

may also be observed for other 3d metal ions.

In conclusion, in all the described examples, a monodentate ligand coordinates to a metal ion which has already a rather saturated coordination sphere. This situation resembles quite well the conditions present in many metalloenzymes, where only some few coordination positions remain accessible for the substrate. For example, in carbonic anhydrase^{35,36} and in carboxypeptidase,^{36,37} Zn²⁺ is coordinated to three imidazole residues, and to one carboxylate and two imidazole groups, respectively; the fourth position at Zn²⁺ is in both enzymes occupied by a water molecule which may be replaced by the substrate.^{36,37} It is striking indeed that imidazole is often observed^{7d} in the coordination sphere of metal ions bound to proteins. On the basis of our results, one is tempted to suggest that this is a way to achieve selectivity toward the substrate,

which is one of the prime goals in enzymic systems. Aside from the use of certain combinations of ligating atoms, the degree of selectivity in nature may be further promoted by making use also of direct intramolecular ligand-ligand interactions which are possible within mixed-ligand complexes.^{7e,38} These interactions may be of, e.g., ionic or hydrophobic nature; in any case selectivity will be improved.³⁹

Acknowledgment. The potentiometric titrations were carried out with the skillful technical assistance of Ms. Rita Baumbusch and Ms. Madeleine Imhof. The computer was made available by the Rechenzentrum der Universität Basel (Univac 1100/81). These supports and research grants from the Swiss National Science Foundation are gratefully acknowledged.

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Photodecomposition of *cis*-Azidoamminebis(2,4-pentanedionato)cobalt(III). The Photoactive State

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Received April 15, 1980

The photodecomposition of *cis*-Co(acac)₂N₃NH₃ (acac = 2,4-pentanedionate) occurs with the formation of Co(acac)₂ and azide radicals. This reaction has been effected with the use of exciting radiations throughout the 250-580-nm region, and in the 250-470-nm region the quantum efficiency for this reaction is surprisingly wavelength independent. Examination of the optical spectra of Co(acac)₂N₃NH₃ and Co(acac)₃ and the respective optical electronegativities of the azide and 2,4-pentanedionate ligands suggests that photooxidation of the 2,4-pentanedionate group should be favored over that of the azido group. Yet photooxidation of the azido group is the only observed reaction. This observation, the relative constancy of the quantum efficiency, and the energy of the threshold for the onset of redox photodecomposition ((21.3-17.2) × 10³ cm⁻¹) suggest that the photoactive state is a triplet charge-transfer state involving the azido group. The photoreaction has an apparent activation energy of 11.7 kcal/mol, and solvent assistance in the loss of the azide radical is implicated.

Introduction

In a recent communication from these laboratories, the photodecomposition of *cis*-azidoamminebis(2,4-pentanedionato)cobalt(III) (Co(acac)₂N₃NH₃) by 350-nm radiation was examined in some detail.¹ Although the photochemistry of metal azido complexes has received considerable attention in recent years,¹⁻¹¹ the reasons for their diverse photochemistry are not yet understood. Metal azides undergo one or more of three reported modes of photodecomposition. These are

substitution of the azido group, oxidation of the azido group, or formation of coordinated nitrene. The 350-nm irradiation of this complex, which corresponds to one or more charge-transfer excitations,^{1,12} yields azide radicals and Co(acac)₂, and only one mode of photodecomposition is observed. The simplicity of the photochemistry is somewhat surprising considering the number of modes of photodecomposition which have been observed for other complexes containing the ligands comprising this complex.¹³⁻¹⁹ Thus it provides an excellent test for the various models which have been proposed for metal azide photochemistry and charge-transfer photochemistry in general.^{5,7,8}

Although one mode of photodecomposition seems to be favored over numerous others, the quantum efficiency for this

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mode of photodecomposition is only 0.019, which is well below the efficiencies observed for the charge-transfer irradiation of other complexes containing one or more of these ligands. The rate constant for the secondary recombination of the radicals formed during photolysis has been estimated to be $7 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ and is thus ruled out as being responsible for the low quantum efficiency for this reaction.¹

The low quantum efficiency for this reaction as well as the surprisingly simple photochemistry raises some interesting questions. In addition, one might expect oxidation of the 2,4-pentanedionato group to be favored over the azido group on the basis of their respective optical electronegativities.^{20,21} Because this system is so well-behaved, and also suggests interesting insights into the photochemistry of cobalt azido complexes, we have elected to further examine this system.

Experimental Section

Materials. $\text{Co}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$ was prepared by the method of Ellan and Ragsdale.²² The product was recrystallized several times from ethanol and dried in air. Prior to use in the preparation of calibration curves, it was dried under vacuum at 55 °C for 6 h to yield $\text{Co}(\text{acac})_2$. Although no problems were encountered in handling these compounds, azides are potentially hazardous compounds, and it is recommended that the scale of these operations not be increased significantly.

