conditions due to a rapid polymerization reaction with CH_2O.[19]

(5) **Dissociation and Aquation.**—After completion of the free radical reaction, the pH of the solvent influences the further course of the reaction. Cobalt(II)-amine complexes are unstable and are readily dissociated.[20] In acidic solutions the Co(II) complexes would dissociate rapidly and the ethylenediamine would be protonated and prevented from entering into further reaction.

(6) **Reoxidation.**—In neutral solutions the liberated ethylenediamine as a moderately strong base causes an increase in the pH of the solution. In the presence of air, reoxidation of the Co(II) occurs with the formation of all possible Co(III)–ethylenediamine–water–hydroxide species. The red material, which formed as a consequence of the photolysis of $[Co(en)_3]^{+3}$ in aqueous solution, was found to contain cobalt(III). The spectrum of this material had no specific absorption peaks. This is the type of optical absorption pattern expected for a mixture of a large number of components with overlapping absorption peaks. The subsequent decomposition of the red material after long irradiation demonstrated that it was a photosensitive intermediate in the over-all photodecomposition of $[Co(en)_3]^{+3}$ in aqueous solution. Continued irradiation of such solutions might lead to the complete decomposition of the ethylenediamine. However, complete decomposition could only be approached slowly since, as the concentration of ammonium ions increased, the $Co(OH)_2$ began to precipitate. As the cobalt ion was removed from solution, the number of coordination sites available was depleted, and in the absence of coordination the ethylenediamine solutions were found to be photochemically stable under the conditions used.

Acknowledgment.—This work was supported in part by a grant from the National Science Foundation.

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[19] J. F. Walker, "Formaldehyde," Reinhold Publishing Corp., New York, N. Y., 1953.

[20] J. C. Bailar, Jr., "The Chemistry of the Coordination Compounds," Reinhold Publishing Corp., New York, N. Y., 1956, p. 428.

Contribution from the Department of Chemistry
The University of Connecticut, Storrs, Connecticut

The Photochemistry of Coordination Compounds in Solution. II. Tris(propylenediamine)cobalt(III) Chloride and Tris(butylenediamine)cobalt(III) Chloride

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The irradiation with ultraviolet light of coordination compounds of Co(III) which contain the diamine ligands ethylenediamine, 1,2-diaminopropane, or 2,3-diaminobutane leads to photodecomposition. The major products are Co(II), NH_3, the diamine, an aldehyde, a monoamine, and an aminocarbonyl. The specific nature of the aldehyde and the monoamine obtained with the different ligands points to a β-elimination reaction; thus the photolysis of $[Co(pn)_3]Cl_3$ results in CH_2O and $CH_3CH_2NH_2$, while from $[Co(bn)_3]Cl_3$ there are obtained CH_3CHO and $CH_3CH_2NH_2$.

A number of studies have been made on the use of ultraviolet irradiation to induce the reduction of Co(III) to Co(II) in coordination compounds that are quite stable under ordinary conditions.[2–5] However, there have been very few detailed product analyses, especially for complexes with neutral ligands.

Due to their observation that $[Co(NH_3)_6]I_3$ was reduced by ultraviolet light of 370 mμ only if an excess of I^- ions was present, Adamson and Sporer felt that electron transfer resulted from ion pairing.[6] On the other hand, it was found[7] that reduction of Co(III) occurred upon irradiation of the solid ethylenediamine (en) complex, $[Co(en)_3]Cl_3$, with no evidence of a corresponding oxidation of the chloride ion; ammonia was the only gaseous product detected. Studies made on the decomposition of the complex ion in aqueous solutions led to the proposing of a mechanism involving the transfer of an electron from one of the nitrogen atoms to the Co(III), followed by the fission of the C–C bond in the diamine.[8] The nature of the products indicated that the use of unsymmetrical diamine ligands would be interesting since subsequent reactions of the radicals formed should produce new amines which could help in the determination of the mechanism. This article describes such a study using 1,2-diaminopropane (pn) as the unsymmetrical diamine and 2,3-diaminobutane (bn) to test further the course of the reaction.

Experimental

Preparations.—$[Co(en)_3]Cl_3$ and $[Co(pn)_3]Cl_3$ were prepared by direct oxidation as described by Work, using Eastman diamines and Baker and Adamson reagent grade $CoCl_2 \cdot 6H_2O$.[9]

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[1] Abstracted in part from the Ph.D. dissertation of William C. Taylor, Jr., The University of Connecticut, 1963.

[2] R. Schwartz and H. Weiss, *Ber.*, **58B**, 746 (1925).

[3] R. Schwartz and K. Tede, *ibid.*, **60B**, 63 (1927).

