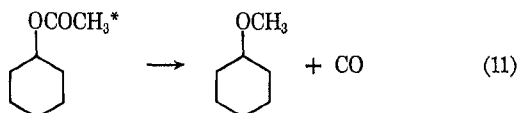
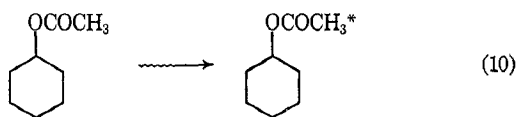


rather than the recombination of the methyl and phenoxy radicals.



Then, phenol may be formed by a process independent of the formation of anisole.

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## Photochemistry of Complex Ions. IX. *trans*-Co(en)<sub>2</sub>(NCS)Cl<sup>+</sup>

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Irradiation of the first ligand field band of *trans*-Co(en)<sub>2</sub>(NCS)Cl<sup>+</sup> in aqueous solution at 22–24° leads to photoaquation in very low quantum yield, with a ratio of thiocyanate to chloride aquation of 1.6. Photoredox decomposition is negligible at this wavelength. Irradiation of the first CT band leads to reaction of total quantum yield 0.013, of which 66% comprises Co<sup>2+</sup> production and the remainder, aquation. The ratio of the two aquation modes is now 6.3. The thermal reaction chemistry of the complex is entirely one of chloride aquation. The results conform to qualitative photolysis rules for Co(III) amines, and those for irradiation of the first CT band are discussed further in terms of a previously proposed homolytic bond fission mechanism. A general conclusion is that the ligand field and CT excited states are exhibiting distinctive chemistries.

### Introduction

The photochemistry of Co(III) complex amines and acidoamines conforms in a general way to the following rules.<sup>1</sup>

*Rule 1.* Irradiation of the first charge-transfer (CT, or actually CTTM) band leads to redox decomposition, while that of a ligand field (L) band leads to substitution type reactions.

*Rule 2.* Quantum yields for redox decomposition,  $\phi_R$ , are high relative to those for substitution; usually aquation,  $\phi_A$ , on irradiation of the first CT and an L band, respectively.

*Rule 3.* Irradiation of the first CT band may lead to a  $\phi_A$  comparable to  $\phi_R$ , in the case of acidoamine complexes, depending on the ease of oxidation of the acido group or, alternatively, on the degree to which the presence of the acido group has produced a bathochromic shift of the CT band maximum.

As examples of rules 1 and 2,  $\phi_R$  is 0.6 to 0.9 for Co(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> at 254 m $\mu$ <sup>2</sup> (the first CT band being at 200 m $\mu$ <sup>3,4</sup>), while  $\phi$  for any reaction is less than 10<sup>-3</sup> at 370 m $\mu$  and 550 m $\mu$ ,<sup>5</sup> wavelengths corresponding to the first and second ligand field bands (L<sub>1</sub> and L<sub>2</sub>). In the case of Co(NH<sub>3</sub>)<sub>5</sub>Br<sup>2+</sup>,  $\phi_R$  is 0.3 at 370 m $\mu$ ,<sup>5</sup> this

wavelength corresponding to a high extinction coefficient shoulder on the first CT band,<sup>3,6</sup> while irradiation at 550 m $\mu$ , or at around the L<sub>1</sub> band maximum, gives only aquation with the low  $\phi_A$  of 0.0014.<sup>5</sup> Rule 3 is illustrated by this same system in that at 370 m $\mu$ ,  $\phi_A$  rises to 0.07.<sup>5</sup> It may be that the aquation is sometimes of an ammonia rather than of the acido group. This is suggested by the special shifts accompanying irradiation of the CT band of Co(NH<sub>3</sub>)<sub>5</sub>Cl<sup>2+</sup>,<sup>7</sup> and in a report on the 254-m $\mu$  irradiation of Co(NH<sub>3</sub>)<sub>5</sub>N<sub>3</sub><sup>2+</sup>.<sup>8</sup>

Rule 1 implies that the CT and L excited-state systems are sufficiently isolated from each other that

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(3) C. K. Jørgensen, *Advan. Chem. Phys.*, **5**, 33 (1963).

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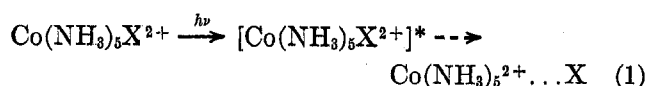
(7) L. Moggi, N. Sabbatini, and V. Balzani, *Gazz. Chim. Ital.*, **97**, 980 (1967).