$\text{K}[\text{trans-Co}(\text{acac})_2(\text{N}_3)_2]$ was prepared by the method of Boucher and Harrington.¹²

$\text{cis-Co}(\text{acac})_2\text{N}_3\text{NH}_3$ was prepared by treating 1.0 g of $\text{K}[\text{trans-Co}(\text{acac})_2(\text{N}_3)_2]$ with 20 mL of methanol which was ca. 50% saturated with ammonia. The suspension was warmed to 60 °C for a few minutes after which time all of the solid had dissolved. The solution was allowed to evaporate to dryness, and the residue was taken up in a minimum of chloroform and filtered. The product precipitated from the filtrate upon the addition of two volumes of mixed hexanes. After it was collected by filtration, it was purified by chromatography on silica gel. The column was developed with 5% (v/v) methanol in chloroform, and the product was isolated from the eluants by the addition of two volumes of mixed hexanes and allowing the product to crystallize overnight. The solid was collected and air dried.

Reagent grade ammonium thiocyanate was recrystallized from ethanol prior to use. Methanol was freshly distilled from magnesium turnings prior to use.

Photolysis Procedures. The optical train used in the photolyses has been described elsewhere.¹ For irradiations requiring visible radiation, McCarthy 100-4750 and 100-5350 filters and a soft glass filter were used to remove the second-order spectrum of the monochromator. Unless otherwise specified, all quantum yield determinations were made at 25.0 ± 0.1 °C and 90% of the exciting radiation was contained in a 10-nm band-pass. Light intensities were determined with the use of both ferrioxalate²³ and Reinecke salt²⁴ actinometry. 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 for secondary photolysis or an internal filter effect. Unless otherwise specified, photolyses were performed without prior deaeration of solutions.

The concentration of cobalt(II) in the photolytes was determined by pipetting 3 mL of the photolytes into 5-mL volumetric flasks and diluting to the mark with 1 M methanolic NH_4SCN and recording the optical density at 618 nm. Calibration curves were prepared with use of authentic samples of $\text{Co}(\text{acac})_2$. In cases in which mixed solvents were used, a separate calibration curve was prepared for each solvent composition.

For studies in which the infrared spectrum in the region from 2200 to 2000 cm^{-1} was monitored during photolysis, 5–15% (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

Table I. Results of the Gaussian Curve Analyses of the Optical Spectra of $\text{Co}(\text{acac})_3$ and $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$ in Methanol

| | $10^{-3}\nu_0$, cm^{-1} | $10^3\epsilon_0$, $\text{M}^{-1} \text{cm}^{-1}$ | $10^{-3}\theta$, cm^{-1} |
|---|--------------------------------------|--|---------------------------------------|
| $\text{Co}(\text{acac})_3$ | 43.80 | 36.16 | 4.88 |
| | 38.17 | 20.50 | 2.54 |
| | 33.89 | 8.22 | 2.14 |
| | 30.32 | 6.69 | 2.05 |
| | 24.06 | 1.15 | 2.23 |
| | 16.95 | 0.122 | 1.98 |
| $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$ | 44.80 | 25.15 | 5.64 |
| | 38.77 | 4.93 | 1.38 |
| | 36.64 | 8.26 | 2.24 |
| | 32.33 | 7.40 | 4.17 |
| | 24.30 | 0.750 | 3.06 |
| | 17.04 | 0.179 | 1.96 |

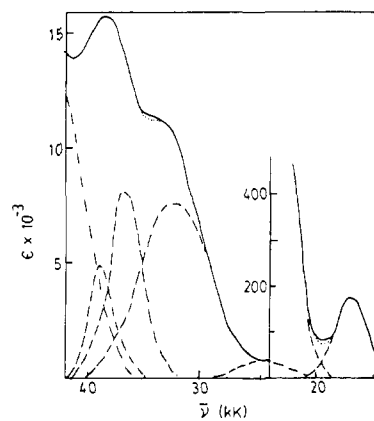


Figure 1. Optical spectrum of $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$ fitted to six Gaussian components: (—) experimental spectrum; (---) computed spectrum; (· · ·) Gaussian components.

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} .

Spectral Curve Analysis. In several cases the absorption spectra were analyzed by fitting the experimental spectra to a set of Gaussian curves. The spectral data were collected from Cary Model 17 or Hitachi Model 100-60 spectrophotometers. The data, which consist of wavelengths with corresponding optical densities and molar concentrations, were treated by a least-squares procedure described by Beech²⁵ which was modified by the method of Fraser and Suzuki²⁶ in order to permit one of the spectral parameters to have a fixed predetermined value. This modification was necessary in order to treat cases in which there were intense high-energy absorptions for which the band maxima could not be determined. In such cases the band maximum for the highest energy band, for which the maximum could be determined, was fixed at the observed value before curve fitting commenced. The curve fitting procedure used only those data which did not reflect a contribution from tails of high-energy bands whose maxima could not be determined.