[4] S. T. Spees, Jr., and A. W. Adamson, *Inorg. Chem.*, **1**, 531 (1962).

[5] S. E. Beacom, Ph.D. Dissertation, The University of Connecticut, 1954.

(6) A. W. Adamson and A. H. Sporer, *J. Am. Chem. Soc.*, **80**, 3865 (1958).

[7] D. Klein, C. W. Moeller, and R. Ward, *ibid.*, **80**, 265 (1958).

[8] D. Klein and C. W. Moeller, *Inorg. Chem.*, **4**, 394 (1965).

[9] J. B. Work, *Inorg. Syn.*, **2**, 221 (1946).

The 2,3-diaminobutane was prepared by modifying the method of Dickey, *et al.*[10] The distillate was evaporated down; the solid residue was washed with ethanol and dried for 12 hr. The per cent chloride found on analysis of the hydrochloride salt indicated that the amino alcohol reported by Dickey was not present but rather it was completely removed, if formed, in one of the operations.

Anal. Calcd. for $C_4N_2H_{14}Cl_2$: Cl, 45.3. Found: Cl, 45.1, 45.7.

The *meso* salt could be separated from the racemic *d,l* mixture by recrystallization from methanol. The isomers can be recognized by their infrared spectra; that of the *meso* compound is simpler than that of the racemic component.

The complex $[Co(bn)_3]Cl_3$ was prepared by three different methods; the preparations and the properties of the complex are described in some detail since they have not been previously recorded.

(1) Four grams (0.011 mole) of $Na_3[Co(CO_3)_3]\cdot 3H_2O$, which was prepared by the method of Bauer and Drinkard,[11] was added to a 250-ml. erlenmeyer flask equipped with a condenser. Then 9.3 g. (0.06 mole) of $(bn)H_2Cl_2$ and 100 ml. of ethanol were added and the sample was refluxed for 12 hr. The brownish yellow product was filtered and dissolved in 50 ml. of concentrated HCl to remove the NaCl. The filtrate was evaporated to dryness yielding a yellow to green solid which was recrystallized from hot methanol to form yellow-orange crystals. The salt was dried for 12 hr. at 110°. A typical preparation resulted in 3.7 g. (0.009 mole) of product or 86% yield.

(2) Following the method of Basolo, Palmer, and Pearson, 10 g. (0.04 mole) of $[Co(NH_3)_5Cl]Cl_2$ was added to a 1-l. evaporating dish.[12] Then 900 ml. of 0.15 M aqueous bn and 2 g. of charcoal were added, and the mixture was heated on a steam bath for 4 hr. After filtration, the filtrate was evaporated to a thick, red sirup which was dissolved in 200 ml. of hot ethanol, boiled down to about 25 ml., and allowed to cool. This step was repeated two or three times until a yellow-orange, crystalline precipitate formed when the solution was cooled. This compound was found to be more difficult to crystallize by this method than were the en and pn complexes.

(3) An aqueous solution containing 8.42 g. (0.095 mole) of bn in 60 ml. was added to 50 ml. of an aqueous solution containing 7 g. (0.03 mole) of $CoCl_2\cdot 6H_2O$. Then 3 ml. of 12 M HCl and 1 g. of charcoal were added, and the solution was oxidized with air for 6 hr. The sample was filtered and evaporated on a steam bath until it became sirupy and formed a film on the surface. To this 500 ml. of hot ethanol was added, and the solution was evaporated to about 100 ml. This step was repeated two or three times until a yellow-orange, crystalline salt formed. The final solution was evaporated to 50 ml. and yielded close to the theoretical amount of product. The analyses of the salts from all three of the methods of preparation were similar.

Anal. Calcd. for $[Co(bn)_3]Cl_3$: Co, 13.7; N, 19.5; Cl, 24.7. Found: Co, 13.7; N, 18.7–18.9; Cl, 23.5–23.6.

The complex $[Co(bn)_3]Cl_3$ is stable thermally up to 250°; beyond this point the compound slowly begins to decompose, releasing the diamine which condenses around the top of the capillary tube. It is stable in acidic and basic solutions at room temperature. The absorption spectrum of a 0.025 M solution in concentrated HCl showed no change in molar extinction coefficient after being stored in the dark for 18 months. A 0.025 M solution in 2.5 M NaOH retained its color for over 6 weeks. In concentrated HCl the compound has three absorption peaks in the visible and ultraviolet regions. These are at 470, 333, and 217 mμ with molar extinction coefficients of 110, 120, and 1.7×10^4, respectively. In the same medium the absorption peaks of $[Co(pn)_3]Cl_3$ are at 465, 340, and 230 mμ with E_M of 95, 100, and 2.1×10^4, respectively.