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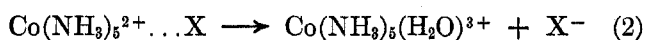
the former, in particular, is able to exhibit its own distinctive photochemistry. Internal conversions within each system are not ruled out. The photochemistry following irradiation of an  $L_2$  band could be due to reaction from an  $L_1$  or a d-d triplet state. The results of photosensitization studies have suggested that redox decomposition of  $\text{Co}(\text{NH}_3)_6^{3+}$  may occur from a CT triplet state.<sup>9</sup> The point is that the CT and d-d excited-state systems do not strongly intercommunicate.

Rule 2 seems not to have been provided with a detailed rationale. In particular, it is not really clear why ligand field excited states should be relatively so inert toward aquation, as compared, for example, with those of Cr(III) complexes. The problem and some *ad hoc* explanations have been discussed.<sup>1</sup>

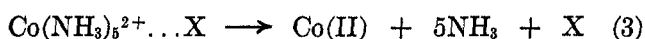
There does exist a mechanism of fairly long standing which accounts for rule 3, however. It was proposed that irradiation of the first CT band led to homolytic bond fission of a Co-X bond, in the case of an acidoammine complex, where X denotes the acido group in question. The proposed primary step, in the case of an acidopentaammine, was



That fraction of excited-state species  $[\text{Co}(\text{NH}_3)_5\text{X}^{2+}]^*$  escaping radiationless deactivation was thus considered to undergo Co-X bond fission to give ground-state  $\text{Co}(\text{NH}_3)_5^{2+}$  and X. Cage reactions then followed, in which X might recoordinate, or might recover an electron from the complex, to escape as  $\text{X}^-$  ion. The resulting partially coordinated Co(III) would then attach an adjacent solvent molecule so that the net reaction would be one of aquation.



Alternatively, if X escaped the above process, net redox decomposition would ensue.



Reaction 3 does not, of course, necessarily indicate the nature of the final oxidation products.

Some of the evidence for the homolytic bond fission-cage mechanism has been summarized elsewhere.<sup>1</sup> One inference, of relevance to the present study, was that reaction 3 should be favored relative to (2) and the yield for (1) increased, the greater the ease of oxidation of the X group, *i.e.*, with decreasing energy for the process



In conjunction with the above mechanism for CT irradiations, it was supposed that irradiation of an L band led to heterolytic bond fission (with or without solvent cooperation), so that the primary step would now be



Thus aquation which occurred on irradiation of an L band was considered to derive from an entirely different mechanism than did that associated with irradiation of a CT band.

Detailed mechanistic hypotheses are notoriously controversial and difficult to establish definitively; the above is not likely to be an exception. It appeared to us, however, that it would be of significance to test the last mentioned prediction, that is, to determine whether there was any spectroscopicity to photoaquation of a Co(III) ammine. This can be done by invoking a complex of the type  $\text{CoA}_4\text{XY}^+$ , for which two relatively similar aquation reactions are possible. Should the ratio of photoaquation of the X group to that of the Y group be spectroscopic, then a wavelength dependent mechanism would be indicated. A similar approach to Cr(III) photochemistry was successful in this respect;<sup>10</sup> it was concluded that at least two different excited states could be precursor to aquation in the case of  $\text{Cr}(\text{NH}_3)_5(\text{NCS})^{2+}$ .

The complex chosen was *trans*- $\text{Co}(\text{en})_2(\text{NCS})\text{Cl}^+$ . The thermal reaction chemistry of aqueous ion has been studied in detail,<sup>11,12</sup> only chloride aquation occurs (the observed product being a 50-50 mixture of the isomers of  $\text{Co}(\text{en})_2(\text{H}_2\text{O})(\text{NCS})^{2+}$ ). The spectra of both the *cis* and *trans* chloride aquation products were known, as well as those of possible thiocyanate photoaquation.<sup>11-13</sup> In addition, analysis for any photoreleased thiocyanate ion would be easy.<sup>14</sup>

