(37) K. S. Murray and R. M. Sheehan, *Chem. Phys. Lett.*, **22**, 406–410 (1973).
(38) K. S. Murray and R. M. Sheehan, *J. Chem. Soc., Dalton Trans.*, 999–1005 (1976).
(39) A. von Zelewsky and H. Fierz, *Helv. Chim. Acta*, **56**, 977–980 (1973).
(40) T. M. Dunn, *Trans. Faraday Soc.*, **57**, 1441–1444 (1961).
(41) A. J. Freeman and R. E. Watson, "Magnetism", Vol. II, G. T. Rado and H. Suhl, Ed., Academic Press, New York, N.Y., 1965, p 167.
(42) M. C. R. Symons and J. G. Wilkinson, *J. Chem. Soc. A*, 2069–2074 (1971).
(43) P. W. Atkins and M. C. R. Symons, "The Structure of Inorganic Radicals", Elsevier, New York, N.Y., 1967.
(44) L. C. Dickinson and J. C. W. Chien, *Inorg. Chem.*, **15**, 1111–1114 (1976).
(45) V. Malatesta and B. R. McGarvey, *Can. J. Chem.*, **53**, 3791–3800 (1975).
(46) W. C. Lin, C. A. McDowell, and D. J. Ward, *J. Chem. Phys.*, **49**, 2883–2886 (1968).
(47) N. S. Hush and I. S. Woolsey, *J. Chem. Soc., Dalton Trans.*, 24–34 (1974).
(48) A. Dedieu, M.-M. Rohmer, and A. Veillard, *J. Am. Chem. Soc.*, **98**, 5789–5800 (1976).
(49) A. Pezeshk, F. T. Greenaway, J. C. Dabrowiak, and G. Vincow, unpublished results.
(50) F. D. Tsay, H. B. Gray, and J. Danon, *J. Chem. Phys.*, **54**, 3760–3769 (1971).

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Photodecomposition of *cis*-Azidoamminebis(2,4-pentanedionato)cobalt(III)

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Irradiation of methanolic solutions of $Co(acac)_2N_3NH_3$ with 350-nm radiation yields azide radicals and $Co(acac)_2$. The quantum yield for cobalt(II) formation was 0.019 ± 0.001 and evidence suggests that secondary recombination is ineffective under the conditions used. The second-order rate constant for secondary recombination is estimated to be 7.1×10^4 M^{-1} s^{-1}. There is no evidence for nitrene or coordinated nitrene formation at this wavelength. The results suggest that although several states are populated by the 350-nm exciting radiation, only the charge transfer to metal state(s) involving the azido group results in photodecomposition.

Introduction

The photodecomposition of coordinated azides is of special interest because of the varied modes of photodecomposition which have been observed involving this ligand.[1-8] In addition, the work of Zink[9] suggests that such complexes illustrate the relationship between the numerous excited states available to such complexes and their observed photoreactions. Nonetheless, relatively few detailed studies have been carried out on azido complexes, and further study will be necessary if an understanding of their photochemistry is to be realized.

Investigations of the azidopentaammines of the cobalt triad suggest that the metal will have a major influence on which modes of photodecomposition will be observed.[2,7,8] Furthermore, replacing the ammines of the azidopentaamminecobalt(III) ion with cyano groups also changes the mode of decomposition.[1] The *cis*-azidoamminebis(2,4-pentanedionato)cobalt(III) complex, $Co(acac)_2N_3NH_3$, has been chosen for investigation in order to judiciously exploit the β-diketonate ligand and its derivatives in hope of probing various features of the photochemistry of coordinated azides. The photodecomposition of a number of tris(β-diketonates) of cobalt(III) have been studied, and their spectra and photochemistry are now reasonably well understood.[11,12] The reactive state is believed to be a singlet ligand to metal charge transfer state, CTTM, and the reactions involve reduction of the metal center and a one-electron oxidation of the β-diketonate ligand.[10] The photochemical behavior of azido complexes, on the other hand, is more varied and less well understood. To date, three modes of photodecomposition involving the azido group have been observed. Photosubstitution involves the loss of the azido group as azide ion,[13] photo oxidation–reduction involves its loss as azide radical and reduction of the metal center,[2-5] and coordinated nitrene formation involves cleavage of nitrogen–nitrogen bond of the azido group to form molecular nitrogen and coordinated nitrene.[6-9]

Furthermore, whereas the electronic state(s) responsible for $Co(acac)_3$ photochemistry has been identified[11-13] and in azide ion, hydrazoic acid, and organic azides internal azide electronic transitions have been identified,[14,15] no such transitions have been identified in azido complexes.[8,16,17] In $Co(acac)_2N_3NH_3$ the charge-transfer states involving the 2,4-pentanedione and azide are similar in energy and one might expect either or both pentanedione or azide radicals to result from charge-transfer excitation. Furthermore, charge-transfer excitations have yielded both nitrene formation and substitution reactions. The 350-nm region has been characterized as the charge-transfer region of $Co(acac))_2N_3NH_3$[11-13] whereas, by analogy to $Co(acac)_3$, one might expect to observe 2,4-pentanedionate radical formation; by analogy to $Co(NH_3)_5N_3^{2+}$ one would expect azide radicals. The behavior of $Rh(NH_3)_3N_3^{2+}$ suggests the possibility of coordinated nitrene intermediacy, and that of $Co(CN)_5N_3^{3-}$ suggests azide ion formation. The compound under study has at least one feature in common with each of these compounds, and a study of its photochemistry will help to unravel the features important to the photochemistry of coordinated azides.

