of the bromo and chloro complexes are notably different from those of the corresponding bands for $Co(EDTA)^-$. The intensity of the second CD band is approximately twice that for $Co(EDTA)^-$ while the intensity of the first band approaches zero for the pentadentate complexes. These changes may be due in part to the very low symmetry of the pentadentate complexes. If approximate C_s symmetry is assumed, one might expect transitions polarized perpendicular to the plane containing the halide ion to have quite different rotational strengths from those polarized parallel to this plane. Another factor which probably contributes to this change in intensities is the decrease in strain in the EDTA chelate system. For complexes similar to $Co(EDTA)^-$ in which the strain of the chelate system has been reduced by enlarging or eliminating the five-membered diamine ring, the intensity of the second CD band is increased more than is that of the lowest energy band.[14]

The CD curves of the bromo and chloro complexes do not vary significantly with the pentadentate ligand used, indicating the relative unimportance of the acetate or hydroxyethyl side chain. By contrast the CD curves for the nitro complexes change markedly as the pentadentate ligand is varied (Figure 5). Possibly the sensitivity of the CD spectra of the nitro complexes to the nature of the pentadentate ligand is due to the π-bonding ability of the nitro group. The π-bonding of the nitro group could be affected by hydrogen bonding to the hydroxyethyl chain or through water to the acetate chain. The electronegativity of the variable portion of the pentadentate ligand cannot explain the observations since the order $-CH_2CH_2OH > -CH_3 > -CH_2COO^-$ is not consistent with the trend of the change in the CD curves. The coordinated nitrogens to which these groups are attached are asymmetric but it is unlikely that this factor would cause variation within the nitro series but not within the series of halide complexes. Thus, although steric and electrical properties of the pentadentate ligands apparently affect the interaction of the nitro group with the metal ion, the exact reason for the changes observed is not now known.

Since the total areas of CD bands in the low-energy region are comparable for $Co(EDTA)^-$, $Co(EDTA)X^{2-}$, $Co(MEDTA)X$, and $Co(YOH)X^-$ ($X^- = Cl^-$ or Br^-), coordination of the fourth acetate group must make little contribution to the total rotational strength of $Co(EDTA)^-$. The small contribution found is contrary to predictions that increasing the number of chelate rings or the strain in a chelate complex should increase its rotational strength. Also the uncoordinated acetate group in $Co(EDTA)X^{2-}$ ($X^- = Cl^-$ or Br^-) apparently makes no significant contribution to the optical activity; this group would be expected to contribute significantly to the optical activity only if it is in a preferred conformation.

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Photochemical Reactions of Nitropentaamminecobalt(III) Ion

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The photochemical behavior of $Co(NH_3)_5NO_2^{2+}$ has been investigated in aqueous solution and in the solid state. Excitations have been performed by radiations at 254, 313, 365, and 442 mμ, corresponding to charge-transfer and ligand-field bands of the complex. The nature of the photoreactions has been established by spectrophotometric measurements in the uv, visible, and ir spectral regions and by chemical analyses of some of the reaction products. In aqueous solution at all of the wavelengths of irradiation, the oxidation–reduction decomposition involving the NO_2^- ligand and the nitro → nitrito linkage isomerization occur simultaneously. In the solid state the nitro → nitrito isomerization occurs at all of the wavelengths of irradiation, accompanied at 254 mμ by a minor oxidation–reduction decomposition. For aqueous solutions the quantum yields of the two photoreactions have been determined. They decrease with decreasing energy of the exciting radiations, but their ratio is almost wavelength independent. The mechanisms of the photoreactions are discussed, and it is proposed that the same photoreactive excited state is involved, independent of the wavelength of irradiation. On the basis of the data obtained, it is also concluded that, even in solution, the linkage photoisomerization must occur through an intramolecular mechanism.

Transition metal complexes may undergo three principal types of photoreactions: (1) photoxidation–reduction reactions, involving changes in oxidation number of metal and/or ligand(s); (2) photosubstitution reactions (generally, photoaquations), involving changes in the composition of the coordination shell; (3) photoisomerization reactions, involving changes in the coordination arrangement of the ligands.

In the case of Co(III) complexes, owing to the high oxidation number of the central metal ion and the general reducing properties of the ligands, the reactions of the first type always consist of an electron transfer from the ligand(s) to the metal, followed by the decomposition of the unstable Co(II) complex so originated.[1] For mixed-ligand complexes, such as $Co(NH_3)_5NO_2^{2+}$, both the photooxidation–reduction and the photoaquation reactions could involve either of the ligands. In addition, $Co(NH_3)_5NO_2^{2+}$ could also undergo a photochemical isomerization since linkage isomerism for the NO_2^- group in cobalt(III) ammine complexes is possible.[2] Therefore, for this complex as many as five different photoreactions may be expected: photoxidation–reduction decomposition involving NO_2^-

$$Co(NH_3)_5NO_2^{2+} \xrightarrow{h\nu} Co^{2+} + 5NH_3 + NO_2 \qquad (1)$$

photooxidation–reduction decomposition involving NH_3

$$Co(NH_3)_5NO_2^{2+} \xrightarrow{h\nu} Co^{2+} + 4NH_3 + NO_2^- + \text{oxidation products of } NH_3 \qquad (2)$$

NO_2^- photoaquation

$$Co(NH_3)_5NO_2^{2+} \xrightarrow[H_2O]{h\nu} Co(NH_3)_5H_2O^{3+} + NO_2^- \qquad (3)$$

NH_3 photoaquation

$$Co(NH_3)_5NO_2^{2+} \xrightarrow[H_2O]{h\nu} \textit{cis-}\text{ and/or } \textit{trans-}Co(NH_3)_4(H_2O)NO_2^{2+} + NH_3 \qquad (4)$$

nitro → nitrito linkage photoisomerization

$$Co(NH_3)_5NO_2^{2+} \xrightarrow{h\nu} Co(NH_3)_5ONO^{2+} \qquad (5)$$

Although a number of investigations have been reported concerning the photochemical behavior of $Co(NH_3)_5NO_2^{2+}$, there has been no agreement regarding both the nature of the reaction products and the mechanism of the photoreactions.