Physical Measurements. Spectral curve fitting was performed with use of a Digital PDP 11/34 minicomputer. Optical spectra were measured on either a Cary Model 17, Hitachi Model 100-60, or a Sargent Welch Model SM optical spectrophotometer. Infrared spectral measurements were made on a Beckman Model 4240 infrared spectrometer.

Results

The optical spectrum of $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$ in methanol contains four readily discernible bands which correspond to four of the seven discernible bands in the spectrum of $\text{Co}(\text{acac})_3$. The spin-forbidden ligand field absorption which is observed for $\text{Co}(\text{acac})_3$ is not observed in the spectrum of

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Table II. Quantum Yields for the Formation of Cobalt(II)

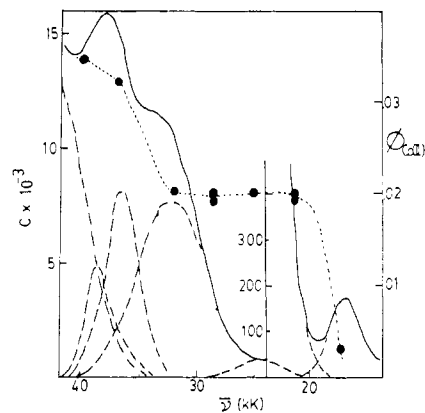
| $\lambda_{\text{ex}}, \text{nm}$ | $\phi_{\text{Co(II)}}$ | $T, ^\circ\text{C}$ | conditions |
|----------------------------------|------------------------|---------------------|-----------------------------------|
| 580 | 0.0028 | 25.0 | in air |
| 470 | 0.019 | 25.0 | in air |
| 400 | 0.020 | 25.0 | in air |
| 350 | 0.019 | 25.0 | in air |
| 350 | 0.020 | 25.00 | under nitrogen |
| 310 | 0.020 | 25.0 | in air |
| 270 | 0.032 | 25.0 | in air |
| 270 | 0.032 | 25.0 | in air |
| 250 | 0.034 | 25.0 | in air |
| 300 | 0.025 | 25.0 | in air and in 20% ethylene glycol |
| 350 | 0.024 | 30.0 | in air |
| 350 | 0.036 | 35.0 | in air |
| 350 | 0.039 | 35.0 | in air |

$\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$. With the use of arguments presented in the Discussion, the optical spectrum of $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$ was fit to six Gaussian components (Table I and Figure 1).

Methanolic solutions of $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$ were irradiated at 25 °C with 250-, 310-, 350-, and 585-nm radiation, and in each case the spectral changes were monitored over the 400–200-nm region. The spectral changes were identical with those observed in the 350-nm photolysis of this compound. In these monitoring experiments with the exception of the 585-nm photolysis, all photolyses were carried to apparent completion. The 585-nm photolysis was carried to only 30% completion because of the low optical densities of the solutions at this wavelength. In all cases, except the 250-nm photolysis, isosbestic points were maintained throughout the photolyses, and they occurred at the positions predicted by the examination of spectra of authentic samples of $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$ and $\text{Co}(\text{acac})_2$. In the cases of the 250-nm photolysis, the isosbestic points were lost after the reaction reacted about 70% completion. A methanolic solution of $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$ made 0.0088 M in LiBr was irradiated with 350-nm radiation. The observed spectral changes and the rate of these changes were identical with those observed for a solution otherwise identical but containing no LiBr. Spectral monitoring of a solution containing LiBr, but which was kept in the dark during the course of the experiment, exhibited no spectral changes during this time period. In addition a 250-nm irradiation of a 4.41×10^{-5} M methanolic solution of $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$ made 20% (v/v) in 2-propanol produced spectral changes identical with those observed in the absence of 2-propanol. There was also an 11% increase in the rate of photodecomposition over an otherwise identical solution not containing 2-propanol. A similar 300-nm irradiation of a 7.64×10^{-5} M $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$ solution made 1.36% (v/v) in ethylene glycol also resulted in spectral changes identical with those observed in the absence of ethylene glycol. A 300-nm irradiation of a 6.74×10^{-5} M $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$ solution made 20% (v/v) in ethylene glycol resulted in a 5-nm red shift of the 298-nm isosbestic point but otherwise identical spectral changes.