Experimental Section

Materials. $Co(acac)_2{\cdot}2H_2O$ was prepared by the method of Ellan and Ragsdale.[18] The product was recrystallized several times from ethanol and dried in air. Prior to use in photolyses or in the preparation of calibration curves, it was dried under vacuum at 55 °C for 6 h to yield $Co(acac)_2$.

cis-$Co(acac)_2N_3NH_3$ was prepared by a modification of the method of Boucher and Herrington.[17] A solution was prepared by dissolving 2.0 g (7.8 mmol) of $Co(acac)_2{\cdot}2H_2O$ in 125 mL of methanol and 5 mL of triethyl orthoformate. Similarly, solutions were prepared by dissolving 2 mL of concentrated ammonia in 10 mL of methanol and 2 mL of triethyl orthoformate and dissolving 3 mL of 30% hydrogen peroxide in 10 mL of methanol and 3 mL of triethyl orthoformate. All three solutions were boiled for 5 min and cooled to room temperatures. Then, 0.75 g (17.8 mmol) of NaN_3 was added to the $Co(acac)_2$ solution, followed by the ammonia solution. The hydrogen peroxide solution was then added dropwise with stirring over a period of several hours. The solvent was allowed to evaporate and the moist residue extracted with chloroform. The extracts were combined, filtered, and dried over sodium bicarbonate. Two volumes of mixed hexanes were added and the product collected by filtration. The product was purified by chromatography on silica gel. The column was developed with 5% (v/v) methanol in chloroform. The product

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was isolated from the eluents by the addition of 2 volumes of hexanes and allowing the product to crystallize overnight. The solid was filtered and dried. Anal. Calcd for $CoC_{10}H_{17}O_4N_4$: C, 38.009; H, 5.42; N, 17.33. Found: C, 37.98; H, 5.24; N, 17.69.

Ammonium thiocyanate was dissolved in a minimum of warm ethanol and precipitated with ether. The solid was collected and dried. This procedure was required in order to remove the highly colored material which formed when commercial NH_4SCN was dissolved in methanol.

$[Co(NH_3)_5N_3](BPh_4)_2$ was prepared by treating aqueous solutions of $[Co(NH_3)_5N_3]Cl_2$, prepared by the method of Tinhard and Flygare, with excess $NaBPh_4$. The product was collected, washed with water, and dried at 110 °C.

All other materials were reagent grade unless otherwise specified. Methanol was freshly distilled from magnesium turnings prior to use. Tetrahydrofuran was freshly distilled from sodium hydroxide. Methanolic ammonia solutions were prepared by bubbling ammonia through freshly distilled methanol, followed by standardization against standard hydrochloric acid.

Photolysis Procedures. Unless otherwise specified an optical train was employed in the irradiations. The light from a 1000-W Oriel Optics high-pressure neon–mercury lamp was focused by means of two quartz lenses through a 14-cm quartz water filter onto the entrance slit of a Bausch and Lomb Model 33-86-08 grating monochromator (1200 grooves/mm). The entrance slit width (3.78 mm) and the exit slit width (1.40 mm) were calculated from the manufacturer's reported dispersion of the grating to yield 90% of the radiation within a 10-mm band-pass. The light from the exit slit of the monochromator passed into a Varian Model 01-44-4200-00 thermostated cell jacket. The cell jacket was modified to place the 12 × 12 mm cell adaptor as close to the exit slit of the monochromator as possible. The jacket was thermostated to 25.0 ± 0.1 °C with a Haake Model FS constant-temperature circulator. The jacket was mounted such that the distance between the exit slit of the monochromator and the cell could be changed, thus permitting the light intensity to be varied. Light intensities were measured by ferrioxalate actinometry.[21]

Quantum yield determinations were made from plots of concentration vs. time of irradiation. These plots were linear and at no time was the reaction carried beyond 5% conversion to products. There was no evidence of secondary photolysis or an internal filter effect.

In studies in which the infrared spectrum in the region 2200–2000 cm^{-1} was monitored during photolysis, 5% (v/v) cyclohexene–tetrahydrofuran was used as a solvent. The same solvent was used as a reference. A Beckman Model VC-01 variable path length cell was used as a reference cell. The path lengths were matched by adjusting the reference cell path length with solvent in both cells and monitoring the infrared spectrum. The solution under study was irradiated in a standard infrared cell with a nominal path length of 1 mm, and after each irradiation the infrared spectrum was recorded in the region 2200–2000 cm^{-1}.