According to some authors, when $Co(NH_3)_5NO_2^{2+}$ solutions are exposed to light, Co^{2+} or other Co(II) species (depending on the pH of the reaction medium) are formed.[3-6] However, Schwarz and Weiss[7] and Tsuneda and Oouchi[8] reported that the complex undergoes a complete photodecomposition *without* any reduction of the central ion, and Shinozuka and Kikuchi[5] found that no more than 30% of the initial Co^{3+} was reduced even after very prolonged irradiation. According to Schwarz and Weiss[7] and Tsuneda and Oouchi,[8] all NO_2^- and NH_3 contained in the original complex were present in the solution after irradiation, while the other authors did not determine the concentration of NO_2^- and NH_3 after the photoreaction. Regarding the mechanism of the photoreactions, the following primary processes have been proposed: (a) intramolecular oxidation–reduction between the central metal and the NO_2^- group (reaction 1);[9] (b) NH_3 aquation (reaction 4);[8] (c) simultaneous NH_3 and NO_2^- aquations (reactions 3 and 4);[5] (d) intramolecular oxidation–reduction between the central ion and the NO_2^- group (reaction 1) simultaneous with the NO_2^- aquation (reaction 3).[6]

A careful examination of the literature reports shows that in several cases the results were either inaccurate or incomplete. In fact, the main reasons for such a general disagreement are clearly associated with (1) the failure to search for the occurrence of other photoreactions besides the most evident or "expected" one, (2) the failure to distinguish between primary photoreactions and secondary thermal and/or photochemical reactions, and (3) the failure to control the reaction medium during irradiation.

As far as the photochemical behavior of $Co(NH_3)_5NO_2^{2+}$ salts in the solid state is concerned, the first significant study is that by Adell,[10] who proved that the red compound obtained from $[Co(NH_3)_5NO_2]Cl_2$ on prolonged exposure to sunlight was the nitrito isomer (reaction 5). This result has been recently confirmed by Wendlandt and Woodlock,[11] irradiating with uv radiations.

The purpose of this investigation was to clarify some of the experimental and theoretical aspects of the photochemistry of $Co(NH_3)_5NO_2^{2+}$.

Experimental Section

Preparation of Compounds.—Both the nitro- and nitritopentaamminecobalt(III) complexes may be prepared as salts of various anions.[12,13] From the investigations by Adell[14] it appears that only the nitro forms are stable (the nitrito complexes are reported to undergo a complete isomerization after standing, even in the solid state); however, Beattie and Satchell[15] found that for the solid $[Co(NH_3)_5NO_2]Cl_2$ there is an equilibrium between the nitro and nitrito forms, with the nitrito form being favored. We prepared $[Co(NH_3)_5NO_2](NO_3)_2$ according to ref 16 and verified by means of infrared spectroscopy[15,17] that this compound did not contain any appreciable amount of the isomeric nitrito form neither when it was freshly prepared nor after standing for 6 months in the dark at room temperature. The electronic absorption spectrum of freshly prepared solutions of the complex agreed well with that reported by Linhard and Weigel,[9] even when the complex had been aged in the solid state. Since both infrared and ultraviolet (see Figure 1) spectra are very sensitive to the presence of the nitrito form, we concluded that our complex was a pure nitro form even after long aging.

The possible photoreaction products of $Co(NH_3)_5NO_2^{2+}$ (see reactions 3–5) were also prepared, in order to know their spectra in detail. The nitritopentaamminecobalt(III) perchlorate, $[Co(NH_3)_5ONO](ClO_4)_2$, was prepared following the method indicated in ref 13. Both infrared[15,17] and ultraviolet[18] spectra

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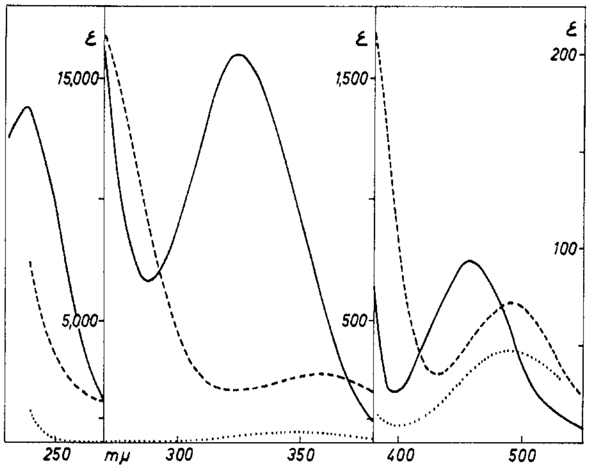