Solutions of $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$ in 5–15% cyclohexene-tetrahydrofuran were irradiated with 270-, 310-, 350-, and 580-nm radiation, and the infrared spectra were monitored over the region of 2200–2000 cm^{-1} . In all cases the band at 2024 cm^{-1} (asymmetric stretching of the azido group in $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$) diminished in intensity and a new band at 2109 cm^{-1} developed. This new band has been attributed to the product of azide radical scavenging by cyclohexene.^{1,5}

The quantum yields for the formation of cobalt(II) have been determined for the irradiation of methanolic solutions of $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$ at 25 °C with 250-, 270-, 310-, 350-, 400-, 470-, and 580-nm radiations (Table II). In that the quantum yield for the formation of cobalt(II) determined under nitrogen in deaerated solutions was identical with yields determined in air, all other direct photolysis yields were determined in air.

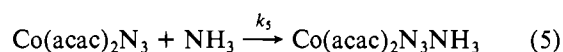
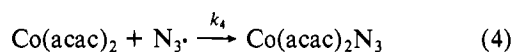
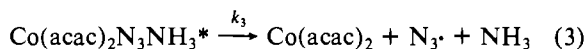
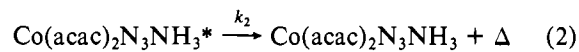
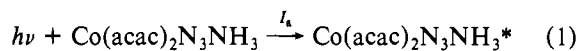
**Figure 2.** Plot of $\phi_{\text{Co(II)}}$ vs. λ_{ex} superimposed on the optical spectrum of $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$.

Furthermore, in that under the conditions used the observed quantum yields for cobalt(II) formation, $\phi_{\text{Co(II)}}$, are numerically equal to the primary yields for cobalt(II) formation, $\phi_{\text{Co(II)}}^1$, the observed yields may be treated as primary yields. Within the limits of experimental error the quantum yields for 310-, 350-, 400-, and 470-nm excitations are identical, which is surprising when the range of states initially populated is considered. There is a 50% increase in quantum efficiency for excitation below 310 nm, and this increase approximately coincides with onset of the $38.77 \times 10^3 \text{ cm}^{-1}$ absorption (Figure 2). The quantum efficiency for 580-nm excitations, which corresponds to the maximum of the ligand field absorption, is 1 order of magnitude lower than for the higher energy excitations.

The quantum yield for the formation of cobalt(II) by 350-nm radiation was also determined at other than room temperature and in mixed solvents. These results may also be found in Table II. Quantum yields were determined at 25, 30, and 35 °C with the use of 350-nm exciting radiation, and an Arrhenius plot ($\ln \phi_{\text{Co(II)}}$ vs. $1/T$) yielded a slope of 5.92×10^3 and an intercept of 15.87. The quantum yield was also determined with the use of 300-nm radiation in methanolic solutions made 20% (v/v) in ethylene glycol. A 25% increase in quantum efficiency was observed.

Discussion

In a recent communication from these laboratories, the photodecomposition of $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$ by 350-nm radiation was discussed in some detail.¹ A single photoreaction is observed which results in a one-electron reduction of the metal and a one-electron oxidation of the azido group. The mechanism proposed for the photodecomposition of $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$ is depicted in eq 1–6.



The primary quantum yield for the formation of cobalt(II), $\phi_{\text{Co(II)}}^1$, is 0.019 and is identical with the observed quantum yield, $\phi_{\text{Co(II)}}$. Kinetic analysis reveals that secondary recombination (eq 4) is unimportant under the conditions used in the determination of quantum yields. Furthermore, the per-

sistence of well-defined isosbestic points throughout the photolyses is strongly indicative of a single mode of photodecomposition. In addition there was no evidence for either free or coordinated nitrene formation or photodecomposition of the 2,4-pentanedionate ligand.

Beck and Schorpp have reported that cyclohexene is an effective scavenger of azide radicals produced during the photolysis of $[\text{Au}(\text{N}_3)_4]^-$ and $[\text{Pb}(\text{N}_3)_6]^{2-}$ ions.⁵ The photolysis of $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$ has been monitored in the infrared region for excitations throughout the region 270–580 nm. The disappearance of the band attributed to coordinated azide and the development of a band attributed to 3,6-diazidocyclohexene are clear indication that azide radical formation is typical of excitation with radiations throughout this region.

The optical spectra (250–400 nm) were also monitored during photolysis, with use of the same range of excitation energies. The observed spectral changes were identical with those reported for the 350-nm photolysis. Thus, as with the 350-nm excitation a single mode of photodecomposition is indicated and the mechanism depicted in eq 1–6 obtains throughout the 250–580-nm region.