The Aminocarbonyl Compounds.—One of the products in the irradiation of $[Co(pn)_3]Cl_3$ was 2-aminopropanal. The compound and its 2,4-dinitrophenylhydrazone derivative were prepared by the method of Baxter, *et al.*[13] The 2-aminopropanal was not isolated from the reaction solution which was decanted from the Hg–Na amalgam into 100 ml. of DNPH reagent and heated to 95° for 30 min. The orange-brown solid that formed was filtered and dried for 2 hr. at 100°; it is stable up to 300°. The compound would not form when the solution merely stood overnight at room temperature. The hydrazones obtained synthetically and from the photolyzed solutions were found to be identical by infrared analyses.

The 3-aminobutanone-2, which was needed for comparison with the aminocarbonyl obtained in the photolysis of $[Co(bn)_3]Cl_3$, was prepared by reducing isonitroethyl methyl ketone with Raney catalyst powder using a similar procedure to that utilized in the preparation of bn.[10] The amino ketone was not isolated but the distillate from the reduction was added to 200 ml. of DNPH reagent and heated to 95° for 1 hr.

Irradiation Studies.—The light sources used in these studies were Hanovia Utility Model quartz lamps, No. 3062, equipped with Type SH "U"-shaped, 100-watt quartz mercury arc tubes. With the exception of the quantum yield measurements, all experiments were made with the ulfiltered light and with the cells at a distance of 10 cm. from the arc tube. At this distance the temperature reached a maximum of 65° during the first hour and remained at that level for the duration of the irradiations. To check the effect of that temperature on the decomposition of the complexes, a 0.05 M solution of $[Co(bn)_3]Cl_3$ in 3 M HCl was heated at 92° for 8 hr.; no Co(II) formation was detectable. With the ultraviolet light used, photolysis was complete in 8 hr. with respect to Co(II) formation.

The cells were 25-ml., fused-quartz, actinometer cells, Hanovia No. 2681. These cells were used in all of the experiments except the quantum yield determination, for which 3.5-ml. Beckman silica cells were utilized.[8] The cells were equipped with nitrogen-filled tubes in order to maintain an inert atmosphere.

Spectra Analyses.—The visible and ultraviolet spectra were measured with a Cary Model 14 recording spectrophotometer using a scanning speed of 50 Å./sec. The optical density measurements were made with a Beckman Model B spectrophotometer.

The infrared spectra were taken with a Perkin-Elmer Infracord, Model 127B, using a 12-min. scanning time. The samples were prepared in Nujol emulsion; each sample preparation was run in duplicate.

Results

Irradiation in 12 M HCl.—When 0.05 M solutions of $[Co(bn)_3]Cl_3$ or $[Co(pn)_3]Cl_3$ in 12 M HCl were irradiated with ultraviolet light, both complexes went through a series of color changes from orange through yellow and green to blue over a period of 20 hr. The irradiation of the bn complex beyond 50 hr. resulted in a color change of the solution from blue-back to green and the formation of precipitates. These substances were not further characterized since the emphasis in this study was on the initial blue solutions. The solutions containing the pn complex underwent no further color changes with continued irradiation, once the blue color had been attained.

The decomposition of the complexes was followed by the examination of their visible spectra. These showed a decrease in the absorption at 470 mμ, where the molar extinction coefficients of the initial complexes are about 100, and an increase in absorption at 690 mμ due to the formation of the chlorocobalt(II) ion

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[10] F. H. Dickey, W. Fickett, and J. J. Lucas, *J. Am. Chem. Soc.*, **74**, 994 (1952).

[11] H. F. Bauer and W. C. Drinkard, *ibid.*, **82**, 5031 (1960).

[12] F. Basolo, J. W. Palmer, and R. G. Pearson, *ibid.*, **82**, 1073 (1960).

[13] R. A. Baxter, G. T. Newbold, and F. S. Spring, *J. Chem. Soc.*, 370 (1960).

with a molar extinction coefficient of 565. With solutions of $[Co(bn)_3]Cl_3$ the absorption went through a minimum at 470 mμ and began to increase again at that wave length after 50 hr. This increase occurred without any decrease at 690 mμ. Treatment of the photolyzed solutions with DNPH reagent resulted in the precipitation of the derivatives of formaldehyde and acetaldehyde from the solutions containing $[Co(pn)_3]Cl_3$ and $[Co(bn)_3]Cl_3$, respectively.

