

Figure 2. Probable configuration of the transition state for isomerization with H_2O exchange. $\text{N}-\text{N}$ represents an ethylenediamine molecule, and $\text{H}_2\text{O} \cdots$ etc. represent weak coordination bonds between an entering water and the Co^{III} and between a leaving water and the Co^{II} .

the activation volume. In this consideration, we do not take account of the relatively small ΔV^\ddagger for isomerization of $\text{Co}(\text{en})_2(\text{H}_2\text{O})_2^{3+}$ because it is obtained at high ionic strength. Accordingly, the relatively small magnitudes of ΔV^\ddagger for isomerizations of $\text{Co}(\text{en})_2(\text{H}_2\text{O})\text{Cl}^{2+}$ and $\text{Co}(\text{en})_2(\text{H}_2\text{O})\text{Br}^{2+}$ can be explained consistently with the I mechanism. On these bases, we prefer the I mechanism as depicted in Figure 2 rather than the D_p mechanism. Our value of $\Delta V^\ddagger = 4.9 \pm 1.3 \text{ cm}^3 \text{ mol}^{-1}$ for isomerization of *trans*- $\text{Co}(\text{en})_2(\text{H}_2\text{O})_2^{3+}$ coincides within the error limit of the $\Delta V^\ddagger = 5.9 \pm 0.2 \text{ cm}^3 \text{ mol}^{-1}$ for water exchange of the same complex at $\mu = 2.0 \text{ M}$ and 35°C .⁴ Thus, the configurational difference between the transition states of isomerization and water exchange is not reflected in their magnitudes of ΔV^\ddagger .⁵ This mechanistic difference concerns the attacking site by a water molecule, as pointed out by Martin and Tobe.²⁰ In isomerization, the entering H_2O will attack the complex at a site opposite to the leaving H_2O (Figure 2), whereas in water exchange it will attack at a site adjacent to the leaving H_2O . We have some ground to consider that this difference of the attacking position does not cause an essential difference in the magnitude of ΔV^\ddagger .²⁷

The large magnitude of $\Delta V^\ddagger = 18.0 \text{ cm}^3 \text{ mol}^{-1}$ for $\text{Co}(\text{en})_2(\text{OH})\text{NH}_3^{2+}$ is compatible with the idea that twisting occurs in an expanded state of the complex. When a sphere with a radius (r) of 4 \AA expands by $\Delta r = 0.17 \text{ \AA}$, a volume increase of $20 \text{ cm}^3 \text{ mol}^{-1}$ can be expected. However, this magnitude of $\Delta V^\ddagger = 18.0 \text{ cm}^3 \text{ mol}^{-1}$ is also compatible with an alternative I mechanism, whereby $\text{Co}-\text{NH}_2\text{R}$ bond dissociation occurs by stimulation of an attacking water molecule and approximately half of an ethylenediamine chain is freed in the transition state.²⁰ The partial molal volume of ethylenediamine $\bar{V}(\text{en})$ is $62.6 \text{ cm}^3 \text{ mol}^{-1}$ at 25°C .²⁸ ΔV^\ddagger for $\text{Co}(\text{en})_2(\text{OH})\text{NH}_3^{2+}$ is larger by $12 \text{ cm}^3 \text{ mol}^{-1}$ than the $\Delta V^\ddagger(\text{Co}-\text{OH}_2) = 6.3 \pm 1.4 \text{ cm}^3 \text{ mol}^{-1}$. This difference is close to the difference between $0.5\bar{V}(\text{en})$ and $\bar{V}(\text{H}_2\text{O}) = 18.0 \text{ cm}^3 \text{ mol}^{-1}$, $0.5\bar{V}(\text{en}) - \bar{V}(\text{H}_2\text{O}) = 13.3 \text{ cm}^3 \text{ mol}^{-1}$. The $\Delta V^\ddagger = 11.4 \text{ cm}^3 \text{ mol}^{-1}$ for $\text{Co}(\text{en})_2(\text{OH})_2^+$ is intermediate between the $\Delta V^\ddagger(\text{Co}-\text{OH}_2)$ and the $\Delta V^\ddagger = 18.0 \text{ cm}^3 \text{ mol}^{-1}$ for $\text{Co}(\text{en})_2(\text{OH})\text{NH}_3^{2+}$. This result corresponds to the fact that only a fraction of one oxygen per ion exchanges for each act of isomerization of $\text{Co}(\text{en})_2(\text{OH})_2^+$.⁵ The fairly large ΔV^\ddagger for $\text{Co}(\text{en})_2(\text{H}_2\text{O})\text{NO}_2^{2+}$ suggests that $\text{Co}-\text{NH}_2\text{R}$ bond dissociation takes some part in the transition state of this reaction. But, at our present state of knowledge, it seems difficult to specify one of the two possible paths proposed by Hughes.²⁹