Optical Spectrum of $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$. There are only four clearly discernible bands in the optical spectrum of $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$ as compared to seven in the spectrum of $\text{Co}(\text{acac})_3$. Furthermore, the spectrum of $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$ should contain all of the transitions observed for $\text{Co}(\text{acac})_3$ plus several additional transitions. The $16.97 \times 10^3 \text{ cm}^{-1}$ band in $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$ has been assigned to a ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{1g}(\text{O}_h)$ transition.²² The facts that attempts to further resolve this band failed and that its band width ($1.96 \times 10^3 \text{ cm}^{-1}$) is slightly smaller than that of the corresponding band in $\text{Co}(\text{acac})_3$ ($1.98 \times 10^3 \text{ cm}^{-1}$, Table I) suggest that the low-symmetry components of the ${}^1\text{T}_{1g}(\text{O}_h)$ must be of very similar energy. Since this transition in the two complexes only differ in energy by 22 cm^{-1} , it is expected that the ligand field parameters should be quite similar. This contention is supported by the fact that whereas ammonia has a higher ligand field strength than the 2,4-pentanedionate ligand, azide has a lower field strength. This similarly suggests that the ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{2g}$ transitions should occur at similar energies. Thus $25.0 \times 10^3 \text{ cm}^{-1}$ was used as an initial guess for this transition in resolving the optical spectrum of $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$.

There are four bands in the optical spectrum of $\text{Co}(\text{acac})_3$ which have energies greater than $25 \times 10^3 \text{ cm}^{-1}$, and all are associated with the 2,4-pentanedionate ligand.²⁷ Of these, three are directly discernible in the spectrum of $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$. This suggests that the energies of these states differ little in these two complexes. The spectrum of $\text{Co}(\text{acac})_3$ was resolved, and the spectral parameters served as first guesses in the resolution of the spectrum of $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$. The optical spectrum of $\text{Co}(\text{acac})_3$ has been assigned by Lintvedt whose assignments were used in assigning the spectrum of $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$ (Table III). The $32.33 \times 10^3 \text{ cm}^{-1}$ band is assigned to the charge transfer to metal transition involving the 2,4-pentanedionate ligand (CTTM(acac)). The optical electronegativities of the azido group (2.8) and the 2,4-pentanedionate group (2.7) differ by only 0.1 which places the charge transfer to metal transition of the azido group (CTTM(N_3)) $3.0 \times 10^3 \text{ cm}^{-1}$ higher in energy than the analogous transition for the 2,4-pentanedionate group (CTTM(acac)) (at $35 \times 10^3 \text{ cm}^{-1}$). With this used as a first guess for this band, the spectrum of $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$ was resolved (Table I). The success in fitting a band in the $35 \times 10^3 \text{ cm}^{-1}$ region supports the contention that the CTTM(N_3) transition is about $3 \times 10^3 \text{ cm}^{-1}$ higher in energy than

Table III. Optical Transitions of $\text{Co}(\text{acac})_3$ and $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$ in Methanol

| | $10^{-3}\bar{\nu}, \text{cm}^{-1}$ | assign |
|---|------------------------------------|---|
| $\text{Co}(\text{acac})_3$ | 43.80 | $\pi \rightarrow \pi^* \text{ }^a$ |
| | 38.17 | $\pi \rightarrow \pi^* \text{ }^a$ |
| | 33.89 | $\pi \rightarrow \pi^* \text{ }^a$ |
| | 30.32 | CTTM(acac) ^a |
| | 24.06 | ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{2g} \text{ }^a$ |
| $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$ | 16.95 | ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{1g} \text{ }^a$ |
| | 44.80 | $\pi \rightarrow \pi^* \text{ }^a$ |
| | 38.77 | $\pi \rightarrow \pi^* \text{ }^a$ |
| | 36.64 | CTTM(N_3) |
| | 32.33 | CTTM(acac) and/or $\pi \rightarrow \pi^* \text{ }^a$ |
| | 24.30 | ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{2g}(\text{O}_h)$ |
| | 17.04 | ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{1g}(\text{O}_h)$ |

^a Assignments taken from ref 27.

CTTM(acac). This is also in reasonable agreement with the position of the same transition in the $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$ ion.²⁸ Care must be taken not to attach too much quantitative significance to these results, but they do provide semiquantitative estimates of spectral parameters.

Other Possible Photoreactions. The respective optical electronegativities of the azido and 2,4-pentanedionate groups predict that the CTTM(acac) state is lowest in energy, and that in event of efficient interconversion among charge-transfer states, only 2,4-pentanedionate photooxidation should be observed. Even if interconversion among charge-transfer states were inefficient, spectral analysis suggests that 350-nm excitation should populate the CTTM(acac) state and yield 2,4-pentanedionate photooxidation. In addition, the photooxidation of the 2,4-pentanedionate ligand in $\text{Co}(\text{acac})_3$ occurs with 1 order of magnitude greater quantum efficiency than does the photooxidation of the azido group in $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$. These results suggest that photooxidation of the 2,4-pentanedionate group should be the dominant mode of photodecomposition for $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$.