Figure 1.—Electronic absorption spectra: ——, $CO(NH_3)_5NO_2{}^{2+}$; - - - - -, $Co(NH_3)_5ONO^{2+}$; · · · · ·, $Co(NH_3)_5H_2O^{3+}$.

indicated that at low temperature (about −5°) this complex can be stored for several months without appreciable isomerization. The aquopentaamminecobalt(III) perchlorate, $[Co(NH_3)_5(H_2O)](ClO_4)_3$, was prepared from the corresponding chloride salt obtained by a published method,[19] slightly modified. The *cis*-nitroaquotetraamminecobalt(III) nitrate, *cis*-$[Co(NH_3)_4(H_2O)NO_2](NO_3)_2$, was prepared following the method of Yalman and Kuwana.[20] The *trans*-nitroaquotetraamminecobalt(III) chloride, *trans*-$[Co(NH_3)_4(H_2O)NO_2]Cl_2$, was obtained according to a published method.[21] The complexes were purified and recrystallized following the procedures indicated in the original papers.

Apparatus.—Radiations of 254 mμ were obtained using the irradiation equipment previously described.[22] Beams of nearly monochromatic radiations of 313 and 365 mμ were obtained from the Hanau Q 400 mercury vapor lamp arranged as already described[22] by using Schott and Gen. interference double filters instead of the glass-solution filters. On the basis of the lamp output at the various wavelengths and of the spectral characteristics of the filters (λ_{max} 313 and 365 mμ; T = 24 and 40%; half-width = 12 and 10 mμ, respectively), we have calculated that the spectral impurities were ~7% for the 313-mμ radiation and ~1% for the 365-mμ radiation. A narrow spectral band centered at 442 mμ was isolated from a Philips Attralux Spot 150-W, 24-V incandescent lamp by means of a Schott and Gen. interference double filter (T_{max} = 35%, half-width = 13 mμ). To reduce heating in the filter, a solution of $CuSO_4$ (4% w/v, in 0.1 N H_2SO_4; thickness = 5 cm) was situated on the optical path, facing the lamp. The light absorbed by the solution, measured by means of the ferric oxalate actinometer,[23] was of the order of 0.5×10^{-6} $Nh\nu$/min at each wavelength used. For solid samples, additional experiments have been made under the following conditions, in order to have a higher light intensity: (a) irradiation with the low-pressure Hg lamp without any filter (about 85% of the emission was the 254-mμ radiation); (b) irradiation with the high-pressure Hg lamp filtered with 2-mm Chance glass OX 1, which is transparent between 300 and 400 mμ; (c) irradiation with the incandescent lamp filtered with a 3-72 Corning glass, which is transparent over 430 mμ. The irradiation of solutions of $Co(NH_3)_5NO_2{}^{2+}$ was performed using spectrophotometer cells housed in thermostated cell holders. The irradiation of solid $[Co(NH_3)_5NO_2](NO_3)_2$ was performed on Nujol mulls or on finely powdered samples of the complex.

Spectrophotometric measurements were carried out with an Optical CF 4 NI spectrophotometer, which makes possible both manual measurements and automatic recording. The infrared spectra were recorded with a Hilger and Watts Model H 900 spectrometer.

Chemical Analyses.—The rate of formation of Co^{2+} as a function of the irradiation time has been determined by measuring the Co^{2+} concentration with the method of Vydra and Pribil.[24] We have verified that the measurements were unaffected by the presence of both the reagent and its aquosubstitution and isomerization products.

The rate of $NO_2{}^-$ formation has been determined by measuring the amount of free $NO_2{}^-$ by the method of Vogel,[25] slightly modified. We have found that under the experimental conditions the nitro complexes did not affect the measure, whereas the nitritopentaammine complex released $NO_2{}^-$ quantitatively.

The determination of NH_3 has been accomplished by means of the Nessler method.[26] Since some intermediate product interfered, quantitative measurements were possible only on solutions completely photodecomposed.

Procedure.—The general procedure for the study of the photochemical behavior of solutions of $Co(NH_3)_5NO_2{}^{2+}$ was as follows. A weighed amount of the complex was dissolved in 0.1 N $HClO_4$ as quickly as possible in red light. Two 1-cm spectrophotometer cells were filled with 3 ml of freshly prepared solution. One of the cells was placed in the thermostated cell holder of the irradiation equipment. During the irradiation the solution was stirred by the bubbling of a stream of purified N_2. In order to provide the control for possible thermal reactions (which, however, should be negligible at 25°[27,28]), the other cell was placed in a thermostated cell holder maintained in the dark at the same temperature. After suitable irradiation periods, both of the cells were brought to the spectrophotometer and the changes in absorbance caused by irradiation were measured by the differential spectrophotometric method in the range 270–530 mμ. Moreover, chemical analyses of the irradiated solution, as well as of the sample kept in the dark (which provided blank values), were accomplished following the methods described above. All of the experiments were carried out at 25°. The complex concentration was between 10^{-3} and 10^{-2} F. With such concentrations, the radiations of 254, 313, and 365 mμ were almost completely absorbed for sufficiently long irradiation periods, while, in the case of the 442-mμ radiations, appropriate corrections for the fraction of light absorbed had to be made in order to calculate the quantum yields.

In order to study the photochemical behavior of the complex in the solid state, ultraviolet spectra and analysis of Co^{2+} were performed after dissolution of the irradiated samples in 0.1 N $HClO_4$. The infrared spectra were directly measured on the irradiated Nujol mulls of the complex.