Hydrazine was determined by the method of Watt and Chrisp.[21] Three milliliters of photolyte and 4.0 mL of hydrazine reagent were pipetted into a 10-mL volumetric flask and diluted to the mark with ca. 2 M hydrochloric acid. The optical density was then measured at 460 nm. The 2 M hydrochloric acid solution was prepared by diluting 10.0 mL of concentrated hydrochloric acid to 60.0 mL with ethanol. A calibration curve was prepared using reagent grade hydrazine hydrochloride.

Chloramine was determined by the method of Basolo and coworkers.[6] A 0.25-mL aliquot of 0.208 M methanolic potassium iodide was pipetted directly into the photolysis cell after irradiation. The optical density was then measured at 410 nm. A calibration curve was prepared using solutions of known iodine concentration.

Physical Measurements. All infrared spectra were recorded on a Beckman Model 4240 infrared spectrometer. Ultraviolet and visible spectra were recorded on a Varian Cary Model 17 UV-VIS-NIR spectrophotometer. Single-wavelength ultraviolet and visible spectral measurements were taken on a Sargent-Welch Model SM spectrophotometer. Carbon, hydrogen, and nitrogen analyses were performed by the Galbraith Laboratories.

Results

Ultraviolet irradiation of methanolic solutions of *cis*-$Co(acac)_2N_3NH_3$ resulted in bleaching of the pale green solutions. Spectrophotometric monitoring (400–200 nm) of the photolysis of a 3.75 × 10^{-5} M solution with 350-nm radiation gave a smooth conversion from starting material to products, as evidenced by the isosbestic points, Figure 1. Isosbestic points were observed at 277 and 293 nm which are the positions predicted from the spectra of authentic samples of *cis*-$Co(acac)_2N_3NH_3$ and $Co(acac)_2$. They were maintained throughout the photolysis. After exhaustive photolysis, the resulting spectrum was qualitatively similar to that of $Co(acac)_2$ and analysis of the photolyte revealed that it was 2.91 × 10^{-5} M in cobalt(II). Within experimental error the final spectrum is consistent with that expected for a mixture 2.91 × 10^{-5} M in $Co(acac)_2$ and 8.40 × 10^{-6} M in $Co(acac)_2N_3NH_3$.

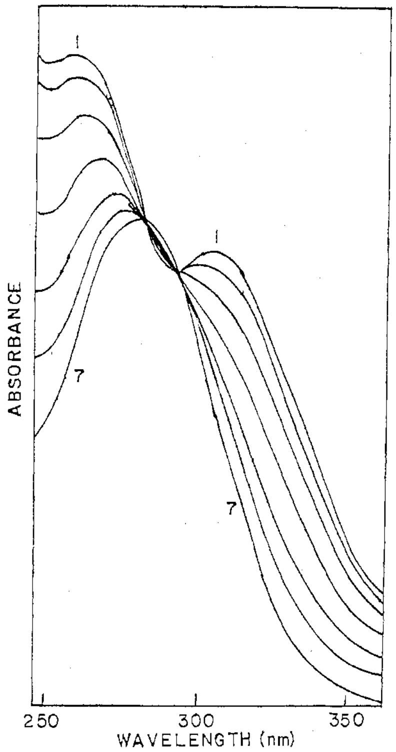

Figure 1. Ultraviolet monitoring of the photolysis of a 3.75 × 10^{-5} M methanolic solution of $Co(acac)_2N_3NH_3$ with 350-nm radiation. Curve 1 is the initial solution and curve 7 is for a 3900-s exposure.

The photodecomposition of *cis*-$Co(acac)_2N_3NH_3$ can be monitored spectrometrically in the infrared (2200–2000 cm^{-1}). Furthermore, Beck and Schorpp have shown that cyclohexene in tetrahydrofuran can effectively scavenge azide radicals produced in the photodecomposition of $Au(N_3)_4^-$ and $Pb(N_3)_6^{2-}$ ions.[3] Accordingly, 2.36 × 10^{-3} M solutions of $Co(acac)_2N_3NH_3$ in 5% (v/v) cyclohexene–tetrahydrofuran were irradiated with 350-nm radiation, and the reaction was monitored in the infrared. Irradiation resulted in a decrease in the absorption band at 2024 cm^{-1} (asymmetric stretching mode of the azido group in *cis*-$Co(acac)_2N_3NH_3$[17]) and a concomitant increase in the absorbance at 2109 cm^{-1}. Photolysis of $[Co(NH_3)_5N_3](BPh_4)_2$ with 320-nm radiation gave similar results. Similar results were obtained by Beck and Schorpp.[3] When solutions which were 2.36 × 10^{-3} M in *cis*-$Co(acac)_2N_3NH_3$ were also made 3.39 × 10^{-3} M in $Co(acac)_2$ and the photolysis was carried out under identical conditions, both the rate of disappearance of the 2024-cm^{-1} band and the rate of appearance of the 2109-cm^{-1} band diminished by about 50%. This decrease was greater than that which would have been expected to occur from an internal filter effect due to the absorbance of $Co(acac)_2$ at 350 nm. A 10% reduction would have been expected.

The 350-nm photolysis of a methanolic solution 1.27 × 10^{-3} M in *cis*-$Co(acac)_2N_3NH_3$ and 1.27 × 10^{-3} M in $(C_2H_5)_2NH_2BF_4$ yielded no detectable hydrazine. This sets an upper

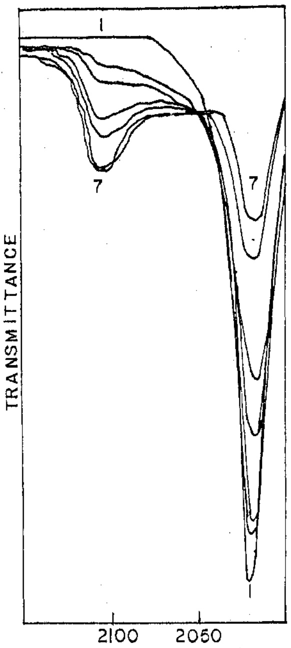

Figure 2. Infrared monitoring of the 350-nm photolysis of a 2.36 × 10^{-3} M $Co(acac)_2N_3NH_3$ solution in 5% (v/v) cyclohexene–tetrahydrofuran. Curve 1 is the initial solution and curve 7 is for a 4000-s exposure.

limit on the quantum yield for hydrazine formation ($\phi_{N_2H_4}$) of 1 × 10^{-5}. Photolysis of a 1.27 × 10^{-3} M *cis*-$Co(acac)_2N_3NH_3$ solution made 1.27 × 10^{-3} M in $(C_2H_5)_2NH_2BF_4$ and 0.46 M in ammonia also yielded no detectable hydrazine. The upper limit on $\phi_{N_2H_4}$ was 1 × 10^{-5}. Assuming that any hydrazine formed was from the reaction of nitrene with ammonia and that the relative rates for nitrene scavenging by water and ammonia and by methanol and ammonia are similar, 61% of any nitrene formed should yield hydrazine. This would place an upper limit on the quantum yield for nitrene formation of 2 × 10^{-5}. Similarily, irradiation of 1.27 × 10^{-3} M *cis*-$Co(acac)_2N_3NH_3$ made 1.27 × 10^{-3} M in $(C_2H_5)_2NH_2BF_4$ and 0.503 M in LiCl yielded no detectable material which was oxidizing to iodide ion. Assuming that any such material resulted from the reaction of coordinated nitrene with chloride ion, the upper limit for the yield of coordinated chloramine formation would be 3 × 10^{-5}. Assuming the relative rates of $Rh(NH_3)_5NH^{3+}$ scavenging by water and chloride ion[23] to be similar to the rates of the scavenging of a cobalt nitrene by methanol and chloride ion, the upper limit for coordinated nitrene formation would be 3 × 10^{-5}.

Irradiation of methanolic solutions of *cis*-$Co(acac)_2N_3NH_3$ resulted in the formation of cobalt(II). Plots of cobalt(II) concentration vs. time of irradiation were linear for reactions carried to less than 10% conversion to products. Curvature was, however, observed after exhaustive photolysis. The quantum yield for cobalt(II) formation ($\phi_{Co(II)}$) under 350-nm irradiation at 25 °C was 0.019 ± 0.001.

Furthermore, in the presence of added $Co(acac)_2$ or under conditions of extensive photolysis, the quantum yield was significantly less than 0.019. The dependence of the quantum yield on the concentration of $Co(acac)_2$ was determined by irradiating solutions 8.56 × 10^{-4} M in *cis*-$Co(acac)_2N_3NH_3$ in which the $Co(acac)_2$ concentration was varied from 0.0 to 2.07 × 10^{-4} M. In all cases, except that in which no $Co(acac)_2$ was added, the concentration of $Co(acac)_2$ formed during photolysis was small compared to the $Co(acac)_2$ added. All determinations were made at the same light intensity. The quantum yield for cobalt(II) formation varied linearly with the concentration of added $Co(acac)_2$ with a slope of −75 ± 3 einstein^{-1} and an intercept of 0.0192 ± 0.0003, Figure 3.

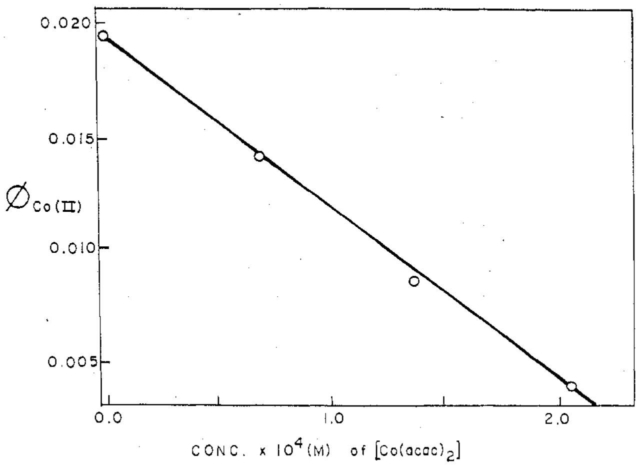

Figure 3. Dependence of $\phi_{Co(II)}$ under 350-nm irradiation on the concentration of $Co(acac)_2$.