Excitation at 250 nm results in the loss of isosbestic points after the reaction reaches about 70% completion. This loss of isosbestic could be attributed to a minor second mode of photodecomposition or to secondary photolysis. A reasonable second mode is the photooxidation of the 2,4-pentanedionate ligand. The quantum efficiency for the photodecomposition of $\text{Co}(\text{acac})_3$ has a large solvent dependence. The ability of the solvent to act as a hydrogen atom donor greatly increases efficiency for this reaction. The hydrogen-donor ability of the solvent is particularly important in the photooxidation of the 2,4-pentanedionate ligand because the primary photoproduct free radical is still bound to the metal, and hydrogen atom abstraction competes with the secondary recombination reaction. Thus, failure to observe photooxidation of the 2,4-pentanedionate ligand for $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$ may be a reflection of the poor hydrogen-donor ability of the solvent. The increased quantum yield observed below 310 nm may be explained in terms of photooxidation of the 2,4-pentanedionate ligand. This explanation is an attractive one also since the onset of increased quantum yield coincides with the onset of absorption into the $37.79 \times 10^3 \text{ cm}^{-1}$ band which is associated with the 2,4-pentanedionate ligand. If this were the case, the presence of 2-propanol, which is a better hydrogen atom donor than methanol, should increase the quantum efficiency for the oxidation of the 2,4-pentanedionate ligand. Both the maintenance of isosbestic points and the very modest increase in quantum efficiency strongly suggest that this is not the case.

For reasons to be discussed shortly, upon CTTM excitation one might expect labilization of the azido group in which case dissociation of the azido group as azide ion might occur upon

(27) R. L. Lintvedt in "Concepts in Inorganic Photochemistry", A. W. Adamson and P. D. Fleischauer, Ed., Wiley-Interscience, New York, 1975.

(28) V. M. Linhard and H. Flygare, *Z. Anorg. Allg. Chem.*, **262**, 328 (1950).

irradiation. If this were the case, in a poorly coordinating solvent such as methanol, there may be no net change in the solution composition and the reaction may go undetected. Nonetheless, photolysis in 0.0088 M LiBr resulted in a change neither in the rate of reaction nor in the products of the reaction. This does not suggest that the azido group is not labilized during photolysis, but it does show that azide ion dissociation does not occur during photolysis.

In a CTTM excitation an electron is removed from a ligand orbital and transferred into a metal orbital. This transfer has several effects on the chemistry of the complex. The ligand undergoes a one-electron oxidation and is thus a free radical which can potentially undergo normal free radical reactions. The one-electron oxidation increases the amount of positive charge on the ligand which decreases its ligating ability and thus weakens the ligand to metal bond. If the ligand is a π donor ligand, removal of one of the π electrons results in diminished ligand-metal π interaction. The metal orbital to which the electron is transferred is a metal e_g or t_{2g} orbital. The e_g orbitals are σ antibonding orbitals and populating either of them weakens the metal-ligand bond(s). The t_{2g} orbitals may be bonding, antibonding, or nonbonding. Thus population of these orbitals may strengthen, weaken, or leave the bonding unchanged.

In an octahedral low-spin d^6 complex, the e_g orbitals are populated upon CTTM excitation. These orbitals are σ antibonding, and weakening of the ligand-metal bonds is expected. The low symmetry of this complex is expected to split the e_g set, and it is expected that the weak field axis will make a dominant contribution to the lower energy orbital. Thus if interconversion among CTTM states is facile, excitation into the CTTM absorption should result in labilization of the azido group. This notwithstanding, optical electronegativity data suggest that the 2,4-pentanedionate group should be the ligand oxidized. The high quantum efficiency for the redox photodecomposition of $\text{Co}(\text{acac})_3$ can be attributed in part to the fact that the same ligand is both oxidized and labilized. This is not expected to be the case for $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$, and one might expect somewhat lower quantum efficiency.

The Reactive State. In the absence of vibrational fine structure, the energy of the vibrationally equilibrated excited state ($\bar{\nu}(0,0)$, ${}^1T_{1g}(0,0)$, etc.) is difficult to determine. It has, nonetheless, been estimated to occur where the intensity of an absorption equals 10% of the maximum intensity of the band.²⁹ For a Gaussian band shape this would be given by eq 7, where

$$\bar{\nu}(0,0) = \bar{\nu}_0 \pm (1.52 \times 10^3)\theta \quad (7)$$

θ is the bandwidth, $\bar{\nu}_0$ is the wavenumber of the maximum in the absorption curve, and the negative sign obtains. Figure 3 is an energy level diagram, depicting the energies of the vibrationally equilibrated excited states of $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$. The shaded areas are given by eq 7 and among other things indicate the degree of overlap among bands. The position of the CTTM(N_3) band was estimated as discussed previously. Care should be exercised not to place too much quantitative significance on the actual energies in Figure 3. Nonetheless it does provide an excellent basis for the discussion to follow. Examination of Figure 1 and comparison to the various excitation energies reveal several things. Excitations in the ultraviolet region (≤ 270) initially populate internal, 2,4-pentanedionate states exclusively, whereas excitations in the near-ultraviolet region initially populate various charge-transfer and internal ligand excited states. At 470 nm ($21.3 \times 10^3 \text{ cm}^{-1}$), a ligand field state is initially populated. Nonetheless, redox photodecomposition occurs with nearly the same quantum efficiency for all these excitations. The ${}^1T_{1g}(O_h)$ state