The decrease in acetaldehyde concentration as well as the color change to green upon long irradiation of the bn complex can be explained by the observation that CH_3CHO polymerizes in 12 *M* HCl. Since CH_2O does not polymerize under these conditions, this must be an aldol condensation which requires that the carbonyl contain an α-hydrogen. That these reactions are catalyzed by acids and bases is well known, and mechanisms for the reactions in both media have been proposed.[14] Formaldehyde cannot undergo a true aldol condensation; however, it is reported that formaldehyde is induced by ultraviolet light to undergo closely analogous reactions but with products that are usually simple compounds.[15]

Irradiation in 3 *M* HCl Solutions.—In order to avoid the polymerization observed with solutions in 12 *M* HCl, studies were made using different acid concentrations in an attempt to find a convenient medium. A series of solutions which were 0.2 *M* in acetaldehyde and from 1 to 12 *M* in HCl were irradiated for 12 hr. It was found that when the HCl concentration was less than 4 *M* polymerization of the aldehyde did not occur. Reoxidation of the Co(II) in air, also, did not occur in these acidic solutions. Therefore, the 3 *M* HCl concentration was selected for most of the irradiation studies.

The color of 0.05 *M* solutions of the complexes changed from orange to pink after about 8 hr. of irradiation. The formation of Co(II) was determined spectrophotometrically by dissolving an aliquot of the irradiated solution in 12 *M* HCl and measuring the absorption at 690 mμ. Treatment of the photolyzed solutions with H_2PtCl_6 solution resulted in the precipitation of yellow crystals which were identified by their infrared spectra as mixtures of the salts of ammonia and the appropriate diamine. Tests with synthetic solutions showed that the anticipated monoamines when in solutions containing ammonia and diamines do not precipitate as chloroplatinates at the low concentrations used. The recoveries for mixtures of ammonia and the diamines were 90 and 70% for pn–NH_3 and bn–NH_3 synthetic mixtures, respectively. The diamines were separated from NH_3 by extraction with benzene, and they were then titrated with alcoholic HCl. Tests with synthetic solutions showed that the recovery was 70 and 80% for solutions containing pn and bn, respectively.

Treatment of the irradiated solutions with DNPH reagent at room temperature resulted in the formation of the derivative of CH_2O from solutions containing $[Co(en)_3]Cl_3$ and $[Co(pn)_3]Cl_3$ and the derivative of CH_3CHO from solutions containing $[Co(bn)_3]Cl_3$. Further studies showed how the amounts of the carbonyl derivatives isolated from the irradiated solutions were related to the irradiation time and the Co(II) formation. Table I indicates the initial increase and later decrease of aldehyde concentration for the pn and bn complexes.

TABLE I

RATE OF FORMATION OF Co(II) AND ALDEHYDES IN IRRADIATED SOLUTIONS

Irradiation time, hr.	Aldehyde and Co(II) found,[a] *M*					
	$[Co(en)_3]Cl_3$		$[Co(pn)_3]Cl_3$		$[Co(bn)_3Cl_3$	
	CH_2O	Co(II)	CH_2O	Co(II)	CH_3CHO	Co(II)
1	0.0033	0.009	0.0039	0.008	0.0140	0.0140
2	0.0106	0.018				
2.5					0.030	0.027
3	0.0138	0.033	0.0167	0.026		
4.5					0.0457	0.047
5	0.0213	0.050				
6			0.0282	0.048	0.0432	0.052
7					0.0391	0.051
8			0.0220	0.051		
8.5	0.0220	0.050				
10					0.0209	0.052
11			0.0192	0.051		

[a] The initial concentrations of the complexes are: $[Co(en)_3]Cl_3$, 0.052 *M;* $[Co(pn)_3]Cl_3$ 0.053 *M;* and $[Co(bn)_3]Cl_3$, 0.051 *M.*

Upon the heating to 90° of the filtrates from the DNPH precipitations, new DNPH derivatives were formed. These substances, which were stable up to 310°, were identified by their infrared spectra as the hydrazones of aminocarbonyls; aminoacetaldehyde, 2-aminopropanal, and 3-aminobutanone-2 were obtained from the irradiated solutions of $[Co(en)_3]Cl_3$, $[Co(pn)_3]Cl_3$, and $[Co(bn)_3]Cl_3$, respectively.

Ethylamine was isolated from the products of irradiated solutions of $[Co(bn)_3]Cl_3$ and $[Co(pn)_3]Cl_3$ by using fractional distillation. To accomplish this the aldehydes had to be distilled from the acidified solutions before the solutions were made basic for the amine distillation. Apparently methylamine, if formed in the $[Co(en)_3]Cl_3$ solutions, polymerized too rapidly with CH_2O to be detected.