Registry No. $\text{Co}(\text{en})_2(\text{H}_2\text{O})_2^{3+}$, 19314-32-0; $\text{Co}(\text{en})_2(\text{H}_2\text{O})\text{OH}^{2+}$, 24458-51-3; $\text{Co}(\text{en})_2(\text{OH})_2^+$, 21772-94-1; $\text{Co}(\text{en})_2(\text{OH})\text{NH}_3^{2+}$, 38246-62-7; $\text{Co}(\text{en})_2(\text{H}_2\text{O})\text{NCS}^{2+}$, 24913-06-2; $\text{Co}(\text{en})_2(\text{H}_2\text{O})\text{NH}_3^{3+}$, 21199-56-4; $\text{Co}(\text{en})_2(\text{H}_2\text{O})\text{NO}_2^{2+}$, 24913-08-4; $\text{Co}(\text{en})_2(\text{H}_2\text{O})\text{Br}^{2+}$, 24913-01-7; $\text{Co}(\text{en})_2(\text{H}_2\text{O})\text{N}_3^{2+}$, 29770-07-8.

(27) Kitamura, Y.; Nariyuki, S.; Kondo, T. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 285-286.

(28) Shahidi, F.; Farrell, P. G.; Edward, J. T. *J. Chem. Soc. Faraday Trans. 1* **1977**, *73*, 715-720.

(29) Hughes, M. N. *J. Chem. Soc. A* **1967**, 1284-1286.

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Photoaquation Reactions of Chromium(III) Polypyridine Complexes Induced by Sequential Biphotonic Irradiations

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Received June 3, 1987

The long-lived, low-lying doublet states of Cr(III) polypyridine complexes have been generated and irradiated by using sequential biphotonic techniques. The detection of products and the time-resolved spectroscopy of the processes have shown that biphotonic irradiation induces a ligand photolabilization independent of acid concentration. Such a reaction cannot be associated with the photolabilization induced in monophotonic irradiations with low light intensities and has been related to processes initiated in upper excited states.

Introduction

Photochemical ligand labilization in Cr(III) complexes with polypyridine ligands has been extensively investigated.^{1,3} These compounds have long-lived, low-lying doublet states, labeled 2E and 2T_1 in an octahedral microsymmetry, whose intrinsic processes, relaxation to the ground state and ligand labilization, are medium-determined.¹⁻³ The sequential biphotonic technique proved to be very useful in our studies of the photochemistry of phthalocyanine radicals.⁴⁻⁶ In this regard, one can use this

technique with Cr(III) complexes in order to promote the population of upper doublet states by using the thermally equilibrated (2T_1 , 2E) states as receptors of a second photon. If the relaxation from the upper states to the lowest quartet and/or doublet states is too fast and competition with chemical reactions is insignificant, no difference between monophotonic and sequential biphotonic excitations are expected. However, the differences must be appreciable if upper states present intrinsic reactivities and such states do not achieve significant populations in monophotonic excitations.

Experimental Section

Photochemical Procedures. The flash photolysis apparatus has been previously described and is based on the synchronous triggering of two flash-pumped dye lasers.⁵ Each experiment involves the generation of the long-lived, lowest lying doublet states of the Cr(III) complexes by

(1) Jamieson, M. A.; Serpone, N.; Hoffman, M. Z. *Coord. Chem. Rev.* **1981**, *39*, 121 and references therein.

(2) Endicott, J. F.; Ramasami, T.; Tamilarasan, R.; Lessard, R. B.; Ryu, Chong Kul. *Coord. Chem. Rev.* **1987**, *77*, 1 and references therein.

(3) Ferraudi, G.; Arguello, G.; Frink, M. J. *Phys. Chem.* **1987**, *91*, 64.

(4) Ferraudi, G. *J. Phys. Chem.* **1984**, *88*, 3938.

(5) Van Vlierberge, B.; Ferraudi, G. *Inorg. Chem.* **1987**, *26*, 337.