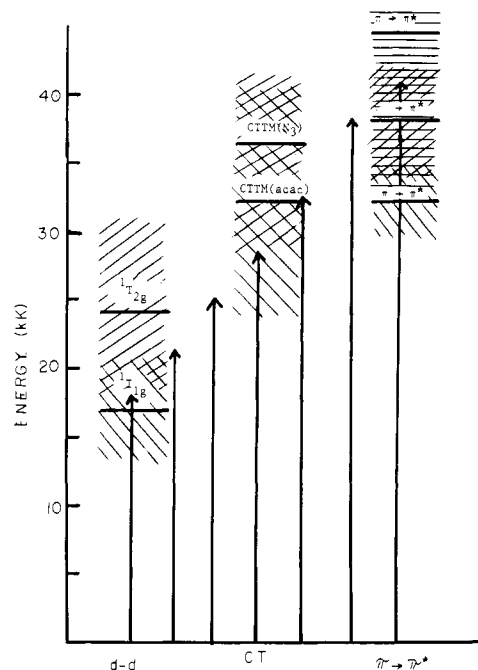


Figure 3. Energy level diagram for $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$. The vertical arrows represent various excitations for which quantum yields were determined.

appears to be below the threshold for redox photodecomposition. Finally, the ${}^1T_{2g}(O_h)$ state appears to be closest in energy to the threshold for redox photodecomposition and hence to the photoactive state. The next highest energy state is the CTTM(acac) excited state.

An examination of Figure 2 would suggest that the energy of the photoactive state can be bracketed between 17.2×10^3 (580 nm) and $21.3 \times 10^3 \text{ cm}^{-1}$ (470 nm). Furthermore, it would seem unlikely that the observed photochemistry should arise from a ligand field or CTTM(acac) state. A CTTM(N_3) state is expected to give rise to the observed photochemistry, but eq 7 and the data in Table I suggest that vibrationally equilibrated CTTM(N_3) state should lie near $33.2 \times 10^3 \text{ cm}^{-1}$ (300 nm). Thus unless one invokes a very large Frank-Condon factor, the spectroscopic CTTM(N_3) state is too high in energy and a ${}^3\text{CTTM}(\text{N}_3)$ photoactive state is indicated.

The constancy of the quantum yield for excitations greater than $21.3 \times 10^3 \text{ cm}^{-1}$ and the number and diversity of the states initially populated upon excitation suggest that interconversion among these states is facile. Failure to observe substitution reactions as a result of 585-nm excitation suggests that the ${}^1T_{1g}(O_h)$ state is probably photochemically inactive. Thus the low quantum efficiency for this reaction can be explained in terms of either facile interconversion among singlet states and inefficient intersystems crossing or facile interconversion among singlet states and facile interconversion to a rather photochemically inactive ${}^3\text{CTTM}(\text{N}_3)$ state. The former case seems more realistic in that intersystems crossing would not be expected to compete favorably with interconversion to the ${}^1T_{1g}(O_h)$ state.

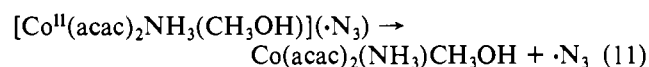
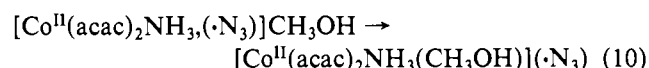
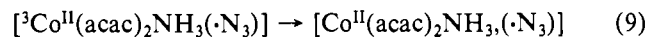
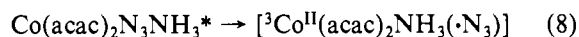
The primary photochemical processes occurring in oxidation-reduction photochemistry have received much attention, and several models have been proposed.^{7,8,30} A plot of $\ln \phi_{\text{Co(II)}}$ vs. $1/T$ yields a slope of $-5.9 \times 10^3 \text{ K}$, which corresponds to an activation energy of 11.7 kcal/mol. This small but significant activation energy indicates a labilized but nonetheless nondissociative excited state. It seems that photophysical

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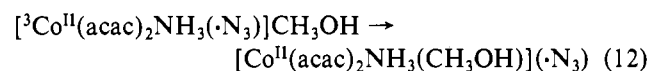
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processes alone could account for such a high activation energy. The processes occurring subsequent to population of the photoactive state are depicted in eq 8-11, where $[^3\text{Co}^{\text{II}}(\text{acac})_2\text{N}_3\text{NH}_3]^*$