Results

Solutions.—Preliminary experiments showed that, as previously reported,[3,7] aqueous solutions of the complex rapidly became clouded upon irradiation, owing to the precipitation of cobalt hydroxides. In order to avoid such trouble, all the experiments were carried out in 0.1 N $HClO_4$ solutions. This reaction medium offered two additional advantages as it prevented both changes in the pH of the solution during irradiation and reoxidation by air of the Co(II) species produced.

The results obtained are qualitatively the same at each one of the wavelengths of irradiation (254, 313, 365, and 442 mμ) and may be summarized as follows.

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(1) During irradiation the absorbance decreased over the entire spectral region examined (270–530 mμ), and Co^{2+}, NO_2^-, and NH_3 were produced.

(2) The changes in absorbance at the various wavelengths and the concentrations of Co^{2+} and NO_2^- increased linearly as the total number of photons absorbed by the solution increased, until 30–50% of the original complex had been decomposed.

(3) After short irradiation times, the concentration of NO_2^- ion was three-fourths of the Co^{2+} concentration.

(4) If a solution was allowed to stand in the dark after a short irradiation time, its spectrum slowly changed; in particular, light absorption increased in the ranges 295–370 and 420–470 mμ, decreased in the ranges 270–295 and 370–420 mμ, and did not change at ~295, 370, 420, and 470 mμ.

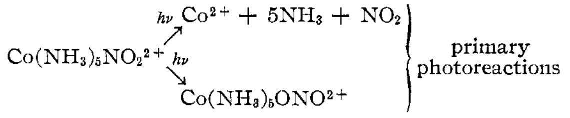
(5) After complete photodecomposition (*i.e.*, when irradiation did not produce any further spectral change), 1 mol of Co^{2+}, 5 mol of NH_3, and 0.5 mol of NO_2^- were present for each mole of the original complex, according to the *over-all* reaction

$$Co(NH_3)_5NO_2^{2+} + 0.5H_2O + h\nu = Co^{2+} + 5NH_3 + 0.5HNO_2 + 0.5HNO_3 \quad (6)$$

(6) Finally, the irradiation of $Co(NH_3)_5ONO^{2+}$ solutions (at the same wavelengths used for irradiating $Co(NH_3)_5NO_2^{2+}$) ultimately led to 1 mol of CO^{2+}, 5 mol of NH_3, and 0.5 mol of NO_2^- for each mole of the original complex.

Observations 1 and 2 show that a primary oxidation–reduction photodecomposition occurred. Since the NO_2^- concentration was lower than the Co^{2+} concentration (point 3), presumably the NO_2^- ligand was involved in the primary photoxidation–reduction reaction (reaction 1). Point 4 indicates that some nitrito isomer was formed upon irradiation (reaction 5), since only the nitrito → nitro thermal isomerization can account for the observed spectral variations (compare with Figures 1 and 2). The detection of NO_2^- ion in the irradiated solutions could indicate the occurrence of the NO_2^- aquation (reaction 3), and/or the oxidation–reduction decomposition involving NH_3 (reaction 2). However, it must be noted that NO_2^- could also originate indirectly from the products of reactions 1 and 5. In fact: (a) reaction 1 requires the production of NO_2 radicals, which are known to disproportionate as: $2NO_2 + H_2O = HNO_2 + HNO_3$; (b) as reported in the Experimental Section, $Co(NH_3)_5ONO^{2+}$ released NO_2^- quantitatively when the reagents for determining the NO_2^- ion were added to solutions containing the complex.

The *quantitative* analysis of the results showed that they were consistent *only* with the following reaction sequence, involving reactions 1 and 5 as simultaneous primary processes



$$Co(NH_3)_5NO_2^{2+} \begin{array}{l} \xrightarrow{h\nu} Co^{2+} + 5NH_3 + NO_2 \\ \xrightarrow{h\nu} Co(NH_3)_5ONO^{2+} \end{array} \Bigg\} \text{ primary photoreactions}$$

$$Co(NH_3)_5ONO^{2+} \xrightarrow{h\nu} Co^{2+} + 5NH_3 + NO_2 \quad \text{secondary photoreaction}$$

$$NO_2 + 0.5H_2O \longrightarrow 0.5HNO_2 + 0.5HNO_3 \quad \text{secondary thermal reaction}$$

In fact: (i) after short irradiation periods, the ratio

$$\frac{\Delta A_{exp} - \Delta A_{redox}}{\epsilon_{nitro} - \epsilon_{nitrito}} = C_{nitrito} \quad (7)$$

where ΔA_{exp} = experimental change in absorbance, ΔA_{redox} = contribution of reaction 1 to the change in absorbance, calculated on the basis of the Co^{2+} concentration, ϵ_{nitro} = molar extinction coefficient of $Co(NH_3)_5NO_2^{2+}$, $\epsilon_{nitrito}$ = molar extinction coefficient of $Co(NH_3)_5ONO^{2+}$, and $C_{nitrito}$ = molar concentration of $Co(NH_3)_5ONO^{2+}$, was constant throughout the spectral region examined (270–530 mμ); (ii) the concentration of NO_2^- was found to be *always* equal to $(X/2) + Y$, where X and Y represent the concentrations of Co^{2+} (directly measured) and of $Co(NH_3)_5ONO^{2+}$ (calculated by eq 7); (iii) the initially linear variation of absorbance and of Co^{2+} and NO^{2-} concentrations (point 2) showed that reactions 1 and 5 were primary photoprocesses; (iv) the observed stoichiometry of the over-all reaction (point 5) can be accounted for, considering the secondary photochemical decomposition of the nitrito isomer formed (point 6).

The quantum yield for reaction 1 has been determined from the amount of Co^{2+} produced, and the quantum yield for reaction 5 has been calculated on the basis of eq 7. Their values are reported in Table I, together with the upper limit values of the quantum yields for the other possible photoreactions, evaluated on the basis of the experimental errors involved in both the absorbance measurements and the chemical analyses.

Solid State.—Irradiation at 254, 313, 365, and 442 mμ converted $[Co(NH_3)_5NO_2](NO_3)_2$ into the nitrito isomer. In fact: (1) the infrared spectra of irradiated Nujol mulls of the complex showed a progressive de-

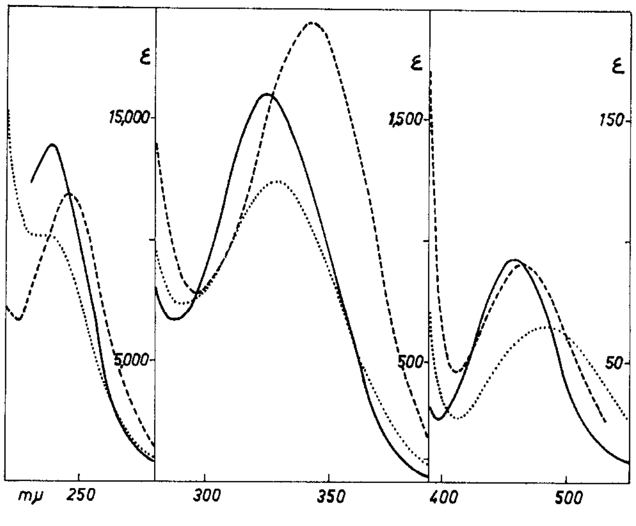


Figure 2.—Electronic absorption spectra: ——, $Co(NH_3)_5NO_2^{2+}$; ----, *trans*-$Co(NH_3)_4(H_2O)NO_2^{2+}$; ·····, *cis*-$Co(NH_3)_4(H_2O)NO_2^{2+}$.

Table I

Quantum Yield Values for the Photoreactions of $Co(NH_3)_5NO_2^{2+}$

Type of reaction (ligand involved)	λ of irradiation, mμ: 254	313	365[a]	442
Redox (NO_2^-)	0.51 ± 0.03	0.41 ± 0.02	0.31 ± 0.04	0.12 ± 0.01
Redox (NH_3)	<0.05	<0.04	<0.05	<0.02
Aquation (NO_2^-)	<0.01	<0.01	<0.01	<0.005
Aquation (*cis*-NH_3)	<0.03	<0.05	<0.03	<0.02
Aquation (*trans*-NH_3)	<0.01	<0.01	<0.02	<0.01
Linkage isomerization	0.13 ± 0.01	0.11 ± 0.01	0.055 ± 0.015	0.035 ± 0.010

[a] Adamson,[6] working at pH ~4, reported $\Phi = 0.65$ for the oxidation–reduction decomposition and $\Phi = 0.35$ for the NO_2^- aquation, irradiating at 370 mμ; Shinozuka and Kikuchi[5] reported $\Phi = 0.32$ for the oxidation–reduction decomposition, irradiating at 365 mμ.

crease in intensity of the bands at 1430, 1315, and 825 cm^{-1}, while new bands arose at 1460 and 1065 cm^{-1};[29] (2) as the irradiation time increased, the electronic absorption spectra of irradiated powder samples of the complex (recorded after dissolution in 0.1 *N* $HClO_4$) decreased in the spectral regions 290–370 and 410–440 mμ, while they increased in the other spectral regions (compare with Figure 1).

By irradiating Nujol mulls, it was possible to obtain an almost complete conversion of the nitro into the nitrito form. When irradiated mulls were placed in the dark at room temperature, a back reaction took place and, at the end, the ir spectrum agreed with the spectrum of the original complex. This result, however, did not allow us to exclude the occurrence of a minor amount of photodecomposition. Therefore, chemical analyses on irradiated powders of the complex were performed. It was found that irradiation at 254 mμ really caused the formation of some Co^{2+}, whereas irradiation at longer wavelengths did not produce any Co^{2+}. For example, on a sample irradiated for 9 hr with unfiltered light from the low-pressure Hg lamp (mainly 254-mμ radiations), 21% of the nitro complex was isomerized and about 1.5% was decomposed. Similar irradiation periods at 300–400 and >430 mμ caused 48 and 62% isomerization, respectively, but no appreciable (<0.2%) decomposition.