(6) Muralidharan, S.; Ferraudi, G. *J. Phys. Chem.* **1983**, *87*, 4877.

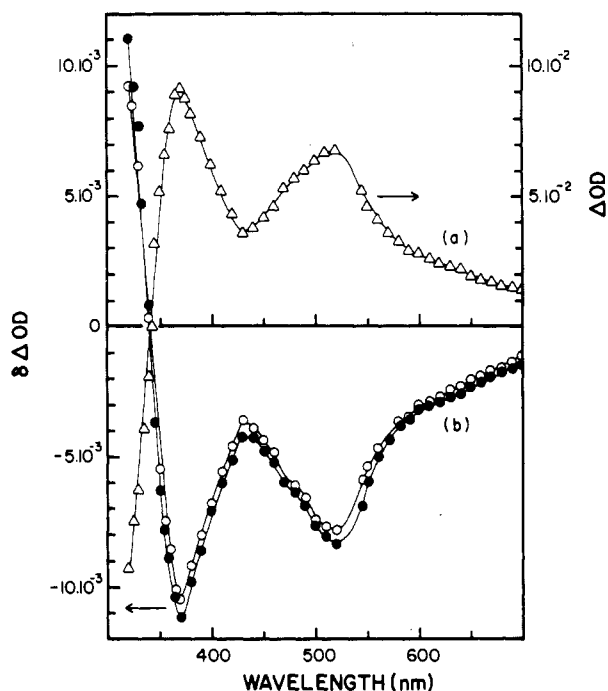


Figure 1. Transient spectra determined in (a) monophotonic and (b) sequential biphotonic excitations of 10^{-4} M $\text{Cr}(\text{phen})_3^{3+}$ in deaerated aqueous acidic (pH 3) solutions. The differential spectrum of ${}^2\text{T}_{1,2}\text{E-Cr}(\text{phen})_3^{3+}$ (a) was recorded $2 \mu\text{s}$ after the irradiation of $\text{Cr}(\text{phen})_3^{3+}$ at 308 nm. Spectral changes induced by sequential biphotonic excitations of $\text{Cr}(\text{phen})_3^{3+}$ are shown in part b. The ordinate, $\delta\Delta(\text{OD}) = \Delta(\text{OD}) - \Delta(\text{OD})_{\text{M}}$, corresponds to the difference between changes in the optical density induced respectively by monophotonic, $\Delta(\text{OD})_{\text{M}}$, and biphotonic, ΔODB , excitations. Values for $\delta\Delta(\text{OD})$ were obtained $0.3 \mu\text{s}$, ●, and $4.0 \mu\text{s}$, ○, after irradiation of ${}^2\text{T}_{1,2}\text{E-Cr}(\text{phen})_3^{3+}$ with a 532-nm laser pulse.

irradiating at λ_{exc} with one of the lasers and by using light intensities that prevent multiphotonic processes, i.e. less than $200 \text{ MW}/\text{cm}^2$. These excited states were then photolyzed at λ_{phot} by a conveniently delayed pulse from another laser. Details of this procedure have been published elsewhere.^{4,5} In experiments where photolysis products were investigated, we used side-on excitations on a 1 cm optical path cell containing 3 cm^3 of the solution. Each sample was irradiated with a maximum of 500 pulses according to the light intensities and the sensitivity of the analytical techniques. In time-resolved measurements, spectra and kinetics were determined with a flash photolysis setup similar to the one described above where we used a XeCl excimer laser ($\lambda = 308 \text{ nm}$) for the generation of excited states and a Nd:YAG pumped dye laser for 532-nm (1,10-phenanthroline complex) or 485-nm (bipyridine complex) photolysis of the excited species. The irradiations were carried out in a flow cell (0.2-cm optical path) with a front face excitation. These photolyses were always carried out with solutions whose pH and ionic strength were adjusted with 8×10^{-3} M Britton-Robinson buffer (same concentrations of phosphoric, acetic, and boric acids) titrated with NaOH and deaerated with streams of ultrapure Ar.

Analytical Procedures. 1,10-Phenanthroline was investigated by complexation with Fe(III) in solutions buffered at pH 5 according to literature procedures.⁷ Blanks for these determinations were prepared with solutions subjected to monophotonic irradiations. In acidic solutions we found that these corrections to the product concentration were negligible.

Materials. The pure Cr(III) complexes $[\text{Cr}(\text{phen})_3](\text{ClO}_4)_3$ and $[\text{Cr}(\text{bpy})_3](\text{ClO}_4)_3$ were available from previous work.³ Other materials were of reagent grade and were used without further purification.

Results

Deaerated solutions of $\text{Cr}(\text{phen})_3^{3+}$, $1.5 \times 10^{-4} \leq [\text{Cr}(\text{phen})_3^{3+}] \leq 2 \times 10^{-3}$ M at pH 3–9, subjected to prolonged sequential biphotonic excitations ($\lambda_{\text{exc}} \sim 440 \text{ nm}$ and $\lambda_{\text{phot}} \sim 520 \text{ nm}$), exhibited spectral changes (with reference to the same solutions exposed to only one of the lasers) that indicate the formation of $\text{Cr}(\text{phen})_2(\text{OH})_2^{3+}$.⁸ Free 1,10-phenanthroline was also found

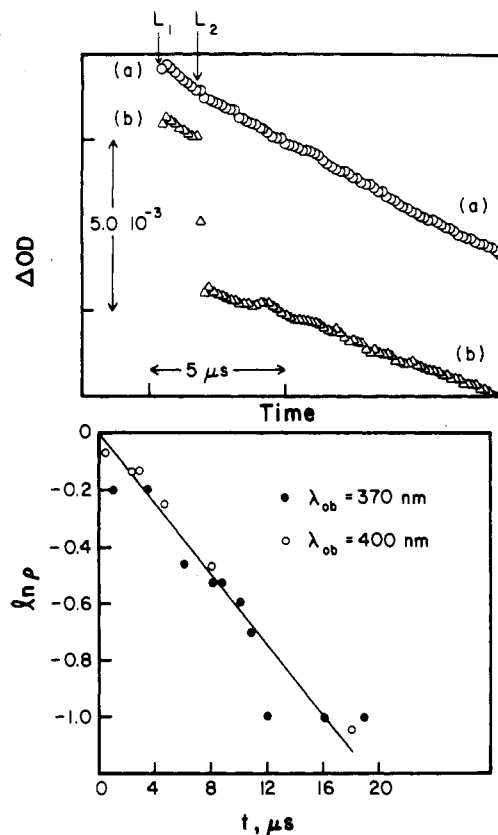


Figure 2. Typical traces (top) recorded in (a) monophotonic and (b) sequential biphotonic irradiations of $\text{Cr}(\text{phen})_3^{3+}$ under the conditions specified in Figure 1. Markers L_1 and L_2 signal the instants when the lasers were fired, and traces a and b represent an average of 50 experiments where optical changes were followed at 400 nm. Traces a and b have been arbitrarily displaced along the vertical scale for a better comparison. In sequential biphotonic excitations similar to that of trace b, the time-resolved changes in ρ (see text) were followed at 370 nm, ●, and 400 nm, ○, respectively. A logarithmic plot of these data is shown in the lower part of the figure.

as a product of the biphotonic irradiation.^{9–11} The amount of 1,10-phenanthroline generated in these irradiations was always less than or equal to 10% conversion of the photolyte to products, i.e. 10^{-4} M phen in photolyses of 10^{-3} M $\text{Cr}(\text{phen})_3^{3+}$, and was in a 1:1 stoichiometry with the aquo complex $\text{Cr}(\text{phen})_2(\text{OH})_2^{3+}$. It must be pointed out that the biphotonic photoaquation of 1,10-phenanthroline takes place in acidic solutions (pH 3) of the complex, i.e. under conditions where (in agreement with previous literature reports^{1,12}) our monophotonic irradiations with either laser failed to produce detectable concentrations of free ligand. Indeed, the significance of the biphotonic photochemistry can be established from the corresponding quantum yield $\phi \sim 10^{-2}$ vs a quantum yield, $\phi \leq 10^{-4}$, for the monophotonic excitation of $\text{Cr}(\text{phen})_3^{3+}$ at pH 3.¹³

In time-resolved experiments, the spectral changes induced by the photolyzing laser pulse (Figure 1) correspond to the bleaching of the excited-state spectrum and the formation of a new absorption band at $\lambda < 340 \text{ nm}$ (Figure 1). Such a bleach, used as a measure of the yield for the biphotonic photoaquation, is