$(\text{acac})_2\text{NH}_3(\cdot\text{N}_3)$ represents the $^3\text{CTTM}(\text{N}_3)$ excited state and $[\text{Co}^{\text{II}}(\text{acac})_2\text{NH}_3(\cdot\text{N}_3)]\text{CH}_3\text{OH}$ and $[\text{Co}^{\text{II}}(\text{acac})_2\text{NH}_3(\text{CH}_3\text{OH})](\cdot\text{N}_3)$ are geminate and secondary (solvent separated) radical pairs. As written a dissociative mechanism has been envisioned, but if an associative mechanism is considered, eq 9 and 10 reduce to eq 12. An activation energy of 11.7



kcal/mol suggests a sufficiently long-lived excited state as to permit the type of solvent involvement required by eq 12. Furthermore, the mechanisms (eq 9 and 10 vs. eq 12) suggest two different types of solvent participation. Whereas the solvent in eq 10 is merely undergoing exchange with a solvent caged but unbound radical, the solvent in equation 12 is undergoing nucleophilic attack on a bound ligand. The latter

process is favored for nucleophilic solvent molecules, but the former is disfavored in viscous media. The quantum efficiency increases in 20% (v/v) ethylene glycol-methanol as compared to methanol as a solvent, although the former is more viscous. In that ethylene glycol is a potentially chelating ligand, it is expected to facilitate reaction 12.

The results of this investigation reveal a number of interesting features in the photochemistry of $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$. Excitations throughout the 250-580-nm region appear to populate a single photoactive state. The ligand field, $^1\text{T}_{1g}(\text{O}_h)$, state appears to be inactive, and the low quantum efficiency and its wavelength dependence can be readily explained in terms of facile interconversion among singlet states and inefficient intersystems crossing into the triplet manifold. The photoactive state has an energy between 17.2×10^3 and $21.3 \times 10^3 \text{ cm}^{-1}$, and a $^3\text{CTTM}(\text{N}_3)$ state is strongly indicated. Studies are currently being carried out in support of this proposition. The photoactive state is nondissociative as evidenced by both the magnitude of the apparent activation energy and the solvent viscosity behavior. The results in mixed solvents suggest that the solvent assists in the displacement of the azide radical from the coordination sphere.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Aeronautics and Space Administration for support of this research.

Registry No. *cis*- $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$, 38977-23-0; $\text{Co}(\text{acac})_3$, 21679-46-9; $\text{Co}(\text{acac})_2$, 14024-48-7.

Contribution from the Inorganic Chemistry Laboratory, Oxford OX1 3QR, England

Ultraviolet Photoelectron Studies on Bonding in Some Metal Carbonyl and Metal Hydrido Carbonyl Clusters

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Received September 11, 1980

He I and He II gas-phase photoelectron spectra are reported for $\text{Ru}_3(\text{CO})_{12}$, $\text{Os}_3(\text{CO})_{12}$, $\text{Co}_4(\text{CO})_{12}$, $\text{Os}_6(\text{CO})_{18}$, $\text{H}_3\text{Re}_3(\text{CO})_{12}$, $\text{H}_4\text{Re}_4(\text{CO})_{12}$, $\text{H}_2\text{Os}_3(\text{CO})_{10}$, and $\text{H}_4\text{Os}_4(\text{CO})_{12}$. The spectra are assigned with the use of fragment molecular orbital analyses of the various electronic structures. Characteristic intensity patterns and ionization energy regions are established for the various types of bonding orbitals. Evidence is presented for treatment of the hydrogen bridge bonds as many-center, two-electron bonds, with a high degree of hydrogen localization. The role of hydrogen in stabilizing the cluster orbitals is noted. The difference between the first ionization energy of a cluster and the work function of metal surfaces is discussed.

As part of a general investigation into the nature of metal-metal bonding in binuclear and polynuclear transition-metal compounds,¹ we have carried out a UV photoelectron (PE) study of some carbonyl and hydrido carbonyl cluster compounds. Preliminary reports on part of this work have already been made.^{2,3} The studies described below have demonstrated that the metal-metal and bridge hydrogen bonds in these cluster compounds can be analyzed satisfactorily in terms of

molecular orbital schemes derived from the frontier molecular orbitals of the $\text{M}(\text{CO})_4$ and $\text{M}(\text{CO})_3$ fragments which have been studied extensively.^{4,5}

This work also provides an opportunity to examine the proposition that clusters of this type can be used as models for metal surfaces involved in heterogeneous catalytic processes. The analogy between the interaction of unsaturated species with molecules, containing three or more metal atoms, and the structure and reactivity of organic species on metal surfaces has been developed in several major review articles⁶⁻¹¹

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