The molar ratios of the decomposition products from the solutions of the three complexes are summarized in Table II. In addition to the major products detected, thin layer chromatographic analyses showed as many as six other products were formed in trace amounts. Their identities were not determined.

Discussion

The photolysis of tris(diamine)cobalt(III) complexes in aqueous or in acid solutions results in the production of Co(II), NH_3, monoamines, diamines, aldehydes, aminocarbonyls, and some polymeric materials. The sum of the C atoms in the corresponding monoamine and aldehyde obtained from a particular complex is

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[14] E. E. Royals, "Advanced Organic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1954, p. 750.

[15] J. F. Walker, "Formaldehyde," Reinhold Publishing Corp., New York, N. Y., 1953, p. 164.

TABLE II

MOLAR RATIOS OF DECOMPOSITION PRODUCTS IN IRRADIATED SOLUTIONS

Complex[a]	Co(II)	Diamine	NH_3	R′CHO	RCH_2NH_2	$RCH(NH_2)C(R')O$
$[Co(bn)_3]Cl_3$	1.0 ∓ 0.05	2.2 ∓ 0.3	1.0 ∓ 0.3	1.0 ∓ 0.05	0.5 ∓ 0.2	0.1 ∓ 0.05
$[Co(pn)_3]Cl_3$	1.0 ∓ 0.05	2.2 ∓ 0.3	1.0 ∓ 0.3	0.55 ∓ 0.1	0.25 ∓ 0.2	0.1 ∓ 0.05
$[Co(en)_3]Cl_3$[b]	1.0 ∓ 0.05	2.5	1.	0.5 ∓ 0.1	Undetected	Present

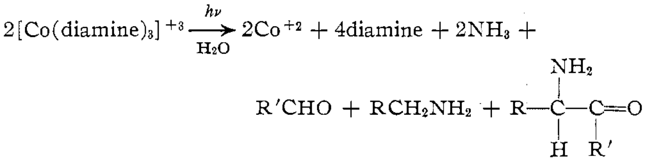
[a] For bn, $R = R' = CH_3$, for pn, $R = CH_3$, $R' = H$; for en, $R = R' = H$. [b] The diamine and NH_3 values for $[Co(en)_3]Cl_3$ are those reported by Klein.[8] In the more acid solutions Klein found higher yields of formaldehyde.

equal to the number of C atoms in the original diamine ligand. These two compounds are consistent with the fission of the C–C bond in the diamine at the two carbon atoms that are bonded to the amine groups. No C–C bond fission has been observed when the diamines alone are irradiated with ultraviolet light. One mole of Co(II) is produced for each mole of complex within a period of about 8 hr. when 0.05 *M* solutions in 3 *M* HCl are irradiated. The solutions of these complexes do not show the presence of any Co(II) after being stored for 2 years in Pyrex flasks in the dark.

In the case of the 2,3-diaminobutane complex at least 1 mole of aldehyde is formed for each mole of Co(II) that is produced. The ethylamine is isolated at only about one-half the molar value of the aldehyde in the case of both $[Co(bn)_3]Cl_3$ and $[Co(pn)_3]Cl_3$. Rate studies made on the production of aldehyde and Co(II) showed that some of the aldehyde was being consumed in a concurring reaction during photolysis. This process continues after all of the Co(III) has been reduced, so that the aldehyde concentration reaches a maximum at the time the cobalt reduction is completed.

The aminocarbonyl, corresponding to the replacement of an amine group by an oxo group in the particular diamine ligand, is formed during the photolysis. The molar amount of this complex isolated is about one-tenth that of the Co(II) formed. The diamine ligand of the complex is regenerated at about twice the molar value of Co(II) and ammonia is produced at about the same rate as the Co(II).

Formation of the Principal Products.—While it is recognized that a mechanism cannot be proposed which excludes all other possible ones, it is considered worthwhile to discuss a reasonable sequence of reactions which could account qualitatively and semiquantitatively for the products observed. The products which were detected and analyzed, and which are summarized in Table II, are indicated in the equation



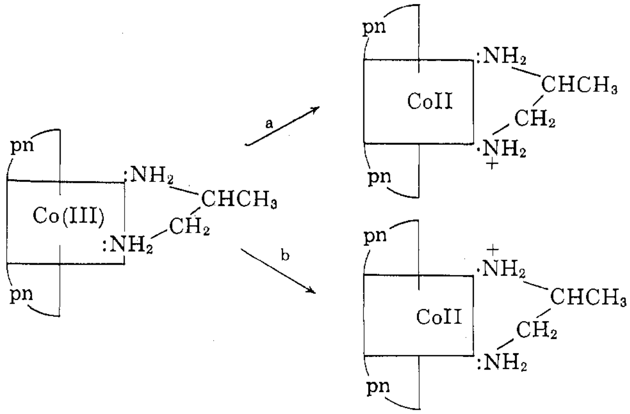
$$2[Co(diamine)_3]^{+3} \xrightarrow[H_2O]{h\nu} 2Co^{+2} + 4diamine + 2NH_3 + R'CHO + RCH_2NH_2 + R\!-\!\underset{H}{\overset{NH_2}{C}}\!-\!\underset{R'}{C}\!=\!O$$