Discussion

Regarding the over-all reaction, our results disagree with those of Schwarz and Weiss[7] and Tsuneda and Oouchi.[8] It should be pointed out, however, that these authors did not work in acid but in aqueous solutions, which became rapidly alkaline because of the liberation of ammonia. According to Linhard and Weigel,[9] the thermal reoxidation of the Co^{2+} produced in the photochemical reaction can account for the stoichiometry observed by Schwarz and Weiss[7]

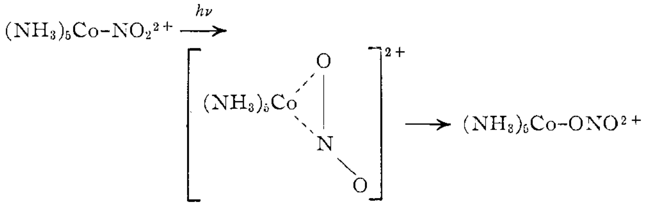
$$Co^{2+} + 2NH_3 + 2H_2O \longrightarrow Co(OH)_2 + 2NH_4^+$$

$$Co(OH)_2 + NH_3 + H_2O + NO_2 \longrightarrow Co(OH)_3 + NH_4^+ + NO_2^-$$

Regarding the primary photoreaction, our results confirm that the oxidation–reduction photodecomposition involving the NO_2^- ligand (reaction 1) takes place,[30] according to the suggestion first advanced by Linhard and Weigel;[9] in addition, the results indicate that some linkage isomerization (reaction 5) occurs simultaneously.

The occurrence of another photoreaction simultaneously with the oxidation–reduction photodecomposition had been already recognized by Adamson.[6] On the basis of the change in absorbance at 330 mμ, he thought that this reaction was the NO_2^- aquation. It should be pointed out, however, that measurements at only that wavelength could not really discriminate between NO_2^- aquation and linkage isomerization (see Figure 1). Finally, we found no evidence for NH_3 photoaquation, which had been assumed to occur by Tsuneda and Oouchi[8] and Shinozuka and Kikuchi[5] (for a critical discussion of these papers, see ref 1).

It has been demonstrated[13] by studies with ^{18}O that the thermal nitrito → nitro isomerization happens even in solution by an intramolecular process. It is interesting to know whether the photochemical nitro → nitrito isomerization in solution occurs through a similar mechanism or *via* NO_2^- photoaquation: (I) intramolecular mechanism



(II) intermolecular mechanism *via* NO_2^- photoaquation

$$(NH_3)_5Co\text{-}NO_2^{2+} \xrightarrow[H_2O]{h\nu} (NH_3)_5Co\text{-}OH_2^{3+} + NO^{2-} \qquad (a)$$

$$NO_2^- + H^+ \rightleftarrows HNO_2 \qquad (b)$$

$$(NH_3)_5Co\text{-}OH_2^{3+} \xrightarrow[HNO_2\text{-}NO_2^-]{k} (NH_3)_5Co\text{-}ONO^{2+} \qquad (c)$$

Our results and the knowledge of the rate constant for the formation of the nitrito complex from the aquo complex (process c) allow us to exclude mechanism II. In fact, we found that the rate of formation of $(NH_3)_5$-$Co\text{-}ONO^{2+}$ was always $\geqslant 5 \times 10^{-8}$ mol/l. sec (depending on the experimental conditions). Therefore, as the rate expression for the formation of the nitrito complex from the aquo complex is given[31] by the equation rate = $k[\text{aquo}][NO_2^-][HNO_2]$, the relation

$$k[\text{aquo}][NO_2^-][HNO_2] \geqslant 5 \times 10^{-8}$$

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[29] For the infrared spectra of $Co(NH_3)_5NO_2^{2+}$ and $Co(NH_3)_5ONO^{2+}$ see ref 15 and 17.

[30] The intramolecular oxidation–reduction reaction of $Co(NH_3)_5NO_2^{2+}$ involving the NO_2^- ligand has recently been proposed to occur also thermally,[27] together with the NO_2^- aquation reaction.[27,28]

[31] R. G. Pearson, P. M. Henry, J. G. Bergmann, and F. Basolo, *J. Am. Chem. Soc.*, **76**, 5920 (1954).

should hold in order for mechanism II to be operative. Since the rate constant is known[31] to be 0.9 l.^{2} mol^{-2} sec^{-1}, the relation above should be verified only for [aquo] $\geqslant 2.5 \times 10^{-2}$ *M*. This is impossible since the initial concentration of $Co(NH_3)_5NO_2^{2+}$, from which the aquo complex should originate, was always $\leqslant 8 \times 10^{-3}$ *M*.

The attribution of the absorption bands in the spectrum of $Co(NH_3)_5NO_2^{2+}$ has been discussed by Linhard and Weigel.[9] They questioned the previous interpretations of the spectrum and first assigned the high-intensity bands at 239 and 325 mμ to charge-transfer transitions from NO_2^- to the central metal ion. Besides these charge-transfer bands, a ligand-field band is present at 458 mμ, whereas the second ligand-field band, which should appear at about 330 mμ, is hidden by the more intense charge-transfer band. It should also be noted that the *free* NO_2^- ion in aqueous solution shows weak absorption bands at 357 mμ (ϵ 29) and 277 mμ (ϵ 9). These intraligand bands, which could change in both position and intensity with coordination, do not appear in the spectrum of the complex. The wavelengths of irradiation used in this work correspond to the high-energy charge-transfer band (254 mμ), to the low-energy charge-transfer band (313 and 365 mμ), and to the ligand-field band (442 mμ).

Two features of the results are of interest: (1) at all of the wavelengths of irradiation, including the one corresponding to the ligand-field band, the same photoreactions take place (*i.e.*, the oxidation–reduction decomposition involving the NO_2^- group and the linkage isomerization); (2) the ratio between the quantum yields of the two photoreactions is practically wavelength independent. These results strongly suggest that the two reactions originate from the same excited state. In addition, the fact that the quantum yields of both of the photoreactions decrease with decreasing energy of the exciting radiations seems to indicate that the two photoreactions compete with a primary recombination (cage effect).