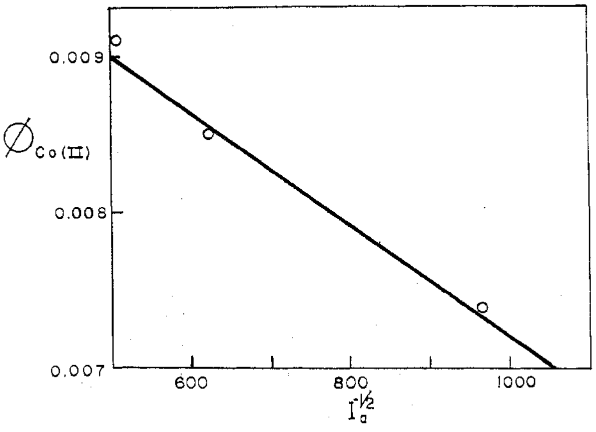

Figure 4. Dependence of $\phi_{Co(II)}$ on the intensity of 350-nm radiation for $Co(acac)_2N_3NH_3$ solution made 1.38 × 10^{-4} M in $Co(acac)_2$.

Table I. Dependence of $\phi_{Co(II)}$ on the Intensity of Exciting Radiation and [$Co(acac)_2$]

Intens × 10^6, einsteins/(L s)	$\phi_{Co(II)}$	10^4[$Co(acac)_2$], M
4.26	0.019 ± 0.001	0.00
2.58	0.020 ± 0.002	0.00
1.10	0.019 ± 0.002	0.00
3.85	0.0091 ± 0.0005	1.38
2.58	0.0085 ± 0.0007	1.38
1.07	0.0074 ± 0.0006	1.38
2.58	0.0038 ± 0.0003	2.07
2.58	0.014 ± 0.001	0.692

Over a range of incident intensities of 4.26 × 10^{-6} to 1.10 × 10^{-6} einstein/(L s) the quantum yield for cobalt(II) formation was independent of incident intensity, Table I. If, however, the solutions were made 1.38 × 10^{-4} M in $Co(acac)_2$, an intensity dependence was observed, Table I.

Discussion

The persistence of isosbestic points during the 350-nm photolysis of methanolic solutions of *cis*-$Co(acac)_2N_3NH_3$ suggests the formation of a single absorbing product. The observation of isosbestic points at predicted positions and the qualitative similarity between the product spectrum and that of $Co(acac)_2$ support the conclusion that the absorbing product is in fact $Co(acac)_2$.

Methanol is an unsuitable solvent for monitoring the reaction by infrared spectroscopy, because of its strong absorbance in the region of interest. Tetrahydrofuran, however, is quite suitable, and the conclusions drawn from the photolyses in tetrahydrofuran are readily extrapolated to photolyses in methanol. The appearance of an absorbance typical of an organic azide (2109 cm^{-1}) is strong evidence for azide radical formation during the photolysis. The observation of identical results in the photolysis of $Co(NH_3)_5N_3^{2+}$, which has been shown to yield azide radicals upon photolysis,[8] and the work of Beck and Schorpp[3] further support this conclusion. This evidence suggests that the primary photochemical step is

$$\textit{cis}\text{-Co(acac)}_2\text{N}_3\text{NH}_3 \xrightarrow{h\nu} \text{Co(acac)}_2\text{NH}_3 + \text{N}_3\cdot \tag{1}$$

The following mechanism is proposed for the photodecomposition of *cis*-$Co(acac)_2N_3NH_3$ under the 350-nm irradiation:

$$\textit{cis}\text{-Co(acac)}_2\text{N}_3\text{NH}_3 + h\nu \xrightarrow{I_a} \text{Co(acac)}_2\text{N}_3\text{NH}_3{}^* \tag{2}$$

$$\text{Co(acac)}_2\text{N}_3\text{NH}_3{}^* \xrightarrow{k_3} \text{Co(acac)}_2\text{N}_3\text{NH}_3 + \Delta \tag{3}$$

$$\text{Co(acac)}_2\text{N}_3\text{NH}_3{}^* \xrightarrow{k_4} \text{Co(acac)}_2 + \text{N}_3\cdot + \text{NH}_3 \tag{4}$$

$$\text{Co(acac)}_2 + \text{N}_3\cdot \xrightarrow{k_5} \text{Co(acac)}_2\text{N}_3 \tag{5}$$

$$\text{Co(acac)}_2\text{N}_3 + \text{NH}_3 \xrightarrow{k_6} \text{Co(acac)}_2\text{N}_3\text{NH}_3 \tag{6}$$

$$2\text{N}_3\cdot \xrightarrow{k_7} 3\text{N}_2 \tag{7}$$

Failure to explicitly consider the formation of a geminate radical pair in the above mechanism is not meant to imply its existence or nonexistence but only the fact that the present investigation has not addressed itself to this question. All photophysical processes resulting in relaxation to the ground state are considered implicitly in eq 3, and all photophysical processes resulting in the reactive state are also included in eq 4. A more detailed investigation of these processes is in progress. Endicott and co-workers have shown that cobalt(II) complexes are effective radical scavengers.[24,25] Equation 6 represents scavenging of azide radicals by the cobalt(II) product. This step is of particular importance under conditions of extensive photolysis. This step is responsible for the failure to effect complete conversion to products even after exhaustive photolysis.