A second prediction could also be tested. The first CT band for  $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$  is at  $228 \text{ m}\mu$ ,<sup>3,15</sup> while that for  $\text{Co}(\text{NH}_3)_5(\text{NCS})^{2+}$  is at the considerably longer wavelength of  $330 \text{ m}\mu$ .<sup>4</sup> This shift in the location of the first CT band suggests that the energy for process (4) is lower for  $\text{X} = \text{NCS}^-$  than for  $\text{X} = \text{Cl}^-$ , and, in terms of the above mechanism, is consistent with the much larger  $\phi_R$  (0.045)<sup>5</sup> for the former as compared to the latter case ( $\phi_R = 0.003$ ),<sup>16</sup> for irradiations around  $370 \text{ m}\mu$ . The implicit assumptions are that the excited state reached through the first CT band is rather localized around the Co-X bond and that the weaker that bond is toward homolytic fission, the less likely is the thermal reverse of (1) to occur.<sup>16</sup>

Since the first CT band for *trans*- $\text{Co}(\text{en})_2(\text{NCS})\text{Cl}^+$  is at  $330 \text{ m}\mu$ , application of the above reasoning sug-

(9) A. Vogler and A. W. Adamson, *J. Amer. Chem. Soc.*, **90**, 5943 (1968).

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(11) M. E. Baldwin and M. L. Tobe, *J. Chem. Soc.*, 4275 (1960).

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gests the Cl excited state to involve primarily the Co-NCS bond. The conclusion suggested by the mechanism is, therefore, that any photoredox decomposition should center around this bond with the consequence that the predicted accompanying aquation should be primarily that of the thiocyanate group.

### Experimental Section

**Materials.** [*trans*-Co(en)<sub>2</sub>(NCS)Cl]ClO<sub>4</sub> was prepared according to Werner's method.<sup>17</sup> The compound was of good spectroscopic purity; its visible and ultraviolet absorption spectrum, shown in Figure 1, agreed well with that reported for an analyzed sample.<sup>12</sup>

**Photolysis Procedures.** The light source used was an AH-6 (General Electric) high-pressure mercury arc and the general arrangement was that previously described.<sup>10</sup> The Pyrex water jacket and collimating lenses limited the ultraviolet radiation emitted to wavelengths over about 330 mμ, and with the interposition of a Schott UG-11 glass filter, the irradiating was confined to 330-390 mμ, or to the region of the first CT band. Alternatively, the filter combination of Corning glass CS-3-69 plus CS-4-96 transmitted light between 515 and 615 mμ, or in the region of the L<sub>1</sub> band of the complex.

The photolyses were carried out in a 10-cm cylindrical spectrophotometer cell, using concentrations of complex such as to have essentially complete light absorption (about 0.005 M for irradiations in the CT region and 0.01 M for those in the L<sub>1</sub> region). The solutions were 0.1 M in perchloric acid, and their temperature 22-24°. An aliquot of the solution to be analyzed was kept in the dark, at the same temperature, so that any thermal aquation could be noted and allowed for. However, the rate constant for the thermal aquation (of chloride) is only 5 × 10<sup>-8</sup> sec<sup>-1</sup> at 25°,<sup>11</sup> and since irradiation times did not exceed 2 hr, correction for such aquation was small.

The total amount of photolysis was limited to about 10% to avoid possible secondary photochemical reactions. Absorbed light intensities were determined by Reineckate actinometry.<sup>14</sup>

**Analytical Procedures.** The possible photolysis products, analysis for which was essential, were free chloride and thiocyanate ions, Co(en)<sub>2</sub>(H<sub>2</sub>O)(NCS)<sup>2+</sup>, Co(en)<sub>2</sub>(H<sub>2</sub>O)Cl<sup>2+</sup>, and Co<sup>2+</sup>. It was not considered necessary to attempt to distinguish *cis* and *trans* isomers in the product aquo complexes, nor did it seem feasible to determine the nature of the final oxidation products accompanying Co<sup>2+</sup> formation.

(1) **Thiocyanate.** Free thiocyanate ion was determined by adding an aliquot of the irradiated (or dark) solution to a fourfold volume of a reagent consisting of 0.1 M ferric nitrate in 0.5 M perchloric acid, and measuring the absorbance due to the resulting ferric thiocyanate complex (ε 4.3 × 10<sup>3</sup> M<sup>-1</sup> cm<sup>-1</sup> at 450 mμ).<sup>14</sup>

