Ligand Field Photochemistry of d^6 Complexes. High Yield Photoaquation Mode in $Co(NH_3)_5N_3^{2+}$

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Summary Irradiation of the 520 nm *d-d* absorption band of $Co(NH_3)_5N_3^{2+}$ has been found to result in relatively high ($\phi \simeq 0{\cdot}2$) yields of ammonia aquation with no other primary photoprocess detectable; this contrasts to what is commonly considered to be the general pattern of cobalt(III) photochemistry.

It has been frequently found that cobalt(III) ammine complexes are relatively insensitive to irradiation of their *d-d* type absorption bands.[1,2] There are also few cobalt(III) complexes which are known to luminesce.[1–3] Both these features contrast to the behaviour of many rhodium(III) and chromium(III) complexes and have led Fleischauer *et al.*, to generalize "... that those complexes which undergo moderately efficient photosubstitution reactions in solution at room temperature also produce luminescence of the *d-d* type at low temperature in rigid media, while the complexes that are not photosensitive toward light in the *d-d* bands are also not luminescent."[2]

We have found a notable exception to the presumed general pattern of photochemical behaviour of cobalt(III) complexes: $Co(NH_3)_5N_3^{2+}$ undergoes "moderately efficient" photosubstitution following *d-d* excitation, while $Rh(NH_3)_5N_3^{2+}$ does not. Luminescence has been observed in the latter complex[4] but not the former.[1–3] It is possible that a very low energy luminescence of cobalt(III) ammine complexes might have gone undetected. Nevertheless, our observations constitute an exception to the Fleischauer–Adamson–Sartori "generalization" and suggest that this generalization may not have a secure foundation in fundamental principles.

Our basic photochemical procedures have been described.[5] Ferrioxalate was used as the reference actinometer.

The ligand field photochemistry of $Co(NH_3)_5N_3^{2+}$ is greatly complicated by secondary photolysis[6]† and the reactivity of azidoaquoamminecobalt(III) complexes. Failure to account for these problems apparently accounts for the early report[7] that photoreduction followed ligand field excitation of this complex. In photolyses at 520 nm, carried out to less than 10% conversion into products, we have been unable to detect any cobalt(II) [$\phi(Co^{2+}) < 10^{-3}$] either by colorimetric analysis of the photolyte using ammonium thiocyanate[5,6] or in cation exchange separations of photolysed solutions. These same solutions exhibit a marked increase in pH (initially $3 \leqslant pH < 4$) following photolysis, while changes in absorption spectra vary from negligible (*e.g.* at 301 nm) to appreciate decreases (*e.g.* at 520 nm). In order to identify photolysis products, photolyte solutions were passed through a Sephadex C-5 Cation Exchange resin. The initial effluents from the resin did not contain detectable N_3^- (determined with either Fe_3^+ or Ag^+), but they did contain significant quantities of NH_4^+ (determined by the method of Bolleter *et al.*[8]). Repeated washings of the resin with $0{\cdot}01$ M-$NaClO_4$ separated the complex cobalt(III) reaction product, apparently $Co(NH_3)_4OH_2N_3^{2+}$, from unchanged photolyte; for 520 nm irradiations we found $\phi(NH_3) = 0{\cdot}20 \pm 0{\cdot}05$ and $\phi(N_3^-) < 10^{-3}$.

Similar procedures were used in the case of $Rh(NH_3)_5N_3^{2+}$ and $Co(CN)_5N_3^{3-}$; we found $\phi(N_3^-) = 0{\cdot}025 \pm 0{\cdot}005$ and $0{\cdot}040 \pm 0{\cdot}002$, respectively, for 350—400 nm irradiations, but no detectable NH_3 or CN^- aquation.

It must be pointed out that[1,6] the possibility of ammonia aquation was apparently not investigated in the early photochemical studies[7] of acidopentamminecobalt(III) complexes. Until this reaction mode is explored in an appreci-

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† Similar complications occur in the charge transfer photochemistry of this complex and have been discussed in ref. 6.

able number of complexes it seems premature to infer that cobalt(III) ammine complexes do not exhibit "moderately efficient" photosubstitution reactions in solution at room temperature.[2]

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