- (9) We have not observed the generation of solvated electrons, characteristic of multiphotonic processes induced with UV light,¹⁰ nor the redox photochemistry reported for the pentaammine complexes.¹¹
- (10) Serpone, N.; Hoffman, M. Z. *J. Phys. Chem.* **1987**, *91*, 1737.
- (11) Siram, R.; Endicott, J. F.; Cunningham, K. M. *J. Phys. Chem.* **1981**, *85*, 38.
- (12) Bolleta, F.; Maestri, M.; Moggi, L.; Jamieson, M. A.; Serpone, N.; Henry, M. S.; Hoffman, M. Z. *Inorg. Chem.* **1983**, *22*, 2502.
- (13) These quantum yields have been calculated from standard definitions. In this regard, the yield for the biphotonic process is the number of moles of the product that are generated by the irradiation of ${}^2\text{E}, {}^2\text{T-Cr}(\text{phen})_3^{3+}$ divided by the number of photons absorbed by the doublets.

(7) Fries, J. *Trace Analysis*; Merck: Darmstadt, West Germany, 1971.

(8) Maestri, M.; Bolleta, F.; Moggi, L.; Balzani, V.; Henry, M. S.; Hoffman, M. Z. *J. Am. Chem. Soc.* **1978**, *100*, 2694.

Table I. Dependence of the 1,10-Phenanthroline Photolabilization Process on Acid Concentration

| pH | ϕ^a | $10^3 \delta \Delta(\text{OD})$ ($\lambda_m = 520 \text{ nm}$) ^b | $10^2 \phi^c$ |
|----|-----------------------|---|---------------|
| 3 | $\sim 0^{12}$ | 6.9 | 2.6 |
| 5 | 5.0×10^{-41} | 7.2 | 2.7 |
| 9 | 6.0×10^{-31} | 7.2 | 2.7 |

^aQuantum yields for 1,10-phenanthroline photolabilization in low-intensity irradiations (monophotonic regime) of $\text{Cr}(\text{phen})_3^{3+}$ at given acid concentrations. Values from this work agree with several literature reports. ^bOptical density changes determined in sequential biphotonic excitations. The optical density change was determined after the irradiation with a laser pulse (532 nm) that was delayed 1 μs following the laser pulse (308 nm) used for the excited-state generation. Experimental errors less than or equal to 5%. ^cQuantum yields for biphotonic photoaquation of 1,10-phenanthroline in photolyses of $\text{Cr}(\text{phen})_3^{3+}$ in deaerated solutions containing the Britton-Robinson buffer. The pH was adjusted with 0.1 M NaOH. The laser intensities (see footnote b) were adjusted to less than 200 MW/cm².

independent of the solution's pH (Table I). Moreover, the investigation of the photoaquation process between 350 and 600 nm (Figure 2) shows that the bleach is followed (in a microsecond time domain) by a small but significant recovery of the optical density. The kinetics of the recovery was investigated in terms of the difference, $\delta \Delta(\text{OD}) = \Delta(\text{OD})_B - \Delta(\text{OD})_M$, between the optical changes that the monophotonic, $\Delta(\text{OD})_M$, and biphotonic excitations, $\Delta(\text{OD})_B$, induced in the solution. The already defined relationship¹⁴

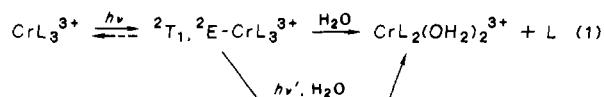
$$\rho = \frac{\delta \Delta(\text{OD})_t - \delta \Delta(\text{OD})_\infty}{\delta \Delta(\text{OD})_0 - \delta \Delta(\text{OD})_\infty}$$

measures the progress of the reaction initiated by photolysis of ${}^2T_1, {}^2E\text{-Cr}(\text{phen})_3^{3+}$. Subscripts refer to a given reaction time whose beginning is marked by the trigger of the photolyzing laser (Figure 2). In this regard, the recovery rate studied in solutions buffered at pH 3 exhibited a wavelength-independent, first-order rate law with $k = (6.3 \pm 0.5) \times 10^4 \text{ s}^{-1}$.¹⁵

The behavior of $\text{Cr}(\text{bpy})_3^{3+}$ in sequential biphotonic irradiations is qualitatively similar to that reported above for $\text{Cr}(\text{phen})_3^{3+}$ in that a detectable ligand photoaquation is induced by the photolyzing pulse (under conditions $1.0 \times 10^{-4} \leq [(\text{Cr}(\text{bpy})_3^{3+})] \leq 5.0 \times 10^{-4} \text{ M}$ and pH 3) where monophotonic irradiations fail to induce similar reactions.¹ However, limitations of the analytical procedures prevented us from making reliable measurements of the quantum yields for the biphotonic process.

