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Photochemical Nitro–Nitrito Isomerization in Bis(acetylacetonato)aminenitrocobalt Complexes[1]

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The photochemically induced linkage isomerization of $Co(NH_3)_5NO_2^{2+}$ ion[3] and the analogous iridium(III) complex[4] have been known for some time; however, neither the mechanism of this photochemical reaction or the generality of its occurrence is known. We wish to report the observation of a thermally reversible photolinkage isomerization in the title compounds and the results of preliminary photochemical studies of this reaction.

Experimental Section

The complexes $Co(acac)_2(A)NO_2$ (A = C_5H_5N, $C_3H_4N_2$, NH_3) were prepared by the method of Bailar and Boucher[5] from Na[$Co(acac)_2(NO_2)_2$] and the appropriate amine and were characterized by spectral measurements. All other materials were reagent grade.

Spectral Measurements.—Infrared spectra were recorded as mulls or in pressed KBr disks using a Perkin-Elmer Model 337 grating infrared spectrophotometer. The visible and near-ultraviolet spectra were obtained with a Cary Model 14R recording spectrophotometer. In the case of solid-phase spectra, Nujol mulls of the appropriate complexes were studied.

Photochemical Experiments.—The photochemical nitro–nitrito interconversion was induced by irradiation of the sample with the total output or some monochromatized segment of the radiation from a PEK 200-W high-pressure mercury arc (825 East Evelyn Ave., Sunnyvale, Calif.). The samples were irradiated as Nujol mulls and in KBr pellets and the photoisomerization was detected by infrared measurement.

Discussion

The assignment of the mode of bonding in nitro–nitrito isomeric pairs has been discussed by numerous authors.[6] The stable isomers of the complexes studied here have been thoroughly studied by Bailar and Boucher[5] and assigned as nitro complexes. In the photoisomers, the infrared band shifts provide the most useful criterion for the bonding mode; in addition, ultraviolet–visible spectra of irradiated mulls are consistent with the proposed nitro → nitrito photochemical conversion. The changes in vibrational spectrum which follow irradiation of a mull containing $Co(acac)_2pyNO_2$ with ultraviolet light are shown in Figure 1. The main diagnostic feature of the infrared spectra of photolyzed samples is a marked increase in absorption in the region 1000–1050 cm^{-1} presumed to be the symmetric stretch[7] of the nitrito ligand; moreover, other changes in the spectra are consistent with such an interpretation. The reversibility of the isomerizations is indicated by the return of the infrared spectra to their preirradiation form in the dark ($\sim$24 hr).

The visible and near-ultraviolet spectrum of a mull containing $Co(acac)_2pyNO_2$ before and after photolysis is shown in Figure 2. For Co(III) complexes the position of nitro and nitrito ligands in the spectrochemical series is $M{-}NO_2 > MO{-}NO$ leading to a red shift in the d–d bands of cobalt(III)–nitro complexes upon conversion to the nitrito form.[8] Although broad bands are observed in the mull spectra, there is a clear-cut shift in absorption maximum to lower frequency following irradiation of a magnitude comparable to that observed for $Co(NH_3)_5NO_2^{2+}$.[3b] The recent spectroscopic test for bonding mode of $-NO_2$ groups suggested by Garner and coworkers[9] did not prove diagnostic for these complexes. This technique depends upon the observation of the vibrational structuring of the overlap forbidden $n \rightarrow \pi^*$ transition of the nitrogen lone pair of the nitrito isomer. The reason this absorption band was not detected must lie in the nature of the electronic states available to the complex and not the spectroscopic technique as the structured band is clearly identified in the mull electronic spectrum of $Co(NH_3)_5ONO^{2+}$.

When $Co(acac)_2pyNO_2$ was photolyzed at 2310, 2800, 3130, and 3650 Å, photolinkage isomerization occurred; however, irradiation of a sample with a broad band of wavelengths longer than 4500 Å did not lead to appreciable isomerization. These results suggest that the d–d excited states of cobalt(III)–nitro complexes are not highly active toward photolinkage isomerization in agreement with the general low photoactivity of the ligand field bands of Co(III) complexes.[10] There is insufficient evidence to allow much speculation concerning the excited state leading to photoisomerization or the mechanism of this photochemical reaction; however, it may be noted that in solution a common mode of reactivity for cobalt(III)–nitro complexes is reduction.[11] A homolytic bond fission mechanism from a charge transfer to metal (CTTM) excited state would accommodate both commonly observed modes of photochemical reactivity in these complexes when the

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[3] (a) B. Adell, *Z. Anorg. Allgem. Chem.*, **279**, 219 (1955); (b) W. W. Wendlandt and J. H. Woodlock, *J. Inorg. Nucl. Chem.*, **27**, 259 (1965); (c) also see A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischauer, and R. D. Lindholm, *Chem. Rev.*, **68**, 541 (1968); see especially p 573; (d) V. Balzani, R. Ballardini, N. Sabbatini, and L. Moggi, *Inorg. Chem.*, **7**, 1398 (1968).

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[10] A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischauer, and R. D. Lindholm, *Chem. Rev.*, **68**, 541 (1968).

[11] See ref 10, p 573 and references therein.

