

are available as with the ligand π to metal e_g^* states of $\text{Co}(\text{phen})_3^{3+}$ and $\text{Co}(\text{bpy})_3^{3+}$. Both $\text{Co}(\text{NH}_3)_6^{3+}$ and $\text{Co}(\text{en})_3^{3+}$ possess two LF bands. Photoexcitation of either LF band leads to a high degree of DNA cleavage. Clearly neither $\text{Co}(\text{NH}_3)_6^{3+}$ nor $\text{Co}(\text{en})_3^{3+}$ bind to DNA via intercalation. Indeed these complexes are known to maintain intimate hydrogen-bonding interactions with the helix.²³ Again, coupling inefficient photo-reactions to DNA binding of all sorts may yield useful photocleavers. These photoactivated cleavage reactions, in particular those with $\text{Co}(\text{NH}_3)_6^{3+}$, might be helpful in mapping and photofingerprinting experiments.

These results indicate that light-induced cleavage of DNA by a range of d^6 metal complexes can occur from CT, LF, and IL states of simple inorganic complexes, albeit via different mechanisms. Cleavage occurs with complexes having positive charges of either 2+ or 3+. The complexes cleave DNA in spite of possessing different binding modes to the DNA (intercalative, hydrogen bonded, and electrostatic). It may therefore be possible to couple the binding mode of interest with the photoactivated cleavage process of the metal complexes to give a variety of site-specific DNA cleavers. Photoactivated cleavage of DNA with simple coordination complexes may be considered a general phenomenon. Moreover, since these reagents are activated by near-UV and visible light, they may provide useful probes for mapping experiments in vivo.

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Photoaquation of the Iodopentaamminechromium(III) Ion in Acidic Aqueous Solution

Sir:

The acidopentaamminechromium(III) complexes¹⁻⁸ $[\text{Cr}(\text{NH}_3)_5\text{X}]^{2+}$ where $\text{X} = \text{Cl}^-$, Br^- , and F^- , together with some of their analogues containing ethylenediamine in place of four ammonias,⁸⁻¹¹ have figured importantly in studies of ligand lability and stereochemistry of the photosubstitution reactions of d^3 complexes.

For the large majority of such complexes the photochemistry is well accounted for by the angular overlap ligand field model^{12,13} of Vanquickenborne and Ceulemans (hereafter VC). For the fluoro compound particularly the theory gave a better description of the photosubstitution modes than Adamson's rule¹⁴ although

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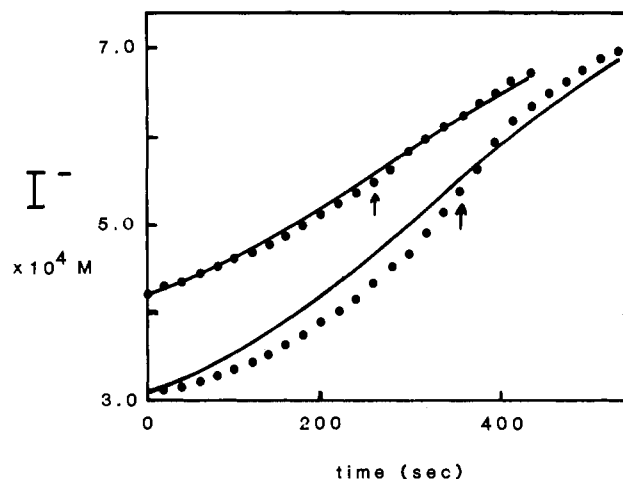


Figure 1. Time dependence of $[\text{I}^-]$ during and after 546-nm photolysis of $[\text{Cr}(\text{NH}_3)_5\text{I}]^{2+}$ in acidic aqueous perchlorate medium at 7 °C: points, experimental data; solid line, theoretical fit (see text). Two data sets are shown corresponding to the best and worst fits found, one displaced 1.2×10^{-4} M upward for clarity. Photolysis begins at zero and ends at the arrow.

the stereochemical results required some extensions.¹⁵ As has been pointed out,¹⁶ the results for the bromo pentaammine compound are somewhat equivocal since the calculated excited-state bond strengths for the Cr-Br and Cr-N bonds are nearly equal, but the molecule efficiently loses mainly ammonia at all wavelengths.

Surprisingly the iodo compound has never been studied photochemically, although it has been reported and its thermal aquation studied polarographically.¹⁷ Probably its lability has deterred photochemical study, the half-life for iodide aquation in 25 °C aqueous solution being only 17 min.