Discussion

The results presented above show that sequential biphotonic excitations induce the absorption of visible light by the lowest excited doublets of CrL_3^{3+} ($L = \text{phen}, \text{bpy}$), a process leading to an overall ligand aquation, eq 1.



Reports of studies carried out under the regime of monophotonic excitations have demonstrated that photolabilization of the first Cr-N bond takes place in association with the radiationless decay of excited adducts ${}^* \text{CrL}_3(\text{OH}_2)_2^{3+}$ or ${}^* \text{CrL}_3(\text{OH})_2^{2+}$.^{1,10,15} Therefore, the recovery of the optical density that follows the sequential excitation in our experiments cannot be related to such a fast process. The final detachment of phenanthroline from a complex with a monodentate ligand, $\text{Cr}(\text{phen})_2(\text{N-N})(\text{OH}_2)_2^{3+}$, was previously investigated by Waltz et al. and is too slow in comparison with the rate of recovery.¹⁶ One possible explanation

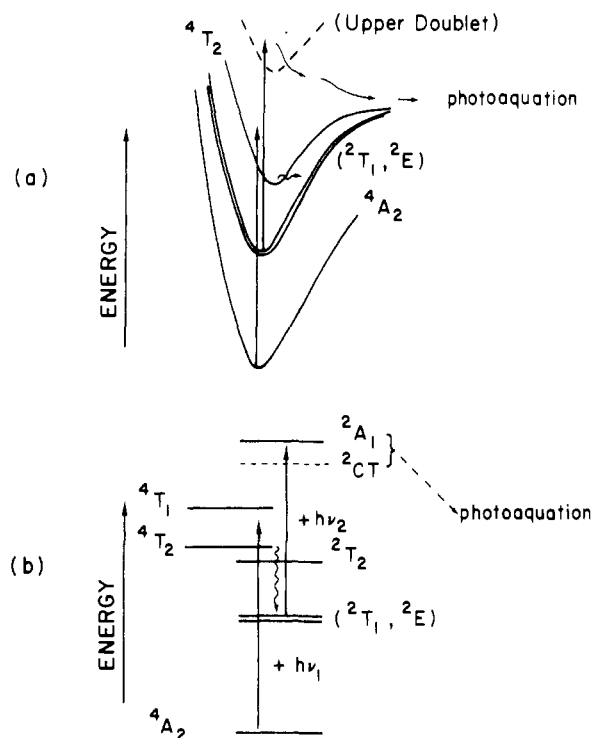
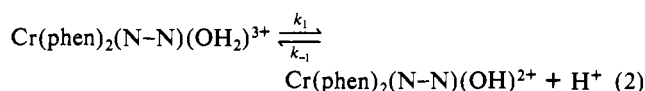


Figure 3. Possible reaction paths for biphotonic photoinduced ligand labilization: (a) reaction involving a rapid relaxation from upper states; (b) reaction initiated in reactive upper states. A group-theoretical nomenclature has been used for the description of the energy levels.³

for our time-resolved observations, in accord with reported acid-base properties of $\text{Cr}(\text{phen})_2(\text{N-N})(\text{OH}_2)_2^{3+}$, is that in biphotonic excitations $\text{Cr}(\text{phen})_2(\text{N-N})(\text{OH})_2^{2+}$ is generated in larger concentrations than in monophotonic excitations. Relaxation of the equilibrium shown in eq 2 could account for the transient



changes in optical density. In this case, the reported $\text{p}K_a$ of the equilibrium¹⁶ and our kinetic data give $k_1 \sim 6 \text{ s}^{-1}$ for the dissociation and $k_{-1} \sim 6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for the association (eq 2).

