

A Pulsed-laser Stimulated Biphotonic Photoreduction of Hexa-amminecobalt(III)

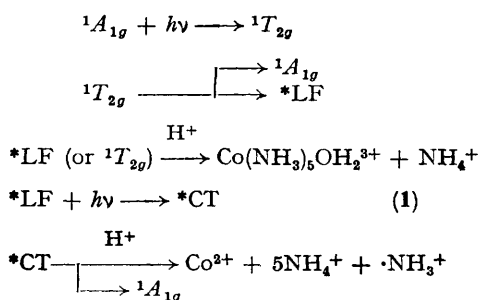
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Summary A photoredox process has been discovered in the 337 nm pulsed laser photolysis of $\text{Co}(\text{NH}_3)_6^{3+}$ which appears to involve two consecutive single photon absorptions; the process is accounted for by generation of a photoactive, charge-transfer state from absorption by a ligand-field excited state, and has considerable mechanistic significance.

STUDIES of the photochemistry of ammine complexes of cobalt(III) have been numerous and it has been observed that the complexes generally exhibit reasonably efficient photoredox decompositions following excitation of charge-transfer absorption bands, while the lower energy ligand-field absorption bands of the same complexes tend to be photoinsensitive.¹ It has been suggested that this photo-inertness may be the result of an exceptionally efficient non-radiative electronic relaxation of the ligand-field excited states of the cobalt complexes,^{1,2} but this hypothesis has recently been questioned by Kane-Maguire and Langford.³ We now report results of pulsed laser photolyses of $\text{Co}(\text{NH}_3)_6^{3+}$, which include the first biphotonic photochemical processes discovered for transition-metal complexes and which provide an experimental approach for

acquiring information about the lifetime of ligand-field excited states.



SCHEME

A Molelectron transversely excited N_2 gas laser with a nominal output of 300 kW at 3370 Å and a pulse duration of 10 ns was used. Photolyses were performed using a repetition rate of 10 pulses s^{-1} and total photolysis times of about 2 h. Beam intensity was decreased in experimentally determined amounts using stacks of No. 1 Corning microscope cover slides. We were able to decrease beam

intensities over a 3-fold range without suffering severe optical problems. Chemical actinometers and a thermopile system were used to monitor beam intensity.

With a columnated laser beam we found the formation of $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$ to be the predominant photochemical process with ϕ_{aq} ca. 5×10^{-3} and $\phi_{\text{aq}}/\phi_{\text{redox}} > 10^2$, consistent with 365 nm photolyses at lower intensities.⁴ When the laser beam was focused so that the beam waist was approximately 0.5 mm \times 2 mm, inside, and toward the front face of the photolysis cell, the ratio of aquation to redox yields was reversed with the redox yield approaching 10^{-2} and the aquation yield being nearly unchanged. In twenty four experiments using the focused beam, the redox yield was found to decrease dramatically with beam intensity; $\log \phi_{\text{redox}} = (2.0 \pm 0.2) \log I_a + \text{const.}$ (I_a = intensity of absorbed radiation).

Since 337 nm is near the absorption maximum of the $^1T_{2g}$ band of $\text{Co}(\text{NH}_3)_6^{3+}$, the laser photolyses may be described as in the Scheme. LF represents the implicated ligand-field excited state (or states). Clearly the ligand-field excited states must have lifetimes comparable to or greater than the laser pulse (*i.e.*, $\geq 10^{-9}$ s). If (1) has an absorption coefficient comparable to that of $^1A_{1g} \rightarrow \text{CT}$ transitions, then a kinetic treatment implies that the *LF lifetime would be of the order of 10^{-8} s. In addition to providing clear evidence that ligand-field excited states of $\text{Co}(\text{NH}_3)_6^{3+}$ have finite, if short, lifetimes, these studies demonstrate at least for $\text{Co}(\text{NH}_3)_6^{3+}$ that the photoaquation and photoredox modes are uncoupled.

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