The diamine in the above equation may be represented by $H_2NCHRCHR'NH_2$, where R and R′ may symbolize CH_3 or H. The ammonia and the amines would be protonated under the acid conditions used, but are represented in the nonprotonated form to simplify the equation. The proposed reaction steps are considered in more detail below.

(1) **Absorption of Energy and Deactivation of the Molecule.**—It is expected that absorption in the electron-transfer band could lead to an oxidation–reduction reaction resulting from the transfer of an electron from the ligand to the metal ion. This process and the possible deactivation of the excited species have been discussed previously.[8] The quantum yields were determined at 254 mμ to be 0.18, 0.11, and 0.07 for the bn, pn, and en complexes, respectively. The low quantum yields indicate that the excited molecules are readily deactivated and only a small percentage undergo permanent electron transfer.

(2) **Electron Transfer.**—The first step in the decomposition of the activated complex is proposed to be a transfer of an electron from one of the coordinated nitrogen atoms to the cobalt. It is known that oxidation or reduction of solutes in aqueous solutions can result from the irradiation of these solutions due to the absorption of energy by the water itself[16]; this is generally the primary process at low concentration of solute and with irradiation by γ-rays or X-rays. However, water is transparent to ultraviolet light down to about 195 mμ and the light sources used in these studies are not expected to provide the energy necessary for photodecomposition of water. In addition, analogous reactions occur in the absence of H_2O.[7,17]

In the cases of $[Co(bn)_3]Cl_3$ and $[Co(en)_3]Cl_3$ only one radical ion is possible by the electron transfer, since in these compounds both nitrogen atoms are equivalent, *i.e.*, $R = R'$. There are two possibilities for the electron transfer with $[Co(pn)_3]Cl_3$, as is shown by the equations



Only formaldehyde was found in the irradiated solutions containing $[Co(pn)_3]^{+3}$ and this is considered to indicate that the reaction proceeds by path a. As will be discussed below, the lack of detectable methylamine

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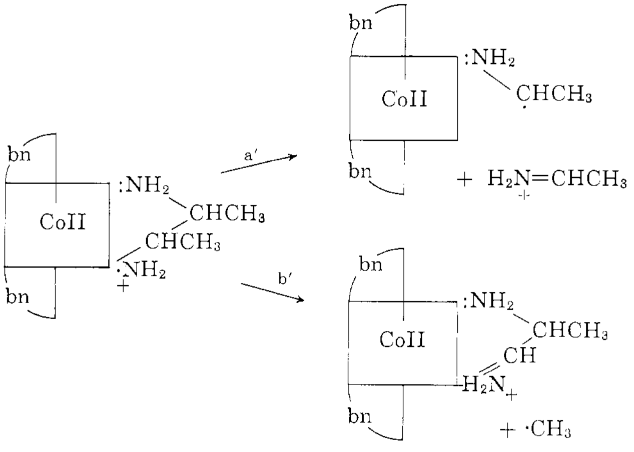
[16] C. Ferradini, *Advan. Inorg. Chem. Radiochem.*, **3**, 171 (1961).

[17] Results of A. L. Plumley and C. W. Moeller, to be published.

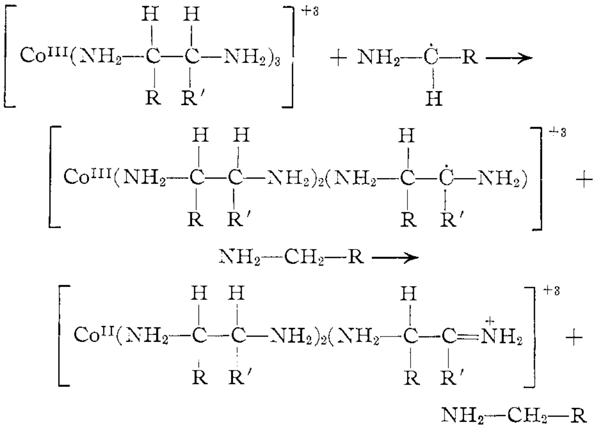
and aminoacetone is in agreement with this conclusion. The preference of path a over path b can be explained in terms of the relative stabilities of the radicals formed by the subsequent reaction of the radical ion, *i.e.*, the stability of a secondary radical compared to a primary.[18,19]