A speculative discussion can then be made concerning the individualization of the photoreactive state. In doing this, a line of reasoning similar to the one given by Porter, *et al.*,[32] in discussing the photochemical behavior of $Co(ox)_3^{3-}$, may be followed.

Since the primary act leading to the oxidation–reduction reaction must be the dissociation of the NO_2 radical (*i.e.*, the oxidized NO_2^- ligand) from the then-reduced metal complex ion, the precursor to the photoreactions must be a $NO_2^- \rightarrow Co^{3+}$ charge-transfer state, *even when irradiation is performed with radiations corresponding to the ligand field band (442 mμ)*. The population of a charge-transfer state *via* ligand-field absorption at 442 mμ seems at first sight impossible, since the charge-transfer bands appear in the spectrum at higher energies than the ligand-field band involved. However, it must be pointed out that, owing to excited-state distortions and Franck–Condon restrictions, band maxima represent "vertical" excitation energies and include vibrational as well as electronic energy. The greater the antibonding character of an excited state, the more it will be distorted and the more its pure electronic energy will differ from that given by the band maximum. Therefore it could occur that the state absorbing at shorter wavelength has actually the lower pure electronic energy (see Figure 3). The photochemical results suggest that this could be the case for $Co(NH_3)_5NO_2^{2+}$ as well as for other Co(III) complexes ($Co(ox)_3^{3-}$,[32] $Co(NH_3)_5I^{2+}$,[1] $Co(NH_3)_5N_3^{2+}$[1]). It can be noted that all of these complexes contain strongly reducing ligands. In fact, since the reducing power of the ligands has the effect of lowering the energy of the charge-transfer states, the more reducing the ligands, the more a situation like that of Figure 3 will be probable.

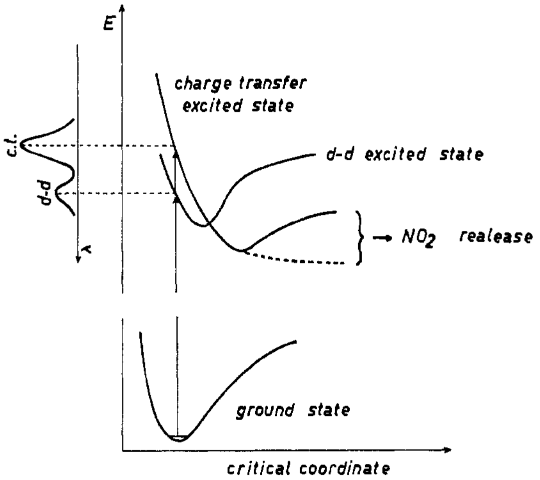

Figure 3.—Schematic representation of a possible relation of charge-transfer and ligand-field excited states.

In conclusion, we envision that by irradiating $Co(NH_3)_5NO_2^{2+}$ at 254, 313, 365, or 442 mμ, the same dissociative excited state is reached, either directly or indirectly (owing to radiationless transitions). The fate of the complex will then depend on the energy of the two fragments produced by the Co–NO_2 homolytic bond fission and on the reaction medium (solid state or solution). Besides the two extreme processes (ultimate separation of the two fragments, *i.e.*, oxidation–reduction decomposition, and primary recombination, *i.e.*, re-formation of the original Co–NO_2 bond), there is also a chance of a Co–ONO bond formation. According to the experimental results, which show that the quantum yields of both of the photoreactions decrease with decreasing excitation energy, the isomerization would compete with the primary recombination and parallel the ultimate separation of the two fragments. In other words, the fragments originating from the Co–NO_2 homolytic bond fission would have two different ways for escaping the primary recombination: (a) diffusive displacements, leading to the ultimate separation of the fragments and resulting in the oxidation–reduction decomposition of the com-

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[32] G. B. Porter, J. G. W. Doering, and S. Karanka, *J. Am. Chem. Soc.*, **84**, 4027 (1962).

plex; (b) rotations of the NO_2 group, creating an opportunity for the formation of a Co–ONO bond. Of course, in the solid state only the second way practically competes with the primary recombination.[33]

Acknowledgment.—The authors are indebted to Professor V. Carassiti for his interest in this work and for his helpful criticism.

(33) As far as the cage effect is concerned, our mechanism is similar to the general mechanism proposed in order to interpret the photochemistry of coordination compounds: A. W. Adamson and A. H. Sporer, *J. Am. Chem. Soc.*, **80**, 3865 (1958). For a critical discussion of Adamson and Sporer's mechanism, see ref 1.