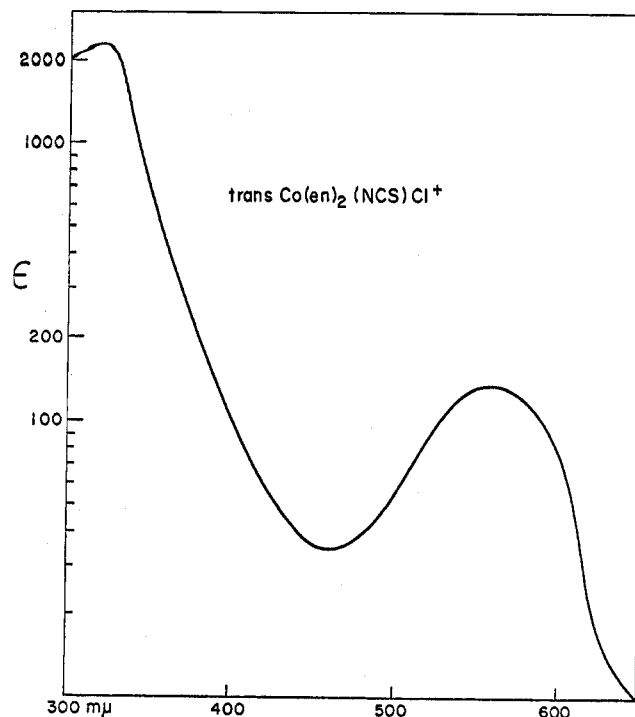


Figure 1. Spectrum of aqueous *trans*-Co(en)<sub>2</sub>(NCS)Cl<sup>+</sup>.

(2) **Cobalt (II).** Cobaltous ion was found by forming the blue complex ion, Co(NCS)<sub>4</sub><sup>2-</sup> in a water-acetone solution and measuring the absorbance (ε 1.7 × 10<sup>3</sup> at 625 mμ), according to a literature procedure.<sup>18</sup>

(3) **Chloride.** The determination of free chloride ion was based on the amount of thiocyanate ion produced by the reaction



as described by Zall and coworkers.<sup>19</sup> The following preliminary procedure was necessary, however. A portion of the solution to be analyzed was adsorbed on a Dowex 50W-X4 ion-exchange column. The free chloride and thiocyanate ions present were eluted with water, and the thiocyanate present in the eluent decomposed by boiling the solution with hydrogen peroxide (prolonged to complete the decomposition of this last reagent). Reaction 6 is not quite complete, and allowance for this was made by means

(16) The characteristic absorption of thiocyanate complexes around this wavelength has alternatively been attributed to an internal CT absorption of the ligand (C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, New York, N. Y., 1962, p 196; L. Di Spiro, L. Oleari, and G. De Michelis, *Coordination Chem. Rev.*, 1, 7 (1966)) and to a ligand to metal CT transition (H. Schmidtke, "Progress in Coordination Chemistry," M. Cais, Ed., Elsevier Publishing Co., New York, N. Y., 1968, p 509). The former interpretation makes more complex the molecular orbital description of the excited state first reached; it is still consistent with our premise that the transition is localized around the Co-NCS moiety. Also, the above rules and predictions are not affected provided the first chemical act is one of homolytic bond fission.

(17) A. Werner, *Ann.*, 1, 386 (1912).

(18) R. E. Kitson, *Anal. Chem.*, 22, 664 (1950).

(19) D. M. Zall, D. Fischer, and M. Q. Garner, *ibid.*, 28, 1665 (1956).

of a set of standardizations using known chloride containing solutions.

(4) *Aquo Products*. The combined amount of  $\text{Co(en)}_2(\text{H}_2\text{O})(\text{NCS})^{2+}$  and  $\text{Co(en)}_2(\text{H}_2\text{O})\text{Cl}^{2+}$  present was first found as follows. A portion of the photolyzed solution was adsorbed on the ion-exchange column, the free thiocyanate and chloride eluted with water, and the initial complex present, by means of 0.3 *M* perchloric acid. The two aquo species were then jointly eluted with 3 *M* perchloric acid. An aliquot of this eluent was then decomposed by boiling with hydrogen peroxide, and the produced  $\text{Co}^{2+}$  determined as described above.

(5)  $\text{Co(en)}_2(\text{H}_2\text{O})(\text{NCS})^{2+}$ . Cobalt(III) amines are subject to rapid base hydrolysis of any acido group present, and this reaction permitted the determination of any  $\text{Co(en)}_2(\text{H}_2\text{O})(\text{NCS})^{2+}$  present in the above eluent solution. An aliquot portion of it was made alkaline by the addition of solid potassium hydroxide, and the resulting mixture was then boiled for 3 hr, and finally reacidified with perchloric acid. The precipitated potassium perchlorate was filtered off, and the free thiocyanate present determined as described above.

