in vacuo* from a degassed solution of potassium in liquid ammonia. In a typical preparation 2 g of complex was placed together with a few small crystals of the relevant ammonium salt in a 100-ml Carius tube and evacuated on the vacuum system to about 10^{-4} Torr. About 20 ml of ammonia was then condensed onto the sample; the Carius tube was sealed and removed from the system. On allowing the reaction mixture to warm to room temperature the complex dissolved to give a ruby red solution which quickly turned orange (*ca.* 10 min). The mixture was then cooled to Dry Ice temperature, the tube opened, and the ammonia allowed to evaporate at its boiling point. The product was then evacuated for a while and stored in a vacuum desiccator overnight to remove most of the excess ammonia. This procedure gave a quantitative yield of crude $[Cr(en)_2NH_3NCS]^{2+}$, either as the bromoperchlorate, or bromothiocyanate, and appeared to contain about equal proportions of the cis and trans isomers. The complex obtained was contaminated with diisothiocyanatobis(ethylenediamine) impurities

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

[2] M. F. Manfrin, L. Moggi, and V. Balzani, *Inorg. Chem.*, **10**, 207 (1971).

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

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

[5] A. D. Kirk, *Mol. Photochem.*, **5**, 127 (1973).

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

[7] A. D. Kirk, K. C. Moss, and J. G. Valentin, *Can. J. Chem.*, **49**, 1524 (1972).

[8] One should perhaps now add thiocyanate to this list of exceptions as photolysis of *trans*-$Cr(en)_2(NCS)_2^+$ gives a significant yield of ethylenediamine aquation: C. Bifano and R. G. Linck, *Inorg. Chem.*, **13**, 609 (1974).

[9] V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, New York, N. Y., 1970, Chapter 7.

[10] E. Zinato, R. D. Lindholm, and A. W. Adamson, *J. Amer. Chem. Soc.*, **91**, 1076 (1969).

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

[12] J. O. Vaughn, O. J. Stvan, and V. E. Magnuson, *Inorg. Chem.*, **7**, 736 (1968).

[13] W. N. Fee, J. N. MacB. Harrowfield, and W. G. Jackson, *J. Chem. Soc. A*, 2612 (1970).

which are difficult to eliminate completely in the subsequent purification steps and which interfered in the later ammonia analyses. Attempts were made to avoid this problem by starting with the perchlorate salt. However this was not effective and introduced difficulties during the isomer separation, apparently due to the great solubility of the perchlorate salts.

Separation of *cis*- and *trans*-$[Cr(en)_2NH_3NCS]^{2+}$. Werner[14] separated the analogous cobalt isomers by fractional crystallization of the thiocyanate salts and trials showed this to work also for the chromium complexes.

Typically 1 g of crude complex was dissolved in a minimum of 40° acidified water (acetic acid), and 2–5 drops of 1 *M* NaNCS added. On standing and cooling slightly, needles of the *trans*-$[Cr(en)_2NH_3NCS](NCS)_2$, which is relatively insoluble, began to crystallize. Some care is required, however, if formation of oils is to be avoided. The thiocyanate concentration was then gradually raised and a number of successive fractions were taken off, typically four. It was found particularly difficult to obtain the quite soluble cis compound crystalline due to oiling out and only one separation in four attempts was really successful in this regard. The products were quite heat sensitive, readily transforming to the diisothiocyanato salts, and were therefore dried in a vacuum desiccator in the dark.

Characterization of Isomers of $[Cr(en)_2NH_3NCS](NCS)_2$. Figures 1–3 show the spectral and X-ray data upon which the characterization of the isomers of $[Cr(en)_2NH_3NCS](NCS)_2$ are based. These data were obtained on the unrecrystallized fractions 1 (A) and 3 (B) from the most successful fractional crystallization mentioned above.