If the steady-state assumption is made for the intermediates $Co(acac)_2N_3NH_3{}^*$ and $N_3\cdot$, the following rate expression may be derived for the quantum yield of cobalt(II):

$$\phi_{\text{Co(II)}} = \Phi_{\text{Co(II)}} + \frac{k_5{}^2[\text{Co(acac)}_2]^2}{2k_7I_a} - \frac{k_5[\text{Co(acac)}_2](k_5{}^2[\text{Co(acac)}_2]^2 + 4k_7I_a\Phi_{\text{Co(II)}})^{1/2}}{2k_7I_a} \tag{8}$$

where I_a is the absorbed intensity and $\Phi_{\text{Co(II)}}$ is the primary yield of cobalt(II).[25] Under conditions where

$$k_5{}^2[\text{Co(acac)}_2]^2 < 4k_7I_a\Phi_{\text{Co(II)}} \tag{9}$$

the terms under the radical can be expanded in a power series in X to yield

$$\phi_{\text{Co(II)}} = \Phi_{\text{Co(II)}} - 2\Phi_{\text{Co(II)}}X^{1/2} + 2\Phi_{\text{Co(II)}}X^{3/2} + \ldots \tag{10}$$

where

$$X = k_5{}^2[\text{Co(acac)}_2]^2/4k_7I_a\Phi_{\text{Co(II)}}$$

It can be shown that under sufficiently low $Co(acac)_2$ concentrations, the first two terms dominate the series and eq 10 reduces to

$$\phi_{\text{Co(II)}} \simeq \Phi_{\text{Co(II)}} - k_5[\text{Co(acac)}_2](\Phi_{\text{Co(II)}}/k_7I_a)^{1/2} \tag{11}$$

Under these conditions $\phi_{\text{Co(II)}}$ is a linear function of $Co(acac)_2$ concentration. Such a dependence is in fact observed, Figure 3. This interpretation of the dependence of $\phi_{\text{Co(II)}}$ on the concentration of $Co(acac)_2$ is further substantiated by the results of the infrared-monitoring experiments. The addition of $Co(acac)_2$ to the $Co(acac)_2N_3NH_3$ solution resulted in a decrease in the rate of both 3,6-diazidocyclohexene formation and $Co(acac)_2N_3NH_3$ disappearance. It is unlikely that the addition of $Co(acac)_2$ would significantly affect $\Phi_{\text{Co(II)}}$. The most reasonable interpretation is that $Co(acac)_2$ competes with cyclohexene for azide radical and in the progress regenerates starting material.

The value of $\Phi_{\text{Co(II)}}$ obtained from the plot of $\phi_{\text{Co(II)}}$ vs. $Co(acac)_2$ is 0.0193 ± 0.0003 and is in excellent agreement with the value of $\phi_{\text{Co(II)}}$ obtained by direct photolysis of $Co(acac)_2N_3NH_3$ solutions. This suggests that secondary recombination is not effective under these conditions and that $\Phi_{\text{Co(II)}}$ may be determined directly from irradiation of $Co(acac)_2N_3NH_3$ solutions. Such experiments do not, however, yield information about primary recombination.

The rate constant for the azide radical coupling reaction (eq 7) has been measured by Treinin and Hayon and found to be 6.8×10^9 M^{-1} s^{-1}.[27] The rate of this reaction in methanol is expected to be similar, and the difference is expected to be much less than the uncertainty in this value (±25%). Equation 11 and the slope of $\phi_{\text{Co(II)}}$ vs. $Co(acac)_2$ concentration can be used to estimate k_5. The value of k_5 determined in this manner is 7.1×10^4 M^{-1} s^{-1}; however, because of the uncertainty in k_7 and the approximations inherent in eq 11, the estimated value of k_5 should be taken as little more than an order of magnitude estimate.

Both eq 8 and 11 suggest that in the absence of $Co(acac)_2$, $\phi_{\text{Co(II)}}$ should be independent of intensity and should be equal to $\Phi_{\text{Co(II)}}$. This is in fact what is observed. However, in the presence of $Co(acac)_2$, $\phi_{\text{Co(II)}}$ is expected to be a linear function of $I_a{}^{-1/2}$ (eq 11). In $Co(acac)_2N_3NH_3$ solutions made 1.38×10^{-4} M in $Co(acac)_2$, $\phi_{\text{Co(II)}}$ was intensity dependent. A plot of $\phi_{\text{Co(II)}}$ vs. $I_a{}^{-1/2}$ yields a reasonable straight line.