(6)  $\text{Co(en)}_2(\text{H}_2\text{O})\text{Cl}^{2+}$ . The above determination of  $\text{Co(en)}_2(\text{H}_2\text{O})(\text{NCS})^{2+}$  plus that of the combined aquo products then permitted the calculation of the amount of  $\text{Co(en)}_2(\text{H}_2\text{O})\text{Cl}^{2+}$  also present in the original solution.

An independent determination was occasionally made as follows. The neutralized and filtered solution described in (5) also contained free chloride ion in amount corresponding to that of any  $\text{Co(en)}_2(\text{H}_2\text{O})\text{Cl}^{2+}$  originally present. An aliquot portion would then be analyzed for chloride by procedure (3). However, this use of successive aliquot portions diminished the amount of sample available, and hence the accuracy of the analysis.

## Results and Discussion

*General Photolysis Results*. The direct analytical results are given in Table I. The total quantum yield,

**Table I:** Photolysis of  $\text{trans-Co(en)}_2(\text{NCS})\text{Cl}^+$

| Product determined                                     | Quantum yield at 22–24°, × 10 <sup>2</sup> |  |
|--|--|--|
|  | 330–390 m $\mu$<br>(CT band)               | 515–615 m $\mu$<br>(L <sub>1</sub> band) |
| Total yield, $\phi_{\text{tot}}$                       | 1.31                                       | ca. 0.01                                 |
| NCS <sup>-</sup>                                       | 1.01 (0.77) <sup>a</sup>                   |  |
| Cl <sup>-</sup>  | 0.94 (0.73) <sup>a</sup>                   |  |
| $\text{Co(en)}_2(\text{H}_2\text{O})(\text{NCS})^{2+}$ | 0.06 (0.046) <sup>a</sup>                  |  |
| $\text{Co(en)}_2(\text{H}_2\text{O})\text{Cl}^{2+}$    | 0.38 (0.28) <sup>a</sup>                   |  |
| $\text{Co}^{2+}$                                       | 0.87 (0.66) <sup>a</sup>                   | <0.001                                   |
| $r^b$  | 6.3  | 1.6                                      |

<sup>a</sup> Yields expressed as fractions, *F*, of the total yield. <sup>b</sup> The ratio, *r*, of yield of  $\text{Co(en)}_2(\text{H}_2\text{O})\text{Cl}^{2+}$  to that of  $\text{Co(en)}_2(\text{H}_2\text{O})(\text{NCS})^{2+}$ .

$\phi_{\text{tot}}$ , is the sum of the yields for  $\text{Co}^{2+}$  and of those for the two aquo products and is thus the yield for disappearance of the parent complex. In the case of irradiation in the region of the L<sub>1</sub> band, this total yield could only be estimated as about 10<sup>-4</sup>, but the sensitivity of the  $\text{Co}^{2+}$  analysis allowed an upper limit of 10<sup>-5</sup> to be placed on the yield for redox decomposition. It was possible, moreover, to determine to 10% accuracy the ratio, *r*, of the yield of  $\text{Co(en)}_2(\text{H}_2\text{O})\text{Cl}^{2+}$  to that for  $\text{Co(en)}_2(\text{H}_2\text{O})(\text{NCS})^{2+}$ .

The results conform generally to the rules given in the Introduction. Thus redox decomposition was essentially confined to excitation in the region of the CT band, and the quantum yield for any reaction was very low in that of the L<sub>1</sub> band. Rule 3 was also obeyed in that aquation contributed 33% of the total photolysis on irradiation of the first CT band.

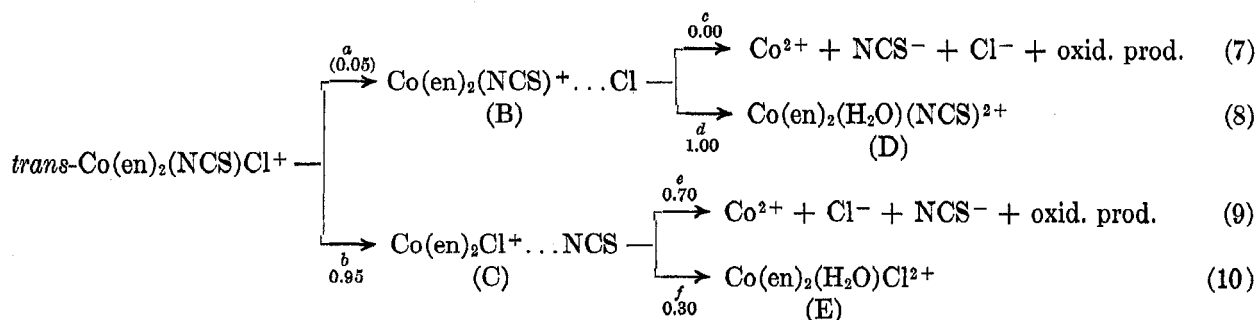
The general predictions based on the homolytic bond fission mechanism are also confirmed. The ratio, *r*, of aquation modes is strongly wavelength dependent, rising from 1.6 for the region of the L<sub>1</sub> band to 6.3 for that of the first CT band. This last value of *r*, moreover, corresponds to the expected predominance of thiocyanate over chloride aquation. The results, then, add support to the premises outlined in the Introduction, namely that the photochemistries following irradiation of the L and first CT bands are characteristic of these two types of excited states. We do not, of course, rule out intersystem crossings between CT and L states; we do conclude that such processes compete with, rather than lead to, the photochemistry that follows irradiation of the CT band.

All of the above effects could simply be attributed to the reaction characteristics of hot ground-state molecules variously energized according to the wavelength of the irradiation. We regard this type of explanation as unlikely to be correct, however. It has so far seemed true of ammine type complexes that quantum yields and ratios of reaction modes do not vary much within the wavelength region of a given absorption band (see reference 1 on Co(III) and Cr(III) complexes), but remain characteristic of that band regardless of the particular wavelength chosen for the irradiation. The implication is that, following excitation, thermal equilibration, and possible internal conversions, an excited state is reached which then exhibits its particular chemistry. It thus appears to us that in the case of  $\text{trans-Co(en)}_2(\text{NCS})\text{Cl}^+$ , redox decomposition and aquation of high *r* value describe the chemistry of a CT excited state reached by irradiation of the first CT band, and that the chemistry of the low-lying d-d excited states is one of aquation only, with a low *r* value.

*Homolytic Bond Fission Mechanism*. As noted above, the results conform to the predictions of this mech-

anism. Assuming this mechanism, then, it is possible to analyze the data in somewhat more detail.

The scheme, as applied to the present system, is the following.



Here, (B) and (C) denote the cage products of Co-Cl and Co-NCS homolytic bond fission, respectively, and  $a$  and  $b$ ,  $c$  and  $d$ , and  $e$  and  $f$ , the bifurcation fractions for the first-stage and the two alternative second-stage processes.

The following material balance statements can be made, in terms of the fractions  $F$  of the total yield.

$$F_{\text{Co}^{2+}} = ac + be = 0.66 \quad (11)$$

$$F_{\text{D}} = ad = 0.046 \quad (12)$$

$$F_{\text{E}} = bf = 0.28 \quad (13)$$

The sum of (11) and (12),  $0.66 + 0.05 = 0.71$ , should give  $F_{\text{Cl}^-}$ . This is essentially the observed value of 0.73, and the agreement confirms the expectation that all released chloride terminates as  $\text{Cl}^-$  ion. Also, the sum of (11) and (13),  $0.66 + 0.28 = 0.94$ , should give  $F_{\text{NCS}^-}$ . The much lower observed value of 0.77 is presumably a consequence of partial oxidation of thiocyanate in step  $e$ . On this basis, path  $be$  must have a relative quantum yield of at least 0.14 (0.94-0.77), corresponding to 100% oxidation of thiocyanate in step  $e$ . However, the experience in the case of

$\text{Co(NH}_3)_5\text{(NCS)}^{2+}$  was that the amount of oxidized thiocyanate was only about a fourth of the  $\text{Co(II)}$  produced.<sup>5,20</sup> Application of this figure of 25% oxidation to the present system suggests that path  $be$  should

be assigned essentially its maximum possible value of 0.66. The individual values for  $a$ ,  $b$ ,  $c$ ,  $d$ ,  $e$ , and  $f$  then follow from the material balance equations and are given in parentheses in the reaction scheme above. These values seem reasonable both in showing a preponderance of Co-NCS over Co-Cl bond fission, and in giving the same ratio of paths  $e$  to  $f$  as was found for  $\text{Co(NH}_3)_5\text{(NCS)}^{2+}$ .

The above assignment of path fractions is not unique, however. Other values follow if the degree of thiocyanate oxidation in step  $e$  is taken to be more than 25%. In summary, while the results of irradiation of the first CT band do not prove the homolytic bond fission mechanism to be correct, the mechanism does appear to provide a chemically reasonable basis for their interpretation.

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(20) Unpublished work in this laboratory.