(3) **β-Elimination in the Radical Ion.**—The decomposition of the radical ion begins with the elimination of a group attached to the carbon atom β to the nitrogen atom having the unpaired electron. Since the C–C bond requires only about 83 kcal./mole for fission compared to about 90 kcal./mole for a C–H bond, it is expected that when both are present it will be the C–C bond that ruptures. In both $[Co(en)_3]Cl_3$ and $[Co(pn)_3]Cl_3$, R = H, and the fission would occur at the only C–C bond present. There are two C–C bonds β to the nitrogen atom with the unpaired electron in the radical ion of $[Co(bn)_3]Cl_3$; this results in two possibilities for the elimination reaction



Here, again, it is presumably the stability of the secondary radical over that of the primary that enhances the reaction through path a′. No 2-aminopropanal, which would form by hydrolysis of the imine of path b′, was detectable in this case; the acetaldehyde and ethylamine predicted for path a′ were found.

(4) **Hydrogen Abstraction by the Radical.**—Under the conditions used in these experiments the products indicate that the principal reactions of the radical are by hydrogen abstraction. Thus, in the case of $[Co(pn)_3]Cl_3$ aminoethane is formed and 2,3-diaminobutane is not detected, showing that dimerization of the aminoethyl radical is not occurring to a significant extent, if at all. Also, the formation of the aminocarbonyls can be explained by a reaction sequence such as in eq. 1. The imine compound would hydrolyze to the aminocarbonyl. The problem of the further reactions of the aminocarbonyls is involved in the interpretation of the quantitative data. The lower yield of 2-aminopropanal from $[Co(pn)_3]Cl_3$ could be due to the readiness of this compound to polymerize in the acid solution. The aminocarbonyl from $[Co(bn)_3]Cl_3$ was found to be quite stable under the reaction conditions and this was further indicated by the smaller amount of polymeric material obtained upon irradiation of this complex.



$$\left[Co^{III}(NH_2-\underset{R}{\overset{H}{C}}-\underset{R'}{\overset{H}{C}}-NH_2)_3\right]^{+3} + NH_2-\underset{H}{\dot{C}}-R \longrightarrow$$

$$\left[Co^{III}(NH_2-\underset{R}{\overset{H}{C}}-\underset{R'}{\overset{H}{C}}-NH_2)_2(NH_2-\underset{R}{\overset{H}{C}}-\underset{R'}{\dot{C}}-NH_2)\right]^{+3} + NH_2-CH_2-R \longrightarrow$$

$$\left[Co^{II}(NH_2-\underset{R}{\overset{H}{C}}-\underset{R'}{\overset{H}{C}}-NH_2)_2(NH_2-\underset{R}{\overset{H}{C}}-\underset{R'}{C}=\overset{+}{N}H_2\right]^{+3} + NH_2-CH_2-R \quad (1)$$

It must be noted that according to exploratory studies the aminocarbonyls could be obtained by reactions of the appropriate aldehydes and monoamines upon irradiation. Thus aminoacetaldehyde can be prepared by irradiating a solution of formaldehyde and methylamine, while ethylamine reacts with formaldehyde or acetaldehyde to produce 2-aminopropanal or 3-aminobutanone-2, respectively. These reactions were very slow compared to the rates of aminocarbonyl formation upon irradiation of the complex ions. The diamines are primary amines and are present in larger concentrations than the monoamines, and it appears that in these systems the aldehydes react preferentially with the diamines.

(5) **Hydrolysis of the Imines.**—The instability of the imines with respect to hydrolysis under the conditions of the experiment is expected and the reactions can be represented by the equation

$$RC{=}NH_2^+ + H_2O \longrightarrow RC{=}O + NH_4^+$$

This would correspond to the formation of about 1 mole of ammonia for each mole of Co(II), which is in approximate agreement with the analytical results. The ammonia would be slower than the monoamines and diamines to react with the aldehydes.[20]

The 1,2-Diaminopropane Complex.—$[Co(pn)_3]Cl_3$ is of particular significance in these reactions because of the unsymmetrical ligand. The equivalent contribution of the two amine groups to the electron-transfer reaction should have led to the formation of both acetaldehyde and formaldehyde in equivalent amounts. The fact that no acetaldehyde was detected and that the infrared analyses would have disclosed amounts corresponding to less than one-tenth those of formaldehyde shows that the predominant electron-transfer reaction is from the amine on the end carbon atom, *i.e.*, path a above. This path is further confirmed by the formation of ethylamine and 2-aminopropanal as significant products. Methylamine might have gone undetected due to rapid condensation with formaldehyde as in the case of $[Co(en)_3]Cl_3$, but there was much less polymerization in the propylenediamine studies so it is felt that methylamine was not formed in appreciable

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[18] W. A. Waters, "The Chemistry of Free Radicals," Oxford University Press, 1948, p. 68.