It is important, however, to fill this gap in our knowledge and to take advantage of the potential offered by this molecule to provide a useful test of the VC theory. Using as ligand field parameters, for ammonia, $E_\sigma = 0.7183 \mu\text{m}^{-1}$ and, for iodide, $E_\sigma = 0.4583 \mu\text{m}^{-1}$ and $E_\pi = 0.065 \mu\text{m}^{-1}$, the VC theory predicts, for the 4E_g lowest excited quartet state, bond energies of 0.72, 0.82, and $1.21 \mu\text{m}^{-1}$ for the Cr-I, Cr-NH₃(ax), and Cr-NH₃(eq) bonds, respectively, unambiguously implying dominant photochemical loss of iodide ion in contrast to the Adamson rule prediction of ammonia loss. We have therefore chosen to study this molecule, recognizing that the problems deriving from the thermal lability of the complex would limit the precision of any results and probably obscure beyond recovery the finer details of the wavelength and temperature dependence of the yields as well as the photostereochemistry.

$[\text{Cr}(\text{NH}_3)_5\text{I}]_2$ was prepared as previously described¹⁷ and characterized by its visible spectrum, which showed bands at 532 nm ($38.1 \text{ L mol}^{-1} \text{ cm}^{-1}$) and 472 (36.4), compared with the literature¹⁷ values 530 (40) and 472 (40). Chromium analysis by oxidation with boiling alkaline hydrogen peroxide and spectrophotometric determination of chromate gave $10.3 \pm 0.25\%$ (five runs), consistent with theory, 10.04%.

Irradiation at 8 °C and 546 nm, into the first ligand field quartet band, of 5×10^{-3} M solutions in 1.319×10^{-3} M $\text{HClO}_4/0.04$ M KClO_4 aqueous medium led to a rise in pH, demonstrating photoaquation of ammonia. Reineckate actinometry together with absorbance measurements and standard additions of H^+ determined a quantum yield of 0.28 ± 0.04 (13 runs) for this process. The thermal lability of the compound caused unusually large scatter in these data and, more importantly, precluded reliable

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correction for effects owing to the concomitant thermal formation of $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$. Here the important effect is a reduction of the fraction of light absorbed by the iodo complex, and hence the measured quantum yield should be considered a reliable lower limit. The true value may well be closer to the value of 0.35 common to the chloro² and bromo⁷ analogues.

Loss of iodide was considerably more difficult to follow for several reasons. First, we found it impossible to obtain either the perchlorate or the nitrate salts by reprecipitation techniques owing to the low solubility of the iodide salt and rapid decomposition of the complex ion. Photochemical iodide loss had therefore to be investigated in solutions from which the iodide ion had been removed by anion exchange through a 3 cm long column (perchlorate form of IRA 400 resin, 100 mesh) near 8 °C. This resulted in a solution of ill-defined composition containing the iodo pentaammine and aquo pentaammine ions. Were time now committed to a spectrophotometric determination of the composition, aquation was subsequently so advanced as to preclude useful photochemical measurements. It was best therefore to directly follow the time course of iodide formation at 7 °C before, during, and after irradiation by using a concentration cell with Ag/AgI electrodes. The resulting curves (Figure 1) show three phases: (1) thermal aquation of iodide prior to photolysis; the measured rate constant (7 °C) for our conditions was $1.23 \times 10^{-4} \text{ s}^{-1}$, in good agreement with the value of $1.0 \times 10^{-4} \text{ s}^{-1} \text{ M}$ calculated¹⁸ from k_{298} and $E_{\text{act}} = 21.4 \text{ kcal mol}^{-1}$; (2) release of additional iodide during the irradiation period, leading to upward curvature in the iodide/time plot; (3) thermal release of iodide at an increased but declining rate after photolysis.

These observations show that any photochemical iodide loss is obscured not only by the thermal loss of iodide from the iodo complex but also, and worse, by rapid thermal iodide aquation from the primary photoproduct of the ammonia loss mode, almost certainly *cis*- $[\text{Cr}(\text{NH}_3)_4\text{H}_2\text{O}(\text{I})]^{2+}$. This phenomenon has been observed previously for the chloro compound.^{3,19} To determine any photochemical quantum yield for iodide therefore, the starting concentrations, the absorbances at 546 nm of all species, the rate constants for the significant thermal reactions, and the light intensity and ammonia quantum yield are required. Five of these were unknowns, namely the exact initial concentrations of the iodo and aquo pentaammines, the iodide aquation rate constant and molar absorptivity at 546 nm of the major photoproduct, and the quantum yield for direct photoaquation of iodide.