Uv-Vis Spectra. In Figure 1, A and B are observed to share the same value for λ_{max} for the first quartet band, 476 nm, and have the same band shapes, but have markedly different extinction coefficients at the maximum, ((A) 80 and (B) 120 l. mol^{-1} cm^{-1}). This is consistent with the claim that they are cis and trans isomers of the type being discussed, that is, where all five amine functions are of the same ligand field strength. Thus one would not expect any difference in λ_{max} for cis and trans configurations of the NH_3 and NCS^- ligands. The difference in extinction coefficients, however, resides in the lower symmetry of the cis isomer and enables one to assign B (ϵ_{max} 120 l. mol^{-1} cm^{-1}) as the cis isomer and A (ϵ_{max} 80 l. mol^{-1} cm^{-1}) as the trans isomer. A parallel situation pertains in the analogous cobalt compounds[15] where *trans*-$[Co(en)_2NH_3NCS](NCS)_2$ has λ_{max} 490 nm and ϵ_{max} 164 l. mol^{-1} cm^{-1}, while *cis*-$[Co(en)_2NH_3NCS](NCS)_2$ has λ_{max} 490 nm and ϵ_{max} 220 l. mol^{-1} cm^{-1}.

The finding that the chromium complexes had λ_{max} at 476 nm was somewhat surprising in light of the fact that the analogous isothiocyanatopentaammine has λ_{max} 490 nm. At first this caused us to believe our product might be the isothiocyanatoaquo complex rather than the ammine. However, in addition to the other evidence presented here, no spectral changes occur on addition of base to the solution. Furthermore the value of 476 nm for λ_{max} is close to that expected theoretically for $[Cr(en)_2NH_3NCS]^{2+}$. Thus there is a question as to why isothiocyanatopentaammine has λ_{max} at 490 nm which seems somewhat low in energy.

Although not shown in Figure 1, the crude reaction product has λ_{max} 476 nm and ϵ_{max} 90–100 l. mol^{-1} cm^{-1}, showing that it is somewhere between 50 and 70% trans. This supports Bailar's contention[16] that the stereoretentive nature of Cr(III) thermal substitutions in aqueous solutions does not apply for reactions in liquid ammonia.

Infrared Spectra. Figure 2 shows the low-frequency region of the ir spectra of A and B. Elsewhere the spectra have the absorptions expected for $[Cr(en)_2NH_3NCS](NCS)_2$ and it is worth noting that absorptions due to H_2O are absent. The purpose of presenting this portion of the spectra is to consider the evidence relevant to isomer characterization.

Hughes and McWhinnie[17] have reported a criterion for distinguishing *cis*- and *trans*-diacidobis(ethylenediamine) complexes based on the number and position of the bands in the Cr–N stretching region from 350 to 650 cm^{-1}. Our system is potentially complicated by the presence of the additional Cr–N linkage due to the ammonia ligand. The above authors noted that all of the *cis*-$[Cr(en)_2XY]^+$ complexes examined show a pattern of four bands in the region of 550–350 cm^{-1}: one, strongly split, at 545 to 535 cm^{-1}, two strong bands at about 480 and 430 cm^{-1}, and a much weaker band at about 405 cm^{-1}. In contrast all except one or two trans complexes show only three bands in this region, at 540 (sometimes split), 490, and 440 cm^{-1}. Figure 2 shows that compound B has a split band at 561–544, strong bands at 494 and 434 cm^{-1}, and a weak band at 406 cm^{-1}, while compound A has only three bands at 557, 488, and 447 cm^{-1}. Except for the somewhat higher frequencies observed for our complexes the correspondence is excellent and supports the assignment of A as the trans and B as the cis complex. Compound B generally shows a more complex ir spectrum, consistent with its being the cis isomer.

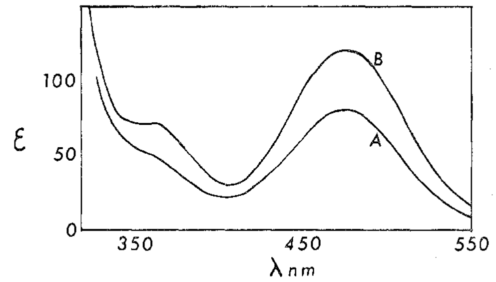

Figure 1. Uv spectra of isomers of $[Cr(en)_2NH_3NCS](NCS)_2$: A, fraction 1, λ_{max} 476 nm, ϵ_{max} 80 l. mol^{-1} cm^{-1}; B, fraction 3, λ_{max} 476 nm, ϵ_{max} 120 l. mol^{-1} cm^{-1}.

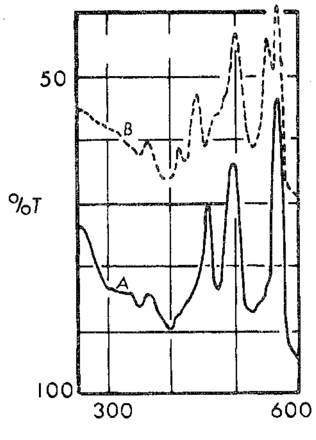

Figure 2. Infrared spectra of isomers of $[Cr(en)_2NH_3NCS](NCS)_2$: A, fraction 1; B, fraction 3.

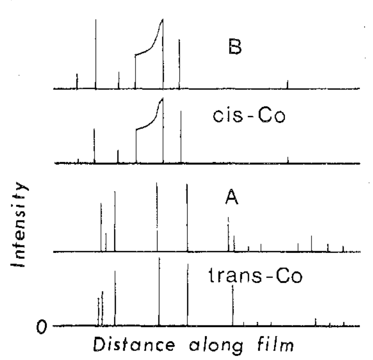

Figure 3. X-Ray powder photographs of isomers of $[Cr(en)_2NH_3NCS](NCS)_2$: A, fraction 1; B, fraction 3; trans-Co ≡ *trans*-$[Co(en)_2NH_3NCS](NCS)_2$; cis-Co ≡ *cis*-$[Co(en)_2NH_3NCS](NCS)_2$.

X-Ray Powder Photographs. Figure 3 shows a line drawing of the powder photographs of A and B and authentic samples of *cis*- and *trans*-$[Co(en)_2NH_3NCS](NCS)_2$, taken with copper Kα radiation. It is seen that very similar line patterns and intensities are given by B and the cis Co compound and by A and the trans Co compound, while the pairs are quite dissimilar. We take this as good evidence of the assignment of B as *cis*- and A as *trans*-$[Cr(en)_2NH_3NCS](NCS)_2$.

Preparation and Purification of *trans*-$[Cr(en)_2NH_3NCS](NCS)_2$. The early fractions from the fractional crystallizations of a total of about 4 g of crude $[Cr(en)_2NH_3NCS](NCS)_2$ were recombined and extracted several times with acetone to remove diisothiocyanato

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[14] A. Werner, *Ber. Deut. Chem. Ges.*, **44**, 876 (1911).

[15] D. A. Buckingham, I. I. Olson, and A. M. Sargeson, *J. Amer. Chem. Soc.*, **90**, 6654 (1968).

[16] J. C. Bailar, private communication.

[17] M. N. Hughes and W. R. McWhinnie, *J. Chem. Soc. A*, 592 (1967).

impurity. The remaining yellow-orange residue was recrystallized several times from acidified warm water to yield finally 0.6 g of purified *trans*-$[Cr(en)_2NH_3NCS](NCS)_2$. Chromatographic analysis (Technicon Autoanalyzer, 10 × 1 cm diameter, Dow CGC 241 column in the Na^+ form, 1-2 *M* NaCl gradient elution, H_2O_2 oxidation to CrO_4^- for detection colorimetrically at 380 nm) of this material showed it to be about 98% pure, the impurity being diisothiocyanato complex which could not be removed by further recrystallizations. Therefore this complex was used in the photochemical work.

Analysis was carried out by Chemanalytics, Tempe, Ariz. *Anal.* Calcd: C, 23.1; H, 5.3; N, 30.8; S, 26.5. Found: C, 23.07; H, 5.44; N, 30.78, S, 25.4. The complex had the infrared and uv-vis spectra reported above for A (Figures 1 and 2) except that careful determination of the molar absorptivity gave the value 77.0 l. mol^{-1} cm^{-1} at 476 nm.

Photolysis Apparatus and Procedure. Monochromatic light was obtained using a water-cooled A-H6 1000-W lamp with a heat-reflecting filter and 479-nm interference filter (Rolyn Corp.). Samples were photolyzed in 1-cm path length rectangular quartz spectrophotometer cells, with magnetic stirring. Two cells could be mounted in line to allow actinometry. All photolyses were at 20° in a water bath. pH was monitored continuously during a run, using a Metrohm EA147 microcombination electrode and Metrohm E388 potentiometric pH meter.

Actinometry was carried out using reineckate (*trans*-$[Cr(NH_3)_2(NCS)_4]^-$) solution contained in a cell behind the sample to measure the total transmitted quanta during irradiation. The quanta absorbed in the sample were calculated using the sample transmittance and a correction was applied for the transmittance of the reineckate solution at the irradiation wavelength. This procedure has been checked in these laboratories and gives results precise to within 2% (for sample transmittance of 0.3-0.7) and consistent with literature values for reineckate and chloropentaamminechromium(III) ions.

Ammonia Analysis. Ammonia analysis was carried out by coulometric titration with bromine as described by Christian, *et al.*[18] The supporting buffer used was prepared by mixing 800 ml of borate buffer, pH 8.60, with 600 ml of 5 *M* sodium bromide. A 15-ml amount of this solution with 25 ml of distilled water gave a blank titration of about 0.1 C. Constant current was obtained from a locally made supply (circuit diagram available on request), monitored continuously by a Dana digital multimeter, while the indicator electrode current was monitored by a Keithley 601c microammeter driving a strip chart recorder.

All titrations were carried out in a total of 40 ml of solution with 15 ml of buffer and with rapid stirring. The lower limit of detection of the method was set by the magnitude of the blank. This can, if necessary, be reduced by pretitration.[18] Calibration of the titration method using standard ammonium sulfate solution gave a linear calibration for titration time *vs.* ammonia over the range 0.5-10 μmol, with the slope of the line within 2% of the theoretical line for three electrons per ammonium ion. It is important to note that the titration is quite nonspecific, so that thiocyanate ion (six electrons), ethylenediamine (eight electrons), and chromium complexes (*e.g.*, 31 electrons for $[Cr(en)_2(NCS)_2]^+$) ideally should be absent from the solution before titration.

Run Procedures. A. Difference Spectrum. A solution of the thiocyanate salt of A at about 10^{-2} *M* was prepared at an ionic strength of 0.1 ($KClO_4$) and a pH of 3.0 ($HClO_4$). One-centimeter spectrophotometer cells filled with this solution were then used to run the base line on the 0-0.1 absorbance unit scale of a Cary 17 spectrophotometer. The spectrum of the sample solution was then run against the reference (dark) after repeated 10-min irradiation periods up to a total of 30 min. This corresponds to a total decomposition of about 15%.

B. Proton Uptake, Ammonia Release, and Quantum Yield Runs. A weighed sample (*ca.* 10 mg) of the thiocyanate salt was washed (2 ml of H_2O) through a 10-cm Amberlite IRA 400 column (ClO_4^- form) to remove the thiocyanate counterions. The eluent was mixed with 3.0 ml of 0.1 *M* $KClO_4$-2.50 × 10^{-3} *M* $HClO_4$ solution and the volume was made up to 6.0 ml. Tests showed that this procedure yielded a thiocyanate-free solution of perchlorate complex of ionic strength 0.05 and starting pH 2.97 ($[H^+] = 1.25 \times 10^{-3}$ *M*).

In runs to compare the yield of ammonia with the proton uptake, such a solution was divided in two, the first half being irradiated until the pH change indicated a suitable extent of photoaquation, the other being kept in the dark. The two solutions were then charged onto identical 2-cm columns of CGC241 resin (200-400 mesh) (Baker Analyzed) in the Na^+ form. The columns were then both washed with 20 ml of water to remove any free thiocyanate (solutions 1 and 2), with 15 ml of 0.7 *M* NaCl to elute any ammonium ion (solutions 3 and 4) (tests showed that some impurity eluted from the complex as well), and with a further 10 ml of 0.7 *M* NaCl to ensure that all ammonium ions had been eluted in the previous step (solutions 5 and 6). All six of these eluents were then titrated coulometrically. The free ammonia in the irradiated sample was calculated from the difference in the titers for the first 15 ml of sodium chloride eluents from the light and dark solutions (3 and 4), and the remaining titers served as checks that free thiocyanate and other photolysis products were not interfering with the free ammonia analysis. The impurity level of the complex was such that the ammonia yield and the impurity titer were about equal for 15% photodecomposition of complex, so that runs with less than about 5% photodecomposition could not be carried out with any degree of precision.

Results and Discussion

The evidence that the complex ion used in this study was truly *trans*-$[Cr(en)_2(NH_3)NCS]^{2+}$ has been presented in the Experimental Section.

As shown in Figure 1, the lowest energy quartet quartet absorption band of the compound is broad, with a maximum in absorptivity at 476 nm. The band shows no features associated with a large splitting of the ^4E and ^4B components and this is parallel to the behavior shown by the acidopentaammine complexes. An irradiation wavelength of 479 nm was selected for the photochemical study as this favors absorption into the ^4E component of the band but is near enough to the maximum to avoid problems with secondary photolysis which would occur to a greater extent at longer wavelengths. On irradiation of acidic solutions of the complex at this wavelength and at 20° the observed photoreaction is loss of base, with consequent proton uptake. The quantum yield for thiocyanate release was observed to be small. These observations are to be anticipated by analogy with the isothiocyanatopentaammine complex for which $\phi_{H^+} = 0.47$ and $\phi_{SCN^-} = 0.02$ at 25° and 492 nm.[10] Several measurements of the quantum yield of proton uptake for *trans*-$[Cr(en)_2NH_3NCS]^{2+}$ gave values in the range 0.47-0.52 in good agreement with expectations.

The central undertaking in this work was to determine whether the loss of amine ligand was confined exclusively to that trans to the isothiocyanate ligand. Comparison of the yield of free ammonia with the proton uptake yield is shown for several runs in Table I. The project was made more difficult by the impurity problems outlined earlier and uncertainties in the corrections for these are largely responsible for the scatter. The data show clearly, however, that in no case are the two yields equal, but the ammonia yield is only 35-45% of the total base released. There does seem to be a trend in the data toward a higher percentage ammonia for low conversions. This could be due to an underestimation in the impurity correction which is relatively much larger for the low-conversion results, or it may reflect secondary photolysis of a product having a lower ammonia quantum yield. In view of this uncertainty it will be assumed in the ensuing discussion that 40 ± 10% of the base released is ammonia. This finding is in contrast to our earlier report of preliminary results[5] on a compound of unestablished stereochemistry. Those results were in error both because the complex was an impure isomer mixture and because the ammonia release data were obtained by inaccurate methods. The earlier report should therefore be disregarded.

The conclusion is that at least this compound does not obey the rule of loss of the strong field, or strong σ-donor lig-

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[18] G. O. Christian, E. C. Knoblack, and W. C. Purdy, *Anal. Chem.*, **35**, 2217 (1963).

Table I. Photolysis of *trans*-$[Cr(en)_2NH_3NCS]^{2+}$ (λ 479 nm, Temperature 20°, $[H^+] = 1.25 \times 10^{-3}$ *M*, $\mu = 0.05$)

$10^2 \times$ [complex], *M*	% photolyzed	Base released (H^+ uptake), μmol	NH_3 found, μmol	% NH_3
1.06	17	2.65	0.86	33
1.15	15	2.67	1.01	38
0.83	13	1.63	(0.81)[a]	(50)[a]
1.10[b]	11	1.9	(0.93)[a]	(49)[a]
1.48[b]	9	1.95	(0.66)[a]	(33)[a]
1.04	3	0.81	0.36	44

[a] In these runs the impurity correction was calculated, not measured. [b] In these runs $[H^+] = 8.6 \times 10^{-4}$ *M* and $\mu = 0.033$.

and on the weak-field axis, with any degree of exclusivity. Comparison of the amine quantum yield for $[Cr(en)_3]^{3+}$ ($\phi = 0.37$) and $[Cr(NH_3)_6]^{3+}$ ($\phi = 0.29$) under similar photolysis conditions suggests that there would be no large preference for loss of ethylenediamine or ammonia per se. If the isothiocyanate ligand played no role, so that the complex showed no preferential activation of any particular axis or plane but all bonds were equally affected by excitation, then one would expect statistical loss of amine, *i.e.*, 20% ammonia, 80% ethylenediamine (or 17%, 83% if weighted according to the above quantum yields for $[Cr(en)_3]^{3+}$ and $[Cr(NH_3)_6]^{3+}$).

The 40% figure found here could thus be interpreted as showing that the weak-field axis is labilized to an extent equivalent to a favoring of the NH_3 ligand by a factor of 2, or slightly more. This interpretation suggests that the phenomenon of weak field axis labilization may play a role, but by no means to the extent that it is exclusive. By analogy one could argue that in the analogous pentaammine, also, loss of the trans ammonia is favored only by a factor of about 2.

This is only one possible interpretation of the results. It is also possible that the effect might reside in a trans group labilization of amine by thiocyanate without any preferential population of the d_{z^2} orbital in the excited state. However, either way the main result is clear; the photolysis rule is only marginally correct, if at all, in this complex. It is probable that, in terms of σ-donor strength of the ligands, this particular complex is quite "octahedral-like" and that the weak-field axis labilization effects might, with the wisdom of hindsight, be expected to be small. The same is likely to be true for *trans*-$[Cr(en)_2NH_3F]^{2+}$, another strong σ-donor "weak-field ligand," and for this reason and because of the fact that our findings open up a new direction for study, we are now preparing and isolating *trans*-$[Cr(en)_2NH_3X]^{2+}$ for $X^- = F^-, Cl^-$, and Br^-. It is our expectation that the trans ammonia yields will be higher in the latter two complexes.

In summary it is clear that the studies of $[Cr(en)_2F_2]^+$,[4] $[Cr(en)_2FCl]^+$,[6] $[Cr(en)_2(NCS)_2]^+$,[8] $[Cr(en)_2NCSCl]^+$,[19] and $[Cr(en)(ox)_2]^-$ [7] and now the present work have thrown considerable doubt on the utility of Adamson's simple criteria for the prediction of photolysis modes. It now appears that, in addition to the problem of separating out the σ- and π-bonding effects for a given ligand,[6] one must also be concerned with the extent to which weak-field axis labilization can be said to occur at all before attempting to predict the photolysis mode.

Because of the specific information obtainable by study of $[Cr(en)_2NH_3X]^{2+}$ complexes we are continuing work on these compounds as indicated above. Of particular interest to us are the comparisons of photoaquation modes for various X groups and the wavelength and temperature dependence of the relative ammonia yields.

As a final comment on the complexity of these systems our work on the difference spectrum due to the product should be mentioned. Early in this study difference spectral runs were carried out. The results were very similar indeed to those obtained for the analogous *trans*-isothiocyanatopentaamminechromium(III) ion, for which, both we[5] and Riccieri and Zinato[11] had concluded, *cis*-isothiocyanatoaquo complex was the main product (*ca.* 95%). Initially it appeared from the difference spectrum for *trans*-$[Cr(en)_2NH_3NCS]$ photolysis that the product was at least 80% *trans*-$[Cr(en)_2H_2ONCS]^{2+}$. However, later results clearly deny this simple product mixture in view of our finding of 60% ethylenediamine photolysis. The products can thus be expected to be *cis*-$[Cr(en)_2H_2ONCS]^{2+}$ and an isomer mixture of $[Cr(en)(enH)H_2O(NH_3)NCS]^{3+}$ as a minimum. This is recounted to indicate how misleading interpretations based on such a crude measure as the difference spectrum can be. We hope in the future to find better methods for product identification in these more complicated systems.

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Registry No. *cis*-$[Cr(en)_2NH_3NCS](NCS)_2$, 51108-57-7; *trans*-$[Cr(en)_2NH_3NCS](NCS)_2$, 51157-26-7.

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(19) M. T. Gandolfi, M. F. Manfrin, L. Moggi, and V. Balzani, *J. Amer. Chem. Soc.*, 94, 7152 (1972).