The work of Basolo and co-workers[8] and Endicott and co-workers[1] suggests that coordinated nitrene formation may also occur in systems where azide radical formation also occurs. Failure to detect either hydrazine or chloramine after irradiation of $Co(acac)_2N_3NH_3$ solutions containing ammonia and chloride ion, respectively, rules out even a minor contribution from this mode of decomposition. Zink has suggested that certain azido complexes should yield coordinated dinitrogen and nitrene upon irradiation,[9] eq 12. Failure to detect hydrazine after the irradiation of $Co(acac)_2N_3NH_3$ solutions containing ammonia also rules out even a minor contribution from this mode of decomposition.

$$\text{M–N}_3 + h\nu \xrightarrow{\text{H}^+} \text{M–N}_2 + \text{NH} \tag{12}$$

It is a generally accepted hypothesis that oxidation–reduction photochemistry arises from states which are predominantly charge transfer in character. Thus oxidation–reduction photochemistry is frequently observed in the ultraviolet photolyses of cobalt(III) complexes. Frequently, the reactions are complicated by trans-ligand aquation. Such is the case in the 254-nm photolysis of the $Co(NH_3)_5N_3^{2+}$ ion. It has been suggested that the aquation results from a large Jahn–Teller distortion in the excited state.[28] Whereas it may be suggested that this mechanism is responsible for the loss of ammonia in the photolysis of $Co(acac)_2N_3NH_3$, the ligand trans to the ligand oxidized is normally labilized. If this were the case, the oxygen of the pentanedionate ligand should be labilized. It seems more likely that ammonia is lost in a thermal reaction subsequent to the photochemical reaction.

Assignments of the electronic spectral transitions of $Co(acac)_2N_3NH_3$ have been made by Boucher and Herrington.[17]

Table II. Visible and Near-Ultraviolet Spectra

Assignment[b]	Abs max[c]	Solvent
	$Co(acac)_2N_3NH_3$[a]	
$^1T_{1g} \leftarrow {}^1A_{1g}$	17.2 (2.02)	CH_3OH
$\pi_L^* \leftarrow t_{2g}$	33	CH_3OH
$e_g^* \leftarrow \sigma_L$	38.9 (4.04)	CH_3OH
	$Co(acac)_3$[d]	
$\pi^* \leftarrow \pi$	38.6 (4.48)	C_2H_5OH
$\pi^* \leftarrow \pi$	33.9 (4.0)	C_2H_5OH
$\pi^* \leftarrow {}^1A_{1g}$	30.6 (3.9)	C_2H_5OH
$^1T_{2g} \leftarrow \pi$, $^1T_{2g} \leftarrow {}^1A_{1g}$	25.0 (2.5)	C_2H_5OH
$^1T_{1g} \leftarrow {}^1A_{1g}$	16.9 (2.1)	C_2H_5OH

[a] L. J. Boucher and D. R. Herrington, *Inorg. Chem.*, 11, 1772 (1972). [b] L refers to the pentanedionate ligand. [c] log ϵ_{max} given in parentheses. [d] R. L. Lindvedt in "Concepts of Inorganic Photochemistry", A. W. Adamson and P. D. Fleischauer Ed., Wiley-Interscience, New York, N.Y., 1975.

Their assignments and those for $Co(acac)_3$ may be found in Table II. The 350-nm exciting radiation lies entirely within the broad band at 303 nm which has been assigned to a charge transfer to ligand (CTTL) transition involving the pentanedionate ligand. It seems unlikely, however, that this band is a single electronic transition. The similarity between the positions of the lowest energy spin-allowed ligand field transition of $Co(acac)_3$ ($^1T_{1g} \leftarrow {}^1A_{1g}$) and the equivalent transition in $Co(acac)_2N_3NH_3$ suggests that both the charge transfer to metal (CTTM) transition involving the pentanedionate ligand and the ligand field transition ($^1T_{2g} \leftarrow {}^1A_{1g}$) are also contained under the envelope of this band. In addition, the optical electronegativity of the azido group (2.8)[29] is somewhat greater than that of the pentanedionate ligand (2.7).[30] It is therefore expected that the CTTM transition involving the azido group should occur about 3.0×10^3 cm^{-1} higher energy than the same transition involving the pentanedionate ligand. Thus the CTTM state involving the azido group is also contained under the envelope of the band at 303 nm. It is reasonable to assume that a CTTM state involving the azido group is responsible for the observed photochemical reaction. However, the presence of such a large number of transitions in this region makes any further interpretation unwarranted without further investigation.

Although 350-nm radiation populates a number of ligand field and charge transfer excited states, it appears that only the CTTM state(s) involving the azido group gives rise to photodecomposition. The reaction occurs with relatively low quantum efficiency. However, this cannot be attributed to secondary recombination since this process is insignificant under the conditions used in the determinations. In contrast to other simpler cobalt(III)–azido complexes, the photochemical behavior of $Co(acac)_2N_3NH_3$ is uncomplicated by other photochemical reactions.