The approach taken was to use the SIMPLEX method with a least-squares criterion for goodness of fit²⁰ to find the parameters in the differential equations for the main thermal and photochemical processes. These equations are

$$\begin{aligned} d[\text{I}^-]/dt &= k_1[\text{CI}] + k_2[\text{CWI}] + \phi_2 I_a \\ -d[\text{CI}]/dt &= k_1[\text{CI}] + I_a(\phi_1 + \phi_2) \\ d[\text{CWI}]/dt &= \phi_1 I_a - k_2[\text{CWI}] \\ d[\text{CW}]/dt &= k_1[\text{CI}] + \phi_2 I_a \end{aligned}$$

where $[\text{CI}] = [[\text{Cr}(\text{NH}_3)_5\text{I}]^{2+}]$, $[\text{CWI}] = [[\text{Cr}(\text{NH}_3)_4\text{H}_2\text{O}(\text{I})]^{2+}]$, $[\text{CW}] = [[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}]$, and $I_a = I_0 f_{\text{CI}}(1 - 10^{-A_{\text{abs}}})$ with Abs the total absorbance of all species at 546 nm, f_{CI} the fraction of absorbed light absorbed by the iodo compound, k_1 and k_2 the iodide aquation rate constants for CI and CWI, respectively, and ϕ_1 and ϕ_2 the ammonia and iodide quantum yields from CI.

Fortunately not all five unknown parameters had to be varied in an unconstrained way. Initial simulations showed that the results were fairly insensitive to the exact value of $\epsilon_{546}(\text{CWI})$. Therefore, on the basis of comparison with the spectra of $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$ and *cis*- $[\text{Cr}(\text{NH}_3)_4\text{H}_2\text{O}(\text{Cl})]^{2+}$, this unknown was set at $40 \text{ L mol}^{-1} \text{ cm}^{-1}$. Simulations with the remaining four unknowns unconstrained led to negative quantum yields of iodide for all four data sets studied. Best fits with ϕ_2 constrained at 0.0

were superior to those where ϕ_2 was 0.1, consistent with this. Figure 1 shows the experimental points with fits (solid lines) for the best and worst data sets that we examined in detail.

We conclude the following:

(1) For all data sets fits can be found having relative standard deviations of 1–5% and giving consistent and physically reasonable parameters. The deviations from experiment are clearly not random but can be partially explained by hysteresis in the iodide electrode response.

(2) The calculated initial concentrations correspond well to a slightly diluted and partially aquated (10–30%) version of the original solution placed on the ion-exchange column.

(3) The rate constant for iodide loss from the ammonia photoaquation product is $(3 \pm 1) \times 10^{-3} \text{ s}^{-1}$ (four runs), about 30 times that for the iodo pentaammine. This factor compares with a factor of about 100 found for the analogous chloro pentakis(methylamino) compound.¹⁹

(4) The "best fit" quantum yield for iodide photolysis is close to zero.

Our results show that the iodo pentaammine, like the chloro and bromo pentaammines, loses ammonia efficiently on irradiation into the ligand field bands with at most a minor yield of iodide. Its photochemistry is therefore also antithermal, inconsistent with the predictions of the VC theory and consistent with Adamson's simpler rule. In terms of fundamental behavior, however, we do not make much of this last point.

It seems that the excited-state bond strength, assuming the VC calculated values may be relied upon, cannot be the only important factor operating. Many years ago, Manfrin et al. pointed out⁴ that much of Cr(III) photochemistry was consistent with another simple rule, preferential aquation of an uncharged ligand. An enhanced escape rate of the neutral ammonia molecule probably accounts for the deviation of this molecule (and the bromo pentaammine) from the VC theoretical predictions.

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Synthesis and Characterization of Substitution-Inert Cobalt(III) Complexes Containing an *N*-Glycoside Derived from Ethylenediamine and a Monosaccharide (D-Mannose, L-Rhamnose, or D-Ribose)

Sir:

We report the first successful synthesis, isolation, and characterization of substitution-inert cobalt(III) complexes containing an *N*-glycoside derived from ethylenediamine (en) and D-mannose (D-Man), L-rhamnose (L-Rha), and D-ribose (D-Rib), the results of which suggest a novel coordination behavior of sugars.

The interaction of carbohydrates with transition metals is of current interest in coordination chemistry and in bioinorganic chemistry. Despite a wide interest in complexes with sugars, very little is known about the structural details of the complexes.¹ Metal complexes are divided into two classes such as substitution inert and substitution labile on the basis of their chemical properties. Therefore, it is desirable to examine these two types of complexes in order to elucidate the interaction of sugars with metals. Recently, we have extensively investigated the synthesis

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