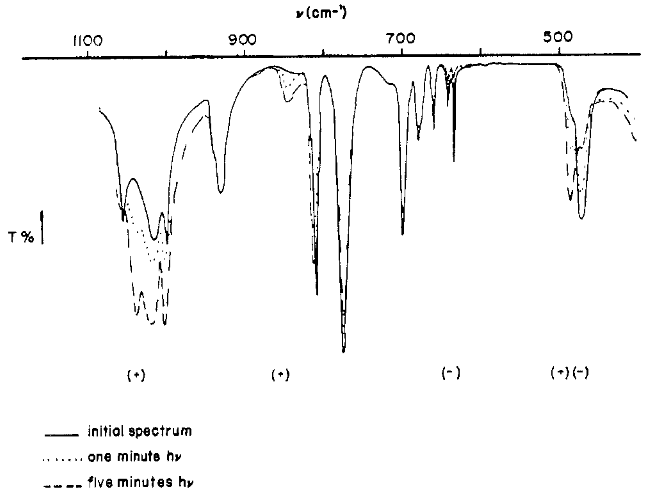

Figure 1.—Infrared spectra of $Co(acac)_2pyNO_2$ before and after irradiation. The regions of maximal change are indicated by (+) or (−) for enhanced and diminished absorption after photoisomerization. The total output of the PEK 200-W lamp was utilized.

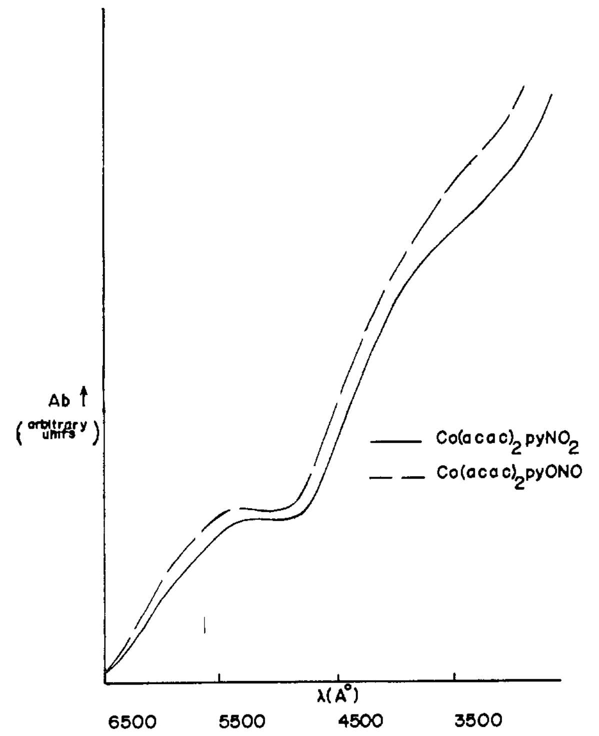

Figure 2.—Electronic spectrum of $Co(acac)_2pyNO_2$ prior to and following irradiation with total output of the PEK lamp. Samples were mulls in Nujol; the absorbance values are only relative.

large cage effect expected in these solid-phase reactions is considered.[3d] The observations in these complexes and other systems under investigation suggest that photolinkage isomerization of nitro groups will be fairly common for cobalt(III). Further work is in progress to ascertain the nature of the influence of the remainder of the coordination sphere upon this photochemical reaction. In general, lower conversion to the nitrito complex occurs for systems showing high rates of the thermal reverse reaction;[3b,12] however, it is not known, at present, whether the low conversion is due entirely to the enhanced rate of the reverse thermal reaction or if some lowering in the quantum yield for the forward reaction also occurs.

[12] D. A. Johnson, and L. E. Poplin, to be submitted for publication.

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The Reaction of Tricarbonatocobaltate(III) with Aqueous Ammonia[1a]

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Two isomers of the diamminedicarbonatocobaltate(III) anion were reported[2] as products from the reaction between ammonium carbonate and the green solutions from which potassium tricarbonatocobaltate(III) can be precipitated.[2] From the reaction sequence

$$Co(CO_3)_3^{3-} \xrightarrow[\text{aq soln, warm}]{\text{ammonium carbonate}} \text{blue } Co(NH_3)_2(CO_3)_2^- \xrightarrow[\text{heating}]{\text{further}} \text{"violet isomer"} \quad (1)$$

the authors suggested[2,3] that the kinetically obtained blue isomer has a *cis* configuration (which requires no change in the positions of the two nonreplaced carbonato ligands) and that the subsequent change to violet is the formation of the *trans* ion of greater thermodynamic stability. The observation of only the *cis* isomer of the $Co(acac)_2(NH_3)_2^+$ cation from reactions of either the blue $Co(NH_3)_2(CO_3)_2^-$ isomer or the "violet isomer" with 2,4-pentanedione[4,5] and a similar result with ethylenediamine[6] have led to further investigation. The visible spectra for violet materials isolated only qualitatively agreed with that given earlier,[2] and the infrared spectrum[5] of one violet sample was not that expected for a $K[Co(CO_3)_2(NH_3)_2]$ salt. In an effort to find a reproducible method for preparing a product consistent with the *trans*-$Co(NH_3)_2(CO_3)_2^-$ structure, we have come to the conclusion that the violet product reported by the original authors is not

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[1] (a) Presented in part at the Northeast Regional Meeting of the American Chemical Society, Boston, Mass., 1968. (b) Texaco Fellow, University of Massachusetts, 1968–1969. (c) Author to whom correspondence should be sent.

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[6] R. D. Archer, B. D. Catsikis, and N. Cooke, presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., 1967.