CN^- ligands leads to a "ring" π molecular orbital.[39]

The spectral difference between the $Cu^{III}(H_{-4}PGGa)^-$ complex and the other deprotonated complexes may be related to interferences of the prolyl ring in forming a N-to-metal π bond. However, if this is the case the effect does not seem to be reflected in the pK_a value for the prolyl complex.

In conclusion, the copper(III) oxidation state facilitates amine deprotonation, indicating very strong Cu(III)–N bonding in which ligand-to-metal π bonding could be important.

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Registry No. $Cu(H_{-3}G_{3a})$, 62801-36-9; $Cu(H_{-3}G_4)^-$, 57692-61-2; $Cu(H_{-3}A_4)^-$, 68628-66-0; $Cu(H_{-3}FGGA)$, 68550-42-5; $Cu(H_{-3}PGGA)$, 24212-63-3; $Cu(H_{-3}G_5)^-$, 68550-43-6; $Cu(H_{-3}G_{4a})^-$, 68550-44-7; $Cu(H_{-3}G_6)^-$, 68550-45-8; $Cu(H_{-3}\text{-}N\text{-}fG_4)$, 68550-46-9; $Cu(H_{-3}\text{-}N\text{-}fG_{3a})$, 68550-47-0; $Cu(H_{-3}\text{-}N\text{-}fG_3)$, 68550-48-1; Cu, 7440-50-8.

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Photoaquation of $[Cr(en)(NH_3)_4]^{3+}$, *cis*- and *trans*-$[Cr(en)_2(NH_3)_2]^{3+}$, and $[Cr(en)_3]^{3+}$. Relative Labilities of Ethylenediamine and Ammonia Ligands

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The total amine aquation yield and the free ammonia yield have been measured for photolysis of $[Cr(en)_x(NH_3)_{6-2x}]^{3+}$ complexes at 366 and 436 nm and at 10 °C in acidic aqueous solutions. For both the bis(ethylenediamine) complexes and the mono(ethylenediamine) complex the ethylenediamine yields were larger than the statistical expectations. The enhancement may involve the steric strain in the ethylenediamine ring; for the bis complexes the rate constant ratio for ethylenediamine to ammonia photoaquation is 2.83, while for the mono(ethylenediamine) complex the analogous ratio is 1.64. The systems provide unequivocal evidence for the importance of factors other than spectroscopic parameters in determining ligand labilities from excited states.

Introduction

Using *trans*-$[Cr(en)_2NH_3X]^{2+}$ compounds as models for the acidopentaamine series, the authors have in recent years carried out experiments[1-3] to try to determine the nature of the excited-state labilizations and ligands lost. Also studies of the wavelength and temperature dependence of these features as a probe of participation in reaction by more than one excited state were undertaken.

Up to this time we have assumed, largely of necessity, that the fact that ethylenediamine and ammonia are closely similar in ligand field spectroscopic parameters[4] gives reason to suppose that they would behave alike as leaving groups in the excited state. This expectation is implied by the currently existing theoretical models of chromium(III) photochemistry.[5,6] There is, however, some reason for uncertainty about this, not so much in regard to the spectroscopic aspect since for ethylenediamine and ammonia the spectroscopic parameters are as well defined as any existing but mainly as a result of the kinetic and structural dissimilarities. As an example, rate constants[7] for amine aquation by ground-state molecules for ethylenediamine complexes are generally greater than for the corresponding ammine complex and appear to arise from smaller activation energies. Also the rate constant for thermal aquation of the first end of an ethylenediamine ligand is larger than that for the second end, possibly due to steric strain in the five-membered chelate ring.

Unfortunately, photochemical evidence is difficult to obtain; comparisons of quantum yields for different molecules cannot be used reliably as a measure of relative leaving-group abilities because of the different excited-state lifetimes and properties

Table I. Quantum Yields for Proton Uptake and Percentage Ammonia Aