

to water activity, the structure of the micellar aggregate and the interactions therein influence the catalytic efficiency of these systems.

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## Stereochemistry of the Photoaquation of Chloropentaamminechromium(III)

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**Abstract:** The  $\text{Cr}(\text{NH}_3)_4(^{15}\text{NH}_3)\text{Cl}^{2+}$  complex ion has been prepared, isotopically labeled either trans or cis relative to chloride, and has been photolyzed at two different excitation wavelengths. The  $^{15}\text{N}/^{14}\text{N}$  ratio of photoaquated ammonia was determined by means of proton magnetic resonance spectra. At 503 nm ( $^4\text{A}_{2g} \rightarrow ^4\text{T}_{2g}$  transition) at least 75% of  $\text{NH}_3$  is photoreleased from the position trans to chloride, *i.e.*, on the weak average-field axis, while only 40 to 50% of  $\text{NH}_3$  labilized at 254 nm (CT transition) was originally trans to  $\text{Cl}^-$ . The configuration of the photoproduct, *cis*- $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}^{2+}$ , shows that the photoreaction, upon d-d band irradiation, involves stereochemical change, a feature which now appears to be general for chromium(III) complexes.

Several  $\text{Cr}(\text{NH}_3)_5\text{X}^{2+}$  type complex ions, with  $\text{X} = \text{Cl},^2 \text{NCS},^3 \text{Br},^4 \text{N}_3,^5$  and  $\text{RCOO},^6$  have been investigated photochemically. The main photoreaction mode upon ligand-field band irradiation is known to be ammonia release while in the dark only the aquation of the acido group, X, is observed.<sup>7</sup> This photochemical behavior is typically "antithermal" and is predictable by a set of semiempirical rules.<sup>8</sup> These state that in mixed-ligand chromium(III) complexes (i) labilization occurs along the axis of the octahedron having the smallest average crystal field and (ii) if the labilized axis contains two different ligands, the one of greater field strength is preferentially aquated. The type of labilization is consistent with the population of the lower lying  $\sigma$  antibonding orbital in the lowest excited quartet state.<sup>9</sup> The principal photoproduct,  $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})\text{X}^{2+}$ , was found to have a cis configuration.<sup>2a, 4, 6, 10</sup> The latter result has given rise to some discussion about the usefulness of the rules.<sup>10, 11</sup> At least three views may be (and have been) taken: (a) the rules imply no more than the data upon which they were constructed, namely that one thereby is

able to predict the type of ligand which is predominantly labilized toward substitution, for example, ammonia in the case of  $\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$ ; (b) the rules specify which actual ligand (if two or more are the same) is labilized, for example, the trans ammonia in the above case; (c) the rules imply not only b but also that the substitution process is stereoretentive, for example, that the product will be *trans*- $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}^{2+}$ . This last view turns out to be an unwarranted mechanistic interpretation. Not only is the cis product obtained in the case of  $\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$  but also with  $\text{Cr}(\text{NH}_3)_5(\text{NCS})^{2+}$ .<sup>12</sup> An important further observation is that *trans*- $\text{Cr}(\text{en})_2\text{Cl}_2^+$  photolyzes primarily to *cis*- $\text{Cr}(\text{en})_2(\text{H}_2\text{O})\text{Cl}^{2+}$ <sup>13</sup> and that the corresponding pattern of behavior applies to the *trans*- $\text{Cr}(\text{en})_2\text{XY}$  family generally<sup>13, 14</sup> and to *trans*- $\text{Cr}(\text{NH}_3)_4\text{XY}$  complexes,<sup>15</sup> that is that the X and/or Y acido group is labilized and that the product is cis. The last group of results does suggest, however, that interpretation b of the rules is valid.

In view of the isomerization that is observed, it was suggested<sup>11</sup> that for Cr(III) ammine complexes change in configuration might be a common photochemical feature, in contrast to the stereoridity of the thermal substitution process.<sup>7, 16</sup> Certainly, the importance of mechanism in the excited-state reaction is indicated by the photoinertness of *trans*- $\text{Cr}(\text{cyclam})\text{Cl}_2^+$ .<sup>17</sup> It appears that the implicated ligand field excited state (probably the first quartet excited state) is reactive only if stereomobility is possible.

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The present investigation was undertaken to determine if interpretation b of the rules would meet a more severe test than that provided by the *trans*-Cr(en)<sub>2</sub>XY series. In this series the labilized ligand occurs only on the weak-field axis so that the behavior is equally predicted under interpretation a or b. In the case of the Cr(NH<sub>3</sub>)<sub>5</sub>X<sup>2+</sup> family, however, a distinction is possible, since under b only the ammonia trans to the X<sup>-</sup> group should be photoaquated. We have chosen Cr(NH<sub>3</sub>)<sub>5</sub>Cl<sup>2+</sup> as an already well studied member of this family, and the experimental approach of determining the <sup>15</sup>N/<sup>14</sup>N ratio for the ammonia released from isotopically labeled complex. Two labeling paths have been used and irradiations have been made both in the region of the first ligand field (L<sub>1</sub>) band and at 254 nm (or the edge of the first charge transfer, CT, band).

### Experimental Section

**Preparation of Complexes.** *trans*-[Cr(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>](ClO<sub>4</sub>) was prepared according to a described procedure by cleavage of *trans*-(NH<sub>3</sub>)<sub>5</sub>Cr(OH)Cr(NH<sub>3</sub>)<sub>4</sub>Cl<sup>4+</sup> with concentrated HCl.<sup>18</sup> The maxima of the absorption spectrum are at 590 nm (ε 25), 470 nm (ε 15) and 397 (ε 29), in agreement with the literature.<sup>19</sup>

[Cr(NH<sub>3</sub>)<sub>4</sub>(<sup>15</sup>NH<sub>3</sub>)Cl]Cl<sub>2</sub> (A). **Reaction of *trans*-[Cr(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>](ClO<sub>4</sub>) with Liquid <sup>15</sup>NH<sub>3</sub>.** Ammonia was handled by a vacuum-line technique. A 0.29 g portion (1 mmol) of finely powdered *trans*-dichlorotetraamminechromium(III) perchlorate was mixed with ca. 22 mmol of <sup>15</sup>NH<sub>3</sub> (500 ml of STP, Bio-Rad, 99.2% <sup>15</sup>N atom content) in a 3-ml Pyrex reaction tube which was sealed. The green slurry was kept at 40° for 1 hr in the dark. The mixture turned into a deep-red solution and a red precipitate separated. Unreacted <sup>15</sup>NH<sub>3</sub> was then transferred directly into another reaction tube containing another portion of starting material, for a subsequent preparation. It was possible to repeat this procedure several times using only ca. 0.4 ml of liquid <sup>15</sup>NH<sub>3</sub>. The solid residue consisted of ~35% unreacted starting complex, ~50% [Cr(NH<sub>3</sub>)<sub>4</sub>(<sup>15</sup>NH<sub>3</sub>)Cl](ClO<sub>4</sub>), and ~15% [Cr(NH<sub>3</sub>)<sub>4</sub>(<sup>15</sup>NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>](ClO<sub>4</sub>). The mixture was treated first with 50 ml of methanol (which dissolved the dichloro complex), then with 25 ml of 1 M HCl in which the hexaammine ion is very soluble while Cr(NH<sub>3</sub>)<sub>5</sub>Cl<sup>2+</sup> is virtually insoluble. The residue was recrystallized, with 95% recovery, by dissolving 0.1 g in 20 ml of 10<sup>-3</sup> M HClO<sub>4</sub>, filtering, and adding dropwise 5 ml of 5 M HCl while the mixture was kept in an ice bath. The crystalline [Cr(NH<sub>3</sub>)<sub>4</sub>(<sup>15</sup>NH<sub>3</sub>)Cl]Cl<sub>2</sub> was filtered off, washed with ethanol and ether, and vacuum dried. *Anal.* Calcd for Cr(NH<sub>3</sub>)<sub>4</sub>(<sup>15</sup>NH<sub>3</sub>)Cl<sub>2</sub>: Cr, 21.26; NH<sub>3</sub>, 35.23. Found: Cr, 21.2; NH<sub>3</sub>, 34.9. The visible absorption spectrum shows maxima at 512 nm (ε 36) and at 375 (ε 38), as reported in the literature.<sup>20</sup> The <sup>14</sup>NH<sub>3</sub>/<sup>15</sup>NH<sub>3</sub> ratio (*vide infra*) was 3.95 ± 0.05.

*cis*-[Cr(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)Cl](ClO<sub>4</sub>)<sub>2</sub> was obtained by reaction of oxalatotetraamminechromium(III) perchlorate with 12 M HCl for 15 min at 50°. The precipitated chloride salt was converted into the perchlorate with concentrated HClO<sub>4</sub>, eliminating ionic chloride as HCl gas.<sup>19</sup> The spectral absorption bands occur at 519 nm (ε 39) and at 384 nm (ε 33) in accordance with reported data.<sup>19</sup>

[Cr(NH<sub>3</sub>)<sub>4</sub>(<sup>15</sup>NH<sub>3</sub>)(H<sub>2</sub>O)](ClO<sub>4</sub>)<sub>3</sub>. **Reaction of *cis*-[Cr(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)Cl](ClO<sub>4</sub>)<sub>2</sub> with Liquid <sup>15</sup>NH<sub>3</sub>.** The general procedure and the amounts of reagents employed were as in the preparation of A. In this case a dark red solution was formed and replacement of coordinated chloride by <sup>15</sup>NH<sub>3</sub> was virtually completed after ca. 20 min at 40°. The water ligand is deprotonated but not displaced by ammonia. The deep purple solid residue, consisting of hydroxopentaamminechromium(III) salt, was dissolved in 10 ml of 0.1 M HClO<sub>4</sub>. The solution was filtered, cooled, and dropwise added an excess of concentrated HClO<sub>4</sub>. The precipitated [Cr(NH<sub>3</sub>)<sub>4</sub>(<sup>15</sup>NH<sub>3</sub>)(H<sub>2</sub>O)](ClO<sub>4</sub>)<sub>3</sub> was collected, washed with ethanol

and ether, and air-dried. The overall yield was 88%. The maxima of the absorption bands are at 483 nm (ε 35) and at 360 nm (ε 30), respectively, in literature agreement.<sup>22</sup> The <sup>14</sup>N/<sup>15</sup>N ratio (*vide infra*) was 3.77 ± 0.07.

[Cr(NH<sub>3</sub>)<sub>4</sub>(<sup>15</sup>NH<sub>3</sub>)Cl]Cl<sub>2</sub> (B) was synthesized, with 80% yield, by chloride anation of labeled aquopentaamminechromium(III) perchlorate in concentrated HCl, and then recrystallized, as described elsewhere.<sup>23</sup> *Anal.* Calcd for Cr(NH<sub>3</sub>)<sub>4</sub>(<sup>15</sup>NH<sub>3</sub>)Cl<sub>2</sub>: Cr, 21.26; NH<sub>3</sub>, 35.23. Found: Cr, 21.4; NH<sub>3</sub>, 35.1. The visible absorption spectrum is identical with that of A, showing maxima at 512 nm (ε 36) and at 375 nm (ε 38).

**Oxalatotetraamminechromium(III) perchlorate derivatives of A and B** were prepared by dissolving 0.1 g either of chloropentaamine or of aquopentaamine complex in 2 ml of water, adding 0.2 g of oxalic acid and 0.1 g of NaClO<sub>4</sub>, and keeping the mixture at 90° for 15 min. An orange-red solid began to separate from the hot solution and precipitation was completed by cooling to room temperature. The product was filtered off, washed with ethanol and ether, and air-dried. The position of the absorption maxima (502 and 374 nm) and their intensity ratio (0.81) agree with the literature,<sup>24</sup> while the apparent extinction coefficients are ~30% smaller, due to the coprecipitation of sodium oxalate. However, the presence of this salt is not an inconvenience in the determination of the ammonia isotope ratio.

**Photolysis Procedures.** Photolyses with both visible and uv light were carried out using 27-ml samples, ~1.2 × 10<sup>-2</sup> M in complex, in 10<sup>-2</sup> M HClO<sub>4</sub>. The solutions were magnetically stirred; the temperature was 18 ± 1° and the reaction time 80 and 60 min, respectively.

Irradiation in the d-d absorption region was accomplished using a 900-W high pressure xenon lamp and the filter combination: B1 750, CS 4-96, CS 3-73, which gave a band centered at 503 nm (T = 70%, 15 nm half-width). Light intensity was determined by reineckate actinometry<sup>25</sup> and was ~3 × 10<sup>-18</sup> einstein sec<sup>-1</sup>. The samples were photolyzed in a 10-cm spectrophotometer cell so that light absorption was complete (ε<sub>503</sub> 35).

For the uv irradiation a low-pressure, pen-type mercury source (Ultra-Violet Products, Inc.) was immersed in the solution of the complex, contained in a 2-cm diameter quartz test-tube, wrapped with aluminum foil. No filters were needed since 97% of the lamp emission occurs at 254 nm. The absorbed intensity (ε<sub>254</sub> 15) was ~4 × 10<sup>-8</sup> einstein sec<sup>-1</sup> and was measured using non-labeled Cr(NH<sub>3</sub>)<sub>5</sub>Cl<sup>2+</sup> as an actinometer and determining the released NH<sub>3</sub>.

**Analytical Procedures.** Separation of free NH<sub>3</sub> from photolysis mixtures was accomplished by an ion-exchange technique. Photolyzed samples were adsorbed in a 3 × 1 cm column of AG 50W-X4 Bio-Rad cation-exchange resin (100-200 mesh) in the hydrogen form, which had previously been washed with 3 M HCl and then treated with 0.5 M HCl. Elution with 50 ml of 0.5 M HCl displaced all the NH<sub>4</sub><sup>+</sup> ion, while all chromium(III) complexes were retained in the column.

The absolute ammonia content either of a solid sample, or of a photolysis eluate was determined by a semimicro Kjeldahl analysis, distilling NH<sub>3</sub> from the solutions made alkaline.

<sup>15</sup>NH<sub>3</sub>/<sup>14</sup>NH<sub>3</sub> ratios were measured by means of the NH<sub>4</sub><sup>+</sup> proton resonance spectra. Samples were prepared by distilling ammonia from solutions made alkaline and collecting it into a test tube containing a suitable amount of HCl. It was found that all NH<sub>3</sub> was recovered in ca. 12 ml of distillate. The latter was then concentrated to a 0.3-0.4 ml volume in a vacuum desiccator over Drierite. The procedure was the same with the above eluates and with solid compounds. The amounts of complexes, of photolyzed NH<sub>3</sub> and of HCl were such that the final concentrations were [NH<sub>4</sub><sup>+</sup>] = 0.2-0.6 M and [HCl] = 1-2 M.

The proton resonance spectra were recorded at 26° by Varian T 60 and Varian DA 60 1 nmr spectrometers. The absorption spectra were measured by Cary 14 recording spectrophotometer.

### Results

**Reactions in Liquid NH<sub>3</sub>.** Little is known in the literature about ammonation of acidoammine complexes

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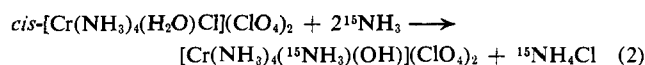
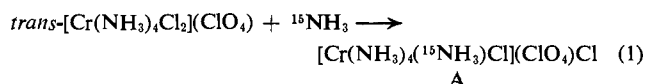
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Table I. Ammonia Isotopic Ratios

	$(^{15}\text{N}/^{14}\text{N})_{\text{obsd}}$	$(^{15}\text{N}/^{14}\text{N})_{\text{corr}}$	$z^a$
A	$0.253 \pm 0.003$	0.250	$0.0025 \pm 0.0025$
B	$0.267 \pm 0.005$	0.250	$0.013 \pm 0.004$
oxA <sup>b</sup>	$0.257 \pm 0.008$		
oxB <sup>b</sup>	$0.252 \pm 0.009$		
Photoreleased $\text{NH}_3$			
From A at 503 nm	$0.972 \pm 0.028$	$\alpha = 0.966 \pm 0.033$	
From A at 254 nm	$0.445 \pm 0.016$	$\gamma = 0.441 \pm 0.019$	
From B at 503 nm	$0.077 \pm 0.003$	$\beta = 0.063 \pm 0.007$	
From B at 254 nm	$0.189 \pm 0.003$	$\delta = 0.174 \pm 0.008$	

<sup>a</sup> Fraction of exchange in the unlabeled positions. <sup>b</sup> Oxalate derivatives of A and B.

of chromium(III). Chloropentaamminechromium(III) has been reported to react with liquid ammonia, in sealed tube, at room temperature, to yield  $\text{Cr}(\text{NH}_3)_6^{3+}$ ; the higher the solubility of the complex salt, the faster the reaction, which is catalyzed by sodamide.<sup>26</sup> Our qualitative observations on the reactions are in agree-



ment with the above report. Reaction 2 appears to be faster than reaction 1, consistent with a higher solubility in liquid ammonia for *cis*-aquochlorotetraamminechromium(III) perchlorate than for *trans*-dichlorotetraamminechromium(III) perchlorate. Also, a semi-quantitative comparison with the rate constants for chloride release in aqueous acid solution for both complexes<sup>18</sup> shows that ammoniation is much faster than aquation.

As mentioned in the Experimental Section, several preparations could be made using a relatively small volume of liquid  $^{15}\text{NH}_3$ , since each batch involved the consumption of *ca.* 5% of the solvent. In both reactions no volatile product was formed and unreacted  $^{15}\text{NH}_3$  was recovered uncontaminated and directly used for other preparations. While hydroxopentaamminechromium(III) is the end product of reaction 2, reaction 1 represents an intermediate stage in the stepwise replacement of coordinated chloride by  $^{15}\text{NH}_3$ , ending with  $\text{Cr}(\text{NH}_3)_4(^{15}\text{NH}_3)_2^{3+}$ .<sup>26</sup> Preliminary tests (with regular  $\text{NH}_3$ ) were carried out in order to establish the conditions for a fair yield of chloropentaamminechromium(III) with the minimum loss of  $^{15}\text{NH}_3$  due to successive ammoniation to hexaammine.

Another problem arose from the possibility of exchange between  $^{15}\text{NH}_3$  solvent and coordinated  $\text{NH}_3$ . The only chromium(III) complex for which  $\text{NH}_3$  exchange studies have been reported is  $\text{Cr}(\text{NH}_3)_6^{3+}$ .<sup>27-29</sup> The exchange rates were investigated over a variety of conditions, and the half-times at 20° were found to range between *ca.* 5 and 700 hr.<sup>29</sup> Even though these results do not necessarily apply to  $\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$ , the rate of exchange was expected to be considerably smaller than that of chloride replacement. This was,

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in fact, the observation. The  $^{15}\text{N}/^{14}\text{N}$  experimental ratios in the  $\text{Cr}(\text{NH}_3)_4(^{15}\text{NH}_3)\text{Cl}^{2+}$  ions are shown in Table I. They are close to the theoretical value, 0.250, and the amount of exchange for each nonlabeled  $\text{NH}_3$  ligand was 0.25 and 1.3% in A and B, respectively. Thus the  $^{15}\text{N}$  content of the ammonia solvent (initially 99.2%) decreased at the most by 0.1–0.3% in each preparation. No correction was then necessary for dilution with normal  $\text{NH}_3$ , the differences being with experimental error.

A point of interest is the geometrical configuration of the products of reactions 1 and 2. The present investigation provides the first information about the stereochemical behavior of chromium(III) complex ions in liquid ammonia. While Cr(III) substitution reactions in aqueous solution generally occur with retention of configuration,<sup>7,16</sup> it is not safe to assume that the same is true in  $\text{NH}_3$ . It is known that in different solvents, such as DMF and DMSO, changes in configuration may take place.<sup>30</sup> For this reason the A and B species have not been designated *a priori* as *trans* and *cis*. Our results (*vide infra*) show, in fact, that both reactions 1 and 2 are accompanied by stereochemical change, yielding two different—but definite—mixtures of *trans* and *cis* labeled compounds. Starting from *trans*- $\text{Cr}(\text{NH}_3)_4\text{Cl}_2^{2+}$  only 49 to 61% of  $^{15}\text{NH}_3$  is found to be in *trans* position to chloride in the chloropentaammine product, whereas the reaction of *cis*- $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}^{2+}$  is more stereospecific, being the configuration retained by at least 94%. In water, instead, at least 92% of the aquation product of the *trans*-dichloro complex is *trans*.<sup>18</sup> Stereomobility may therefore be usual for Cr(III) ions in ammonia solvent.

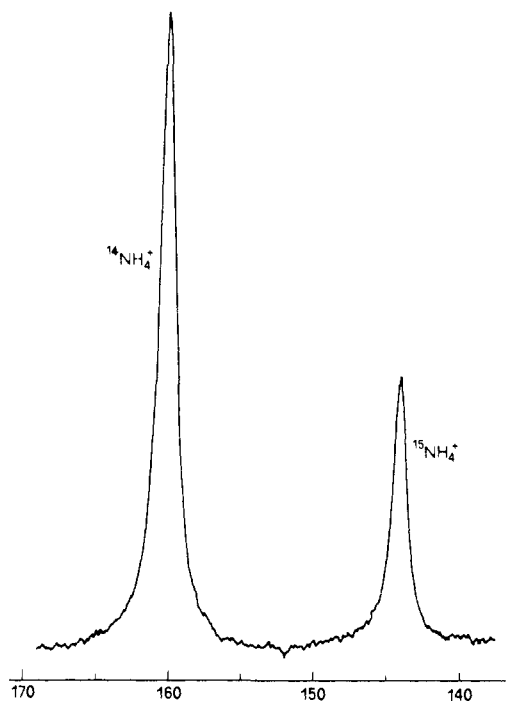
Also the reaction of *trans*- $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}^{2+}$  with liquid  $\text{NH}_3$  was preliminarily investigated and like reaction 2 it was found to produce hydroxopentaamminechromium(III).

**Photolyses.** The photochemistry of chloropentaamminechromium(III) has been accurately investigated.<sup>2</sup> The only thermal reaction is one of chloride aquation with a rate constant of  $3.7 \times 10^{-6} \text{ sec}^{-1}$  at 18°.<sup>31</sup>

Irradiation of the  $L_1$  and  $L_2$  absorption bands ( $^4A_{2g} \rightarrow ^4T_{2g}$  and  $^4A_{2g} \rightarrow ^4T_{1g}$  transitions, respectively, in  $O_h$  approximation) produces ammonia photoaquation with  $\phi_{\text{NH}_3} = 0.35\text{--}0.40^{2a}$  and, to a much smaller extent, chloride photorelease with  $\phi_{\text{Cl}} = 0.005\text{--}0.007$ .<sup>2b</sup> The main photoreaction product is *cis*- $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}^{2+}$ .<sup>10</sup> In the uv region  $\phi_{\text{Cl}}$  increases to 0.3 at 254 nm, while

(30) See, for example, D. A. Palmer and D. W. Watts, *Inorg. Chim. Acta*, **6**, 197 (1972), and references therein.

(31) Extrapolated value from ref 20.



**Figure 1.** A detail of the 60-MHz proton magnetic resonance spectrum of a solution of  $^{14}\text{NH}_4^+$  and  $^{15}\text{NH}_4^+$  in the 4:1 ratio (reference water 0.0 ppm).

$\phi_{\text{NH}_3}$  remains virtually unchanged,<sup>2</sup> and the mechanism of chloride photoaquation may be different from that postulated for the visible.<sup>2,4</sup>

Both A and B were photolyzed at two different excitation wavelengths. The purpose was to find out whether the steric distribution of the labilized ammonia ligands upon charge-transfer irradiation is different from that relative to d-d excitation although the overall  $\phi_{\text{NH}_3}$  is the same.

The reliability of the analytical procedure was checked by performing some total  $\text{NH}_3$  quantum yield determinations at 503 nm.  $\phi_{\text{NH}_3}$  was found to match the previously reported value of 0.37.<sup>2a</sup> The extent of  $\text{NH}_3$  photorelease was  $\sim 15$  and  $\sim 10\%$  at 503 and at 254 nm, respectively, such that in each run an amount of free  $\text{NH}_3$  (0.05–0.03 mmol) suitable for the isotopic analysis, was produced. The reason for a smaller percentage at 254 nm was that in the uv region the total reaction is more extensive, since a comparable amount of chloride simultaneously photoaquates. Secondary photolyses were negligible under these conditions. The temperature of  $18^\circ$  was sufficiently low that the effect of any thermal aquation reaction of  $\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$ ,<sup>20</sup> *cis*- $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}^{2+}$ ,<sup>18</sup> and  $\text{Cr}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$ ,<sup>22</sup> could be disregarded within the photolysis time.

It seemed appropriate to use a sample of nonlabeled  $\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$  as an actinometer at 254 nm with  $\phi_{\text{NH}_3} = 0.37$ ,<sup>2</sup> since the photochemical behavior has been well characterized at this wavelength.

**Determination of the  $^{15}\text{N}/^{14}\text{N}$  Ratios.** The measurement of the nitrogen isotopic distribution was based upon the difference between the proton magnetic resonance spectra of labeled and unlabeled ammonia in aqueous acid solution. A different N–H nuclear spin–spin interaction gives rise to three adsorption

peaks in the spectrum of  $^{14}\text{NH}_4^+$  ( $^{14}\text{N}$  has a nuclear spin  $I = 1$ ) while the proton resonance spectrum of  $^{15}\text{NH}_4^+$  consists of two peaks (the  $^{15}\text{N}$  nuclear spin is  $I = 1/2$ ).<sup>33</sup>

The most laborious step was the preparation of the  $\text{NH}_4^+$  samples (see Experimental Section) of a concentration such as to minimize the noise-to-signal ratio in the spectra (less than 5% in the most unfavorable cases). The acidity of the solution was such that no excessive broadening of the absorption lines occurred, due to proton exchange with the solvent water. The proton resonance of  $\text{H}_2\text{O}$  was used in reference. Generally, only a portion of the spectrum, containing one  $^{14}\text{NH}_4^+$  peak and one  $^{15}\text{NH}_4^+$  peak was scanned with high resolution. A typical nmr spectrum is shown in Figure 1. The relative amounts of  $^{15}\text{N}$  and  $^{14}\text{N}$  were evaluated from the ratios of the peak areas (each  $^{15}\text{NH}_4^+$  peak is more intense than each  $^{14}\text{NH}_4^+$  peak by a factor 1.5). The areas were independently measured by weight, by electronic integration, and geometrically, the last method appearing as the most precise one. The average deviation was 2–4%. The observed  $^{15}\text{N}/^{14}\text{N}$  ratios for the chloropentaammine complexes A and B and for their oxalato derivatives are reported in Table I, together with the fractions  $z$ , of  $^{14}\text{N}$  replaced by  $^{15}\text{N}$  due to exchange, and evaluated from

$$(^{15}\text{N}/^{14}\text{N})_{\text{obsd}} = (1 + 4z)/(4 - 4z) \quad (3)$$

As already mentioned, the amount of exchange in both complex ions is not extensive; for A it is within the limits of experimental error.

Table I shows also the observed isotopic ratios in  $\text{NH}_3$  released upon visible and uv photolysis of A and B, respectively; as well as the values corrected for exchange according to

$$(^{15}\text{N}/^{14}\text{N})_{\text{corr}} = (^{15}\text{N}/^{14}\text{N})_{\text{obsd}}(1 - z) - z \quad (4)$$

It is immediately evident that the distribution of the photolabilized  $\text{NH}_3$  ligands is different in each type of photolysis.

The visible photolysis of A was carried out twice, and the results were in excellent agreement. The emphasis, however, was on having several independent nmr measurements (under different conditions and using two different instruments) on a given photolysis sample, rather than on repeated photolyses (which might improve the determination of the absolute amounts of released ligands, but not particularly the isotopic ratios).

**Treatment of Data.** As mentioned above, no data appear to have previously been reported in the literature about the stereochemical course of chromium(III) solvolysis in liquid ammonia. Therefore the possibility of scrambling of the ammonia ligands could not be ruled out.  $^{15}\text{NH}_3$  may be partially coordinated in a position different from that pertaining to the displaced chloride, *i.e.*, in A a fraction of labeled ammonia may occupy a position *cis* to chloride while in B some  $^{15}\text{NH}_3$  may be *trans* to  $\text{Cl}^-$ . Four unknowns are thus involved, namely the distribution of labeling in A and B and the distribution of the photolabilized  $\text{NH}_3$  positions upon visible and uv irradiation, respectively. The problem

(33) See, for example, A. J. R. Bourn, D. G. Gillies, and E. W. Randall, "Nuclear Magnetic Resonance in Chemistry," Academic Press, New York, N. Y., 1965, p 277.

(32) J. H. Espenson and D. W. Carlyle, *Inorg. Chem.*, **5**, 586 (1966).

may be solved by introducing the following four variables:  $a$  = fraction of  $^{15}\text{N}$  trans to  $\text{Cl}^-$  in A,  $a'$  = fraction of  $^{15}\text{N}$  trans to  $\text{Cl}^-$  in B,  $x$  = fraction of time that an ammonia ligand trans to  $\text{Cl}^-$  is photoaquated upon visible irradiation,  $x'$  = fraction of time that an ammonia ligand trans to  $\text{Cl}^-$  is photoaquated upon uv irradiation. These variables can be correlated to the four  $(^{15}\text{N}/^{14}\text{N})_{\text{corr}}$  experimental ratios relative to photo-released  $\text{NH}_3$ , designated as  $\alpha$  and  $\beta$  when they refer to the visible and  $\gamma$  and  $\delta$  for the uv photolysis of A and B, respectively.

If for example the 503 nm photolysis of A is considered, the isotopic ratio is

$\alpha =$

$$\frac{[^{15}\text{NH}_3]}{[^{14}\text{NH}_3]} = \frac{ax + \frac{1-a}{4}(1-x)}{(1-a)x + \left(1 - \frac{1-a}{4}\right)(1-x)} \quad (5)$$

hence

$$x = \frac{\alpha(3+a) + a - 1}{(1+\alpha)(5a-1)} = f(\alpha, a) \quad (6)$$

similarly, three more relations may be defined

$$x = f(\beta, a') \quad (7)$$

$$x' = f(\gamma, a) \quad (8)$$

$$x' = f(\delta, a') \quad (9)$$

All four variables have physical meaning when they range between 0 and 1. It may be noticed that when  $a$  or  $a'$  equal 0.2,  $x$  and  $x'$  cannot be determined. This situation corresponds to an equal percentage of labeling in each of the five ammonia ligands, so that any distribution of the labeled positions would yield the same value (0.25) for the  $^{15}\text{N}/^{14}\text{N}$  ratio.

Contrary to appearances, the four relations (6–9) cannot be solved simultaneously to give unique values for the four unknowns,  $a$ ,  $a'$ ,  $x$ , and  $x'$ . The problem is that the equations relate the unknowns only two at a time. For example, given values for  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  then if  $a$  is specified,  $x$  follows from eq 6 and  $x'$  from eq 8. Further, knowing  $x$ ,  $a'$  follows from eq 7, and eq 9 is redundant. To illustrate this point using our actual isotope ratios, elimination of  $a$  from eq 6 and 8 gives

$$x' = 0.368x + 0.126 \quad (10)$$

and elimination of  $a'$  from eq 7 and 8 gives

$$x' = 0.364x + 0.127 \quad (11)$$

or essentially identical equations. While this result is reassuring as to the consistency of the data, it does not allow determination of unique values for  $x$  and  $x'$ .

The situation would be disastrous were it not that none of the four unknowns are allowed to have values outside of the range 0–1, if the results are to be physically meaningful. This simultaneous limitation on the four quantities acts to limit the range of acceptable values for each. A convenient procedure at this point is the following graphical one.

As shown in Figure 2, a plot is made of each of the functions 6–9 using the experimental values of  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$ . Each variable appears in two functions and must, of course, have the same value in both of them.

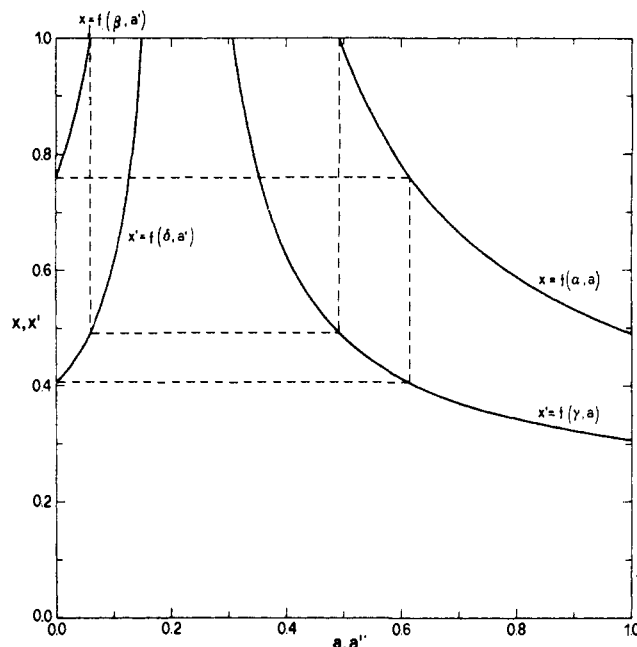


Figure 2. Graphical solution for the distribution of  $^{15}\text{N}$  labeling and the photolabilized  $\text{NH}_3$  ligands. The coordinates are defined in the text:  $\alpha = 0.966$ ;  $\beta = 0.441$ ;  $\delta = 0.174$ .

A consistent set of  $a$ ,  $a'$ ,  $x$ , and  $x'$  values is therefore that given by the corners of a rectangle, each corner touching one of the four plots. The range of possible rectangles is that shown in the figure. Thus  $a'$  is restricted to the range 0–0.06,  $x$  to the range 0.76–1.00, etc., as summarized in Table II. The graphical pro-

Table II. Limiting Solutions<sup>a</sup> and Partial Ammonia Photoaquation Quantum Yields<sup>b</sup>

Quantity <sup>c</sup>	Lower limit <sup>d</sup>	Upper limit <sup>d</sup>
$a$	$0.614 \pm 0.006$	$0.491 \pm 0.008$
$a'$	$0.000 \pm 0.000$	$0.059 \pm 0.006$
$x$	$0.763 \pm 0.025$	$1.000 \pm 0.000$
$x'$	$0.405 \pm 0.021$	$0.491 \pm 0.017$
503 nm $\phi_{\text{ax}}$	$0.28 \pm 0.01$	$0.37 \pm 0.01$
$\phi_{\text{eq}}$	$0.09 \pm 0.01$	0.00
254 nm $\phi_{\text{ax}}$	$0.15 \pm 0.01$	$0.18 \pm 0.01$
$\phi_{\text{eq}}$	$0.22 \pm 0.01$	$0.19 \pm 0.01$

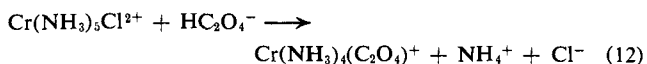
<sup>a</sup> The variables are defined in the text. <sup>b</sup> Based on the over-all  $\phi_{\text{NH}_3}$  values of ref 1 and 2. <sup>c</sup> The subscripts ax and eq denote the labeled positions on the  $\text{NH}_3\text{-Cl}$  axis and on the plane perpendicular to it, respectively. <sup>d</sup> Each column contains a set of consistent solutions.

cedure confirms that only three of the isotope ratios are needed to obtain a set of values for the four parameters, and that the fourth ratio provides a check on the experimental accuracy. Thus while the values of  $\alpha$ ,  $\gamma$ , and  $\delta$  establish the location of the fourth corner of any rectangle in the admissible range, it is a confirmation that the locus of these corners is in fact the experimental function  $x = f(\beta, a')$ .

A further point is that the upper and lower limits given in Table II must be taken as separate sets; for example, the equations are not satisfied if the upper limits are taken for  $a$  and  $a'$  and the lower limits for  $x$  and  $x'$ . On this ground, the extreme values for  $a$ ,  $a'$ ,  $x$ , and  $x'$  have smaller error limits than would be

found by assuming a propagation of errors in the experimental isotope ratio values.

An attempt was made to determine  $a$  and  $a'$ , and hence  $x$  and  $x'$ , through an experiment which it was hoped would provide an additional, independent relationship. If the reaction



is stereorigid, an ammonia cis to the chloride will be displaced. If the reactant is compound A, the ammonia isotope ratio for the product should be

$$\epsilon = \frac{{}^{15}\text{N}}{{}^{14}\text{N}} = \frac{a + 3\left(\frac{1-a}{4} + z\right)}{(1-a) + 3\left(1 - \frac{1-a}{4} - z\right)} \quad (13)$$

The observed value of  $z$  (Table I) in combination with the allowed range of  $a$  values (Table II) gives the range 0.283–0.296 for the allowed  $\epsilon$  values. The observed value of 0.257 (Table I) lies outside this range and in the direction corresponding to scrambling of the ammonia ligands in reaction 12. For the case where the reactant was compound B, the isotope ratio for the oxalato product,  $\xi$ , was found to be 0.252, as compared to the range (from  $z$  and the allowed range of  $a'$  values) 0.246–0.251. While  $\xi$  is within experimental error of the upper limit of allowed values, the similarity of  $\epsilon$  to  $\xi$  is suspicious; we consider it to be a further indication of ammonia scrambling in reaction 12.

## Discussion

Irradiation of the  $L_1$  band leads to the range 0.75–1.00 for possible fractional labilization of the trans ammonia. The former value requires that zero scrambling or stereospecific substitution have occurred in the preparation of B. This situation seems unlikely in view of the rather large degree of scrambling that occurred in the reaction producing A. (It must be kept in mind that the various ranges of values pertain to allowed sets of results and are due not to experimental error but rather to lack of sufficient independent data). We believe that  $a'$  is more likely to have its highest possible value of 0.06, in which case  $x = 1.00$  and the photolysis is 100% stereospecific with respect to the trans ammonia.

We conclude that interpretation b of the rules is at least well obeyed and is probably rather accurately obeyed. This point supports current ligand field analyses which have assumed that the consequences of expected  $\sigma$ - and  $\pi$ -bonding changes in the  $L_1$  excited state can profitably be discussed in terms of the retained geometry of the ground state,<sup>9</sup> and as though mechanism need not be considered.

Mechanism must be important, however, since even where the stoichiometry of the photo and thermal reactions are the same, as with *trans*-Cr(en)<sub>2</sub>XY<sup>+</sup> complexes, the stereochemistry is different; only with *trans*-Cr(cyclam)Cl<sub>2</sub><sup>+</sup> is the stereochemistry the same in both cases, but now the quantum yield is anomalous. It is interesting to note that *cis*-Cr(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)Cl<sup>2+</sup> is produced in the  $L_1$  photolysis of Cr(NH<sub>3</sub>)<sub>5</sub>Cl<sup>2+</sup>, *trans*-Cr(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub><sup>+</sup>,<sup>15</sup> and *trans*-Cr(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)Cl<sup>2+</sup> with virtually the same quantum yield (0.37–0.40).

This uniformity in quantum yield in the face of a considerable variation in the nature of the labilized ligand, NH<sub>3</sub>, Cl<sup>-</sup>, and (presumably) H<sub>2</sub>O, suggests that the yield may be set by a photophysical rather than a photochemical property. Specifically, it may be that following excitation, relaxation to a thermally equilibrated excited (thexi) state occurs with about 40% efficiency in each case, and that the thexi state is committed to reaction. By this supposition the quantum yield is determined primarily by the competition between the radiationless deactivation of the vibrationally hot excited state and its thermalization, a process perhaps largely controlled by the nature of the solvent. A related possibility is that the low quantum yield in the case of *trans*-Cr(cyclam)Cl<sub>2</sub> is due significantly to an enhanced radiationless deactivation rate relative to that for less rigid complexes.

The stereochemical uniformity of product implies the same reaction path for the thexi state including the existence of a common intermediate whose collapse yields the *cis*-aquochloro complex. Either an associative or a concerted mechanism seems to be more consistent with this picture than does a dissociative one, since rearrangement through a pentacoordinated intermediate is likely to yield a mixture of isomers. However, more experimental data will be needed in order to establish if the final configuration of the product is due to stereospecificity of the photoreaction (determined by the type of distortion of the thexi state) or simply reflects a greater thermodynamic stability of the *cis* over the *trans* isomer.

Turning to the 254-nm irradiation the results show that excitation of the CT absorption band leads to 40–50% labilization of the ammonia originally *trans* to the chloride ligand. The allowed range of value is narrow enough that to a good approximation it appears that an equal chance is present of labilizing either the axial (that is, the weak field axis) ammonia or an equatorial ammonia. Random ammonia labilization would have led to 20% release of the *trans* ammonia and random labilization of one of the three pseudooctahedral axes would have led to 33% release of the *trans* ammonia.

A possible explanation is that there is a more or less random ammonia labilization in the CT state, but with extensive intersystem crossing to a ligand field excited state for which *trans* labilization is highly preferred. While such an interpretation cannot be ruled out, it is at least intriguing to consider that the  $x'$  value reflects a purely CT photochemistry. As a crude approximation the CT states of a Cr(III) complex can be thought of as ligand field states of the corresponding Cr(II) species (with one or more ligands electron deficient).<sup>34</sup> Our result would then correspond to an equal probability of having an antibonding electron in either the  $d_{z^2}$  or the  $d_{x^2-y^2}$  orbital of the nominal Cr(II) complex, assuming that axial or equatorial ammonia labilization then followed, respectively.

The quantum yields of Table II may be compared with those relative to *trans*-Cr(NH<sub>3</sub>)<sub>4</sub>XY-type complexes. Visible light excitation of these systems produces aquation of X and/or of Y, and  $\phi_{\text{NH}_3}$  is less

(34) See G. A. Crosby and G. D. Hager, Abstracts, 165th Meeting of the American Chemical Society, Dallas, April 9–13, 1973, for a similar interpretation in the case of Ru(II) complexes, that is, in terms of Ru(III) and reduced ligand.

than 0.01,<sup>15</sup> while in the uv photolysis all three types of ligands are labilized with  $\phi_{\text{NH}}$ , rising to 0.2,<sup>35</sup> or to the same value as found here for  $\phi_{\text{eq}}$  at 254 nm.

As a last comment, our preparative experiences suggest that considerable caution should be exercised in making assumptions about the stereospecificity of a substitution reaction. Reactions 1 and 2, both run in liquid ammonia, behaved quite differently in this respect; in particular, we did not expect reaction 1 to be so poorly stereospecific. Cr(III) substitutions are generally thought to be stereospecific in aqueous media,

(35) P. Ricciari and E. Zinato, unpublished results.

yet it appears that in reaction 12 the displaced ammonia is not primarily the one originally cis to the chloride.

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## Nitrogen-Bound and Carbon-Bound Imidazole Complexes of Ruthenium Ammines<sup>1</sup>

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**Abstract:** Complexes of a series of imidazoles including imidazole, 1-methylimidazole, 4-methylimidazole, 4,5-dimethylimidazole, and benzimidazole with pentaammineruthenium in the II and III oxidation states are described. Except for 4,5-dimethylimidazole, good yields of complexes having imidazole bound to ruthenium through the N-3 nitrogen are obtained by reaction of the imidazole with aquopentaammineruthenium(II) followed by air oxidation. Electronic and pmr spectral features of the Ru(II) and Ru(III) states of these complexes are described. The Ru(II) complexes are not stable below pH  $\sim$ 2, largely reverting to the aquopentaammine species. Kinetic data on this aquation reaction are given for the imidazole complex. The aquation leads to low conversion to derivatives of tetraammineruthenium(II) in which an imidazole ligand is bound to ruthenium through atom C-2. 4-Methylimidazole and benzimidazole give similar carbon-bound species. An analogous carbon-bound complex is the principal product of the reaction of 4,5-dimethylimidazole with pentaammineruthenium(II). The Ru(III) trichloride complexes have been isolated as crystalline solids. Carbonylated derivatives of the Ru(II) complexes of imidazole and 4,5-dimethylimidazole have been prepared and characterized. Spectral data indicating the novel carbon-bound structures are discussed. The results of an X-ray structure determination of the carbonylated derivative of the carbon-bound dimethylimidazole complex as the hexafluorophosphate salt which confirm the carbon-bound structure are presented.

Imidazole and its derivatives have been of substantial interest as ligands because the imidazole ring of histidine plays a prominent role in the biological chemistry of transition metal ions.<sup>3</sup> This study was undertaken to gain further insight into the properties of the imidazole ring as a ligand by extending earlier studies of pyridine complexes of ruthenium ammines.<sup>4-6</sup> In particular, many of the unique properties of the ruthenium(II) complexes of pyridine-type bases can be related to strong metal-ligand  $\pi$  bonding. The imidazole ring contains a pyridine-type nitrogen but its ability to

act as a  $\pi$ -acceptor is expected to be attenuated by the  $\pi$ -donor characteristics of the pyrrole-type nitrogen which serves as an internal electron donor substituent.<sup>7</sup> In this paper we describe the preparation and characterization of a number of pentaammineruthenium complexes of imidazole and its derivatives which are bound through N-3, the pyridine nitrogen, of the imidazole ring. In addition, the isolation of novel complexes in which the ligand is the imidazolium ylide, bound to ruthenium at C-2 of the ring, is described. Structural assignments based largely on nmr evidence and a structure determination by X-ray diffraction methods for one of these compounds are reported.

### Experimental Section<sup>8</sup>

**General Procedure for Pentaammineimidazolruthenium(III) Trichlorides.** The preparation of pentaammine-4-methylimidazole-

(1) Isolation, characterization, and spectral studies were carried out at Stanford University with the support of NSF Grant GP 24726X, NIH Grant GM 13638-07, and NIH Special Research Fellowship GM 50833-01. Structural conclusions based on these studies have been published in a preliminary communication.<sup>2</sup> Determination of the crystal structure of compound 8d was carried out at the University of Virginia.

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(7) K. Schofield, "Hetero-Aromatic Nitrogen Compounds. Pyrroles and Pyridines," Plenum Press, New York, N. Y., 1967, Chapters 2 and 3.

(8) Abbreviations: Im = imidazole; 1-MeIm = 1-methylimidazole; 4-MeIm = 4-methylimidazole; DMIm = 4,5-dimethylimidazole; BzIm = benzimidazole.