The reason for the different concentrations of $\text{Cr}(\text{phen})_2(\text{N-N})(\text{OH})_2^{2+}$ generated under biphotonic and monophotonic excitation regimes must be related to differences in the excited states that are populated in each case. Indeed, our observations suggest that the biphotonic photoreactivity cannot be straightforwardly associated with repopulation of doublet and/or quartet states from higher placed excited states of similar multiplicity. A mechanism by which the sequential biphotonic excitation can induce photoaquation consists, however, in the population of high-energy vibrational modes of the lowest lying doublet and/or quartet states were the photoaquation must compete with the rapid internal conversion (Figure 3a).² It is equally possible that the observed reaction involves an upper doublet state that can only achieve population under the sequential biphotonic excitations used in our experiments (Figure 3b).² In this case, the labilization of the ligand must compete to some extent with the rapid conversion of the upper doublet state(s) to the lowest lying excited state. The photonic energy of the photolyzing light and the reported positions of the upper excited states^{3,17} suggest that either the metal-centered 2A_1 or a low-lying charge-transfer state or both could be the reactive states (Figure 3b). Insofar as upper doublets are expected to exhibit very small distortions with respect to the ground state, the biphotonic ligand labilization seems to be more likely related

(14) Frost, A. A.; Pearson, R. G. *Kinetics and Mechanism*; Wiley: New York, 1953; pp 28, 29.

(15) The recovery rate exhibited a pH dependence that is in qualitative accord with the relaxation of an acid-base equilibrium.

(16) Lillie, J.; Waltz, W. L.; Lee, S. H.; Gregor, L. L. *Inorg. Chem.* **1986**, *25*, 4487.

(17) Hauser, A.; Mader, M.; Robinson, W. T.; Murugesan, R.; Ferguson, J. J. *Inorg. Chem.* **1987**, *26*, 1331.

to the participation of states with a strong charge-transfer character.

Acknowledgment. We are indebted to Dr. P. K. Das for his assistance in some of the time-resolved experiments. The research

described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2995 from the Notre Dame Radiation Laboratory.

Registry No. phen, 66-71-7; Cr(phen)₃³⁺, 15276-16-1; Cr(phen)₂(OH)₂³⁺, 47667-82-3.

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Preparation and Characterization of Ni(BiF₆)₂ and of the Ternary Adducts

[Ni(CH₃CN)₆](BiF₆)₂ and [Ni(CH₃CN)₆](SbF₆)₂. Crystal Structure of

[Ni(CD₃CN)₆](SbF₆)₂

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Received August 10, 1987

Ni(BiF₆)₂ was prepared from the reaction of NiF₂ with BiF₃ in anhydrous HF, followed by removal of the excess of BiF₃ by sublimation. The compound was characterized by elemental analysis, X-ray powder data, and vibrational spectroscopy. Both Ni(BiF₆)₂ and Ni(SbF₆)₂ react with acetonitrile to give ternary adducts of the formula NiF₂·2MF₆·6CH₃CN, with M = Bi or Sb. These isomorphous adducts are stable at room temperature and were characterized by elemental analyses, X-ray powder data, and infrared and electronic spectroscopy. In these ternary adducts the Ni²⁺ ion is octahedrally coordinated by six acetonitrile molecules via the nitrogen, and the counterions are MF₆⁻. The [Ni(CD₃CN)₆](SbF₆)₂ complex was characterized by X-ray diffraction methods, crystallizing in the trigonal space group R $\bar{3}$ with $a = 11.346(3)$ Å, $c = 17.366(6)$ Å, $V = 1936$ Å³, $Z = 3$, and $R = 0.034$. The Sb atoms lie on C₃ sites and are octahedrally coordinated by six F atoms with two nonequivalent Sb-F distances of 1.80 (1) and 1.83 (1) Å. The octahedrally coordinated Ni atoms lie on C₃ sites with Ni-N distances of 2.07 (1) Å. It is shown that coordination of the Ni²⁺ ions by six CH₃CN molecules lessens the strong polarizing effect of these ions on the MF₆⁻ counterions, which had been found for the Ni(MF₆)₂ salts, and reduces their distortion from octahedral symmetry.

Introduction

The preparation and characterization of Ni(SbF₆)₂ have been described in a recent paper,² and preliminary results concerning Ni(BiF₆)₂ and the acetonitrile adducts of both salts have been presented at a meeting.³ This paper gives a full report on the preparation and characterization of Ni(BiF₆)₂ and the acetonitrile adducts. The previous formulation² of NiF₂·2SbF₅·6CH₃CN as [Ni(CH₃CN)₆]²⁺(SbF₆)₂ was confirmed by elemental analysis, vibrational and electronic spectroscopy, and a crystal structure determination. Furthermore, it was interesting to determine how coordination of the Ni²⁺ ion by CH₃CN influences its interaction with the MF₆⁻ counterions.