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New Stilbenediamine Complexes of Nickel(II)

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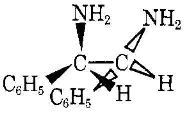
The preparation and electronic spectra are reported of the paramagnetic compounds $[Ni(ms\text{-}1,2\text{-diphenylethylenediamine})_2L_2](ClO_4)_2$ (L = pyridine or β-picoline) and $[Ni(rac\text{-}1,2\text{-diphenylethylenediamine})_2(DMSO)_2](ClO_4)_2\cdot 2DMSO$, and of the diamagnetic complexes Ni(*ms*- or *rac*-1,2-diphenylethylenediamine)$_2(ClO_4)_2L_2$ [L = $(C_6H_5)_3PO$ or $(C_6H_5)_3AsO$], $Ni(ms\text{-}1,2\text{-diphenylethylenediamine})_2(ClO_4)_2(DMSO)_4$, and $Ni(ms\text{-}1,2\text{-diphenylethylenediamine})_2(ClO_4)_2(\alpha\text{-picoline})_2$. It is suggested that in the diamagnetic compounds the nickel ions may be six-coordinate. The preparation of $[Ni(ms\text{-}1,2\text{-diphenylethylenediamine})_3](ClO_4)_2$ is also reported. The *Dq* values of *ms*- and *rac*-1,2-diphenylethylenediamine in the tris-chelate cations are very similar (~11,000 cm^{-1}) although $Ni(ms\text{-}1,2\text{-diphenylethylenediamine})_3^{2+}$ is formed much less readily than its analog with the racemic base. The band in the region 22,000–23,500 cm^{-1} for the diamagnetic complexes is probably due to the transition $d_{xy} \rightarrow d_{x^2-y^2}$.

Introduction

The relationship among the magnetic properties, colors, and structures of nickel(II) complexes with 1,2-diphenylethylenediamine[1] and related ligands has occasioned interest ever since they were first described by Lifschitz and his coworkers.[2-4] Although the main features of the unusual behavior of these compounds are now fairly well understood,[5] certain aspects merit further study. For example, whereas the "blue," fully paramagnetic complexes $Ni(diamine)_2X_2$ or their hydrates have distorted octahedral configurations with the anions or water molecules in axial positions,[6] the coordination numbers of the nickel(II) ions in the "yellow," diamagnetic complexes are less firmly established. The diamagnetism of a complex NiL_4X_2 does not necessarily differentiate between planar $[NiL_4]X_2$ and six-coordinate, tetragonal NiL_4X_2. In $[Ni(ms\text{-stien})_2(CHCl_2CO_2)_2]_3\cdot 2C_2H_5OH\cdot 4H_2O$ one-third of the nickel(II) ions are present as planar, diamagnetic $Ni(ms\text{-stien})_2^{2+}$ species,[6] but diamagnetic $Ni\{C_6H_4[As(CH_3)_2]_2\}_2I_2$ is pseudo-octahedral.[7] With anions as the potential axial ligands it is often difficult without an X-ray study to determine whether they are, in fact, coordinated.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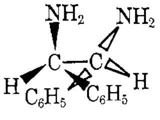
II

Also there is, as yet, insufficient information concerning the extent to which steric and electronic factors contribute to produce either a spin-singlet or a spin-triplet ground state.

We have prepared some complexes of the type $Ni(stien)_2L_2(ClO_4)_2$ (where L is a monodentate, neutral ligand) with both *ms*- and *rac*-stien, to examine the effect on the magnetic properties of varying the steric requirements and donor strength of L. We report here the results of this work and also the preparation of $Ni(ms\text{-stien})_3(ClO_4)_2$.

Experimental Section

Preparation of Compounds. **$Ni(ms\text{-stien})_3(ClO_4)_2$.**—A concentrated ethanolic solution of $Ni(ClO_4)_2\cdot 6H_2O$ (0.73 g) was added dropwise to a mechanically stirred solution of *ms*-stien (2.54 g) in ethanol (20 ml). The resulting solution was immediately filtered, and after 2 hr the fine violet precipitate was filtered off and dried *in vacuo* (50% yield). *Anal.* Calcd for $C_{42}H_{48}Cl_2N_6NiO_8$: C, 56.39; H, 5.41; N, 9.40; Ni, 6.56. Found: C, 55.93; H, 5.51; N, 9.14; Ni, 6.58.

$Ni(rac\text{-stien})_3(ClO_4)_2$.—This violet compound was obtained in 80% yield as for the *ms*-stien analog. The *rac*-stien complex precipitated immediately and was filtered off and dried to constant weight at 115°. *Anal.* Calcd for $C_{42}H_{48}Cl_2N_6NiO_8$: Cl, 7.93; N, 9.40; Ni, 6.56. Found: Cl, 7.71; N, 9.77; Ni, 6.59.

$Ni(ms\text{-stien})_2[(C_6H_5)_3PO]_2(ClO_4)_2$.—A mixture of triphenylphosphine oxide (1.39 g) and finely powdered $Ni(ms\text{-stien})_2(ClO_4)_2$[2] (1.36 g) in 1-butanol (150 ml) was boiled for 30 min and then filtered. On standing overnight, the deep yellow solution deposited bright yellow crystals (27% yield). *Anal.* Calcd for

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(1) Commonly called stilbenediamine (abbreviated here as stien) which can be obtained as *meso* and racemic forms (I and II, respectively)

(2) I. Lifschitz, J. G. Bos, and K. M. Dijkema, *Z. Anorg. Allgem. Chem.*, **242**, 97 (1939).

(3) I. Lifschitz and J. G. Bos, *Rec. Trav. Chim.*, **59**, 407 (1940).

(4) I. Lifschitz and K. M. Dijkema, *ibid.*, **60**, 581 (1941).

(5) J. R. Miller, *Advan. Inorg. Chem. Radiochem.*, **4**, 172 (1962).

(6) S. C. Nyburg and J. S. Wood, *Inorg. Chem.*, **3**, 468 (1964).

(7) N. C. Stephenson, *Acta Cryst.*, **17**, 592 (1964).