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Registry No. *cis*-$Co(acac)_2N_3NH_3$, 38977-23-0; $Co(acac)_2$, 14024-48-7.

References and Notes

(1) G. J. Ferraudi and J. F. Endicott, *J. Am. Chem. Soc.*, **95**, 2371 (1973).
(2) J. F. Endicott, M. Z. Hoffman, and L. S. Beres, *J. Phys. Chem.*, **74**, 1021 (1970).
(3) W. Beck and K. Schorpp, *Angew. Chem., Int. Ed. Engl.*, **9**, 753 (1970).
(4) C. Bartocci and F. Scandola, *Chem. Commun.*, 531 (1970).
(5) G. J. Ferraudi and J. F. Endicott, *Inorg. Chem.*, **12**, 2389 (1973).
(6) J. L. Reed, F. Wang, and F. Basolo, *J. Am. Chem. Soc.*, **94**, 1773 (1972).
(7) H. D. Gafney, J. L. Reed, and F. Basolo, *J. Am. Chem. Soc.*, **95**, 7998 (1973).
(8) J. L. Reed, H. D. Gafney, and F. Basolo, *J. Am. Chem. Soc.*, **96**, 1363 (1974).
(9) J. I. Zink, *Inorg. Chem.*, **14**, 446 (1975).
(10) N. Filipescu and H. Way, *Inorg. Chem.*, **8**, 1763 (1969).
(11) D. W. Barnum, *J. Inorg. Nucl. Chem.*, **21**, 221 (1961).
(12) D. W. Barnum, *J. Inorg. Nucl. Chem.*, **21**, 183 (1962).
(13) R. L. Lintvelt in "Concepts of Inorganic Photochemistry", A. W. Adamson and P. D. Fleischauer, Ed., Wiley-Interscience, New York, N.Y., 1975, pp 316–321.
(14) I. Burak and A. Treinin, *J. Chem. Phys.*, **39**, 189 (1963).
(15) W. D. Closson and H. B. Gray, *J. Am. Chem. Soc.*, **95**, 237 (1973).
(16) H. H. Schmidtke, *J. Chem. Phys.*, **45**, 305 (1965).
(17) T. J. Boucher and D. R. Herrington, *Inorg. Chem.*, **11**, 1772 (1972).
(18) J. B. Ellan and R. O. Ragsdale, *Inorg. Synth.*, **11**, 82 (1960).
(19) M. Tinland and H. Flygare, *Z. Anorg. Chem.*, **262**, 328 (1950).
(20) D. Katakis and A. O. Allen, *J. Chem. Phys.*, **38**, 1359 (1964).
(21) D. Watt and J. D. Chrisp, *Anal. Chem.*, **24**, 2006 (1952).
(22) $Rh(NH_3)_5NH_2Cl^{3+}$ generated by the photolysis of $Rh(NH_3)_5N_3^{2+}$ in HCl does not appear to react with $(C_2H_5)_2NH_2BF_4$.
(23) T. S. Roche and J. F. Endicott, *Inorg. Chem.*, **13**, 1575 (1974).
(24) T. S. Roche and J. F. Endicott, *J. Am. Chem. Soc.*, **94**, 8622 (1972).
(25) $\Phi_{Co(II)} = k_4/(k_4 + k_3)$.
(26) A. Treinin and E. Hayon, *J. Chem. Phys.*, **50**, 538 (1969).
(27) T. T. Kelly and J. F. Endicott, *J. Am. Chem. Soc.*, **94**, 1797 (1972).
(28) H. H. Schmidtke and D. Garthoff, *J. Am. Chem. Soc.*, **89**, 1317 (1967).
(29) C. K. Jorgenson, *Acta Chem. Scand.*, **16**, 2406 (1962).

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Spectroscopic Studies of the Photoactive $^4T_{2g}$ Excited State of Hexaamminechromium(III)

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Detailed low-temperature, high-resolution polarized single-crystal spectroscopic studies on the $^4T_{2g} \leftarrow {}^4A_{2g}$ transition for a new class of $Cr(NH_3)_6^{3+}$ molecular crystals are described. The $^4T_{2g}$ excited state is experimentally shown to undergo both large totally symmetric and Jahn–Teller distortions. These produce the approximate change in the geometry of the $^4T_{2g}$ excited state relative to the $^4A_{2g}$ ground state of an expansion of 0.12 Å in Cr–NH_3 bond lengths along two axes and a contraction of 0.02 Å along the third axis. The photochemical implications of these distortions are discussed.

I. Introduction

Octahedral chromium(III) complexes form the most well-characterized inorganic systems in terms of their photochemistry.[1] The photochemical studies to date strongly support the $^4T_{2g}$ state as being primarily responsible for the observed photoactivity. The photosubstitution reaction pathways often differ from those of the ground state, and an extensive amount of data has led to empirical rules[2] and ligand

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