Experimental Section

Apparatus. Volatile materials were manipulated in an all-metal vacuum line equipped with Teflon or metal valves. Solid products were handled in a glovebox flushed with dry nitrogen. The high-pressure reactor used has previously been described.⁴ Infrared spectra were recorded in the range 4000–200 cm⁻¹ on a Perkin-Elmer Model 283 spectrophotometer. Spectra of solids were obtained by using dry powders pressed between AgCl or AgBr windows in an Econo press (Barnes Engineering Co.). The low-frequency parts of the spectra were also recorded as halocarbon (Voltaflex) or Nujol mulls between silicon plates. Raman spectra were recorded on a Coderg Model T 800 spectrophotometer by using the 514.5-nm exciting line of an Ar ion Spectra Physics laser or the 647.1-nm exciting line of a Kr ion Spectra Physics laser. Sealed quartz capillaries were used as sample containers in the transverse-viewing-transverse-excitation mode. Low-temperature spectra

were obtained with a Coderg liquid-nitrogen cryostat and a Coderg RC 200 regulator. The electronic absorption spectra were recorded on a Beckman UV 5240 spectrophotometer, the solution being contained in a 1 mm thick quartz cell fitted with a Teflon-TFE Rotaflow stopcock. X-ray diffraction powder patterns of the samples sealed in 0.3 mm o.d. quartz capillaries were obtained by using a Phillips camera (diameter 11.46 cm) using Ni-filtered Cu K α radiation. Crystals suitable for structure determination were transferred into quartz capillaries in the drybox.

Materials. Anhydrous nickel difluoride⁵ was obtained by the treatment of nickel acetate with HF at 270 °C followed by fluorination with F₂ at 200 °C. Bismuth and antimony trifluorides were from Ozark Mahoning Co., and their purities were checked by infrared spectroscopy and X-ray diffraction. Fluorine (Union Carbide Co.) was passed over NaF pellets to remove HF. Bismuth pentafluoride was prepared by the reaction of BiF₃ with F₂ at 350 °C at a pressure of 20 atm. Acetonitrile (Prolabo) and acetonitrile-*d*₃ (CEA) were refluxed over P₂O₅ followed by treatment and storage on 5A molecular sieves. The adduct Ni(SbF₆)₂ was prepared as described previously² except that NiF₂ and SbF₃ were used instead of Ni and SbF₅, respectively. Microanalyses were by Analytische Laboratorien, Elbach, West Germany.

Preparation of Ni(BiF₆)₂. A mixture of NiF₂ (2.57 mmol) and BiF₃ (5.15 mmol) was loaded in the drybox into half of a prepassivated Teflon double-U metathesis apparatus.⁶ Dry HF (≈ 10 mL) was added on the vacuum line to the half containing NiF₂-BiF₃, and the resulting mixture was stirred for 6 h at 25 °C. The metathesis apparatus was inverted, and the resulting solution, pressurized by 2 atm of dry nitrogen, was filtered into the other half of the apparatus. The HF solvent was pumped off for 12 h at 25 °C, leaving 1.4749 g of a pale yellow solid. The X-ray powder diffraction patterns indicated that this solid consisted of a mixture of Ni(BiF₆)₂ and BiF₃ and that the filter cake contained NiF₂ and Ni(BiF₆)₂. The solid residue obtained from the evaporation of the solution was ground and loaded in the drybox into a prepassivated 30 cm long sapphire tube, which was connected to an aluminum valve by a Swagelock compression fitting using Teflon ferrules. The lower part of the tube was

- (1) (a) Centre d'Etudes Nucléaires de Saclay. (b) Rocketdyne.
- (2) Christe, K. O.; Wilson, W. W.; Bougon, R.; Charpin, P. *J. Fluorine Chem.* 1987, 34, 287.
- (3) Bougon, R.; Charpin, P.; Lance, M.; Isabey, J.; Christe, K. O.; Wilson, W. W. Presented at the 8th Winter Fluorine Conference of the American Chemical Society, St. Petersburg, FL, Jan 25–30, 1987.
- (4) Hagenmuller, P. *Preparative Methods in Solid State Chemistry*; Academic: New York and London, 1972; p 423.

- (5) Sample kindly supplied to us by M. Bergez, CEA/IRDI.
- (6) Christe, K. O.; Schack, C. J.; Wilson, R. D. *Inorg. Chem.* 1977, 16, 849.