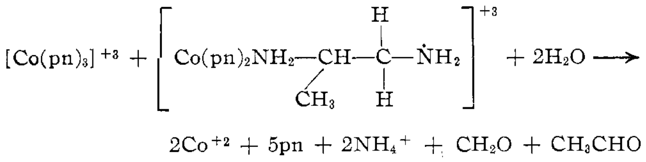
[19] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, Chapter 16.

[20] J. F. Carson and H. S. Olcott, *J. Am. Chem. Soc.*, **76**, 2257 (1954).

amounts, if at all. The attempts to detect aminoacetone, the alternative to 2-aminopropanal, were unsuccessful. Studies of the infrared spectra of the DNPH derivatives of synthetic mixtures of aminoacetone and 2-aminopropanal showed that, while the aminoacetone peaks are somewhat masked by those of the aminopropanal, amounts of the substituted acetone in excess of about one-tenth the concentration of 2-aminopropanal would be detectable.

It was felt that there might be sufficient stabilization of the aminoethyl radical formed in the β-elimination to allow it to dimerize. This termination of the radical reaction could account for the low yield of ethylamine compared to formaldehyde. However, the dimerization product, 2,3-diaminobutane, was not found, so it is concluded that dimerization does not represent an important radical removal reaction. In addition, attempts to detect the alternate product ethylenediamine which might have formed from aminomethyl radicals were not successful.

An alternative to steps (3) and (4) would be the reaction of the excited complex with more $[Co(pn)_3]^{+3}$.



$$[Co(pn)_3]^{+3} + \left[Co(pn)_2NH_2-\underset{CH_3}{CH}-\overset{H}{\underset{H}{C}}-\dot{N}H_2 \right]^{+3} + 2H_2O \longrightarrow 2Co^{+2} + 5pn + 2NH_4^+ + CH_2O + CH_3CHO$$

This would be analogous to a step proposed for the thermal and photochemical decomposition of $[Co(C_2O_4)_3]^{-3}$.[21] The absence of acetaldehyde demonstrates that this reaction path is not involved in the photolysis of the diamine complexes. However, the excited complex might act as a reducing agent for another Co(III) complex ion to form the imine which hydrolyzes to the aminocarbonyl.

Summary.—The coordination compounds $[Co(en)_3]Cl_3$, $[Co(pn)_3]Cl_3$, and $[Co(bn)_3]Cl_3$ decompose when solutions containing them are irradiated with ultraviolet light. The major decomposition products are Co(II), NH_3, the ligand diamines, and an aldehyde. Formaldehyde is obtained from the decomposition of $[Co(en)_3]Cl_3$ and $[Co(pn)_3]Cl_3$, while acetaldehyde is formed from $[Co(bn)_3]Cl_3$. The ratios of the amounts of products change as the irradiation times of the solutions are increased. If the irradiation is continued beyond the time required to reduce all of the cobalt to Co(II), the aldehyde concentration decreases. Ethylamine could be isolated from solutions containing the bn and pn complexes, while similar experiments with solutions of the en complex yielded only a resinous nitrogen-containing material. It is considered that methylamine had formed but reacted with formaldehyde too rapidly to be detected. The irradiated solutions of each of the coordination compounds contained aminocarbonyl compounds; the compounds formed are aminoacetaldehyde, 2-aminopropanal, and 3-aminobutanone-2 from $[Co(en)_3]Cl$, $[Co(pn)_3]Cl_3$, and $[Co(bn)_3]Cl_3$, respectively. In the case of $[Co(pn)_3]Cl_3$ perhaps as significant as the products found were those that were sought but which could not be detected: acetaldehyde, methylamine, aminoacetone, 2,3-diaminobutane, and ethylenediamine.

No examinations of optical activity changes were made in these studies. The 2,3-diaminobutane used was a mixture of 50% *meso* and 50% *d,l* racemic isomers. The mixture can be separated into the *d,l* and the *meso* components by recrystallization of the chloride salts from absolute methanol, the *meso* salt being less soluble. Photochemical studies using the separated isomers of bn as ligands are planned in an attempt to disclose further the course of the decomposition reactions.

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(21) T. B. Copestake and N. Uri, *Proc. Roy. Soc.* (London), **A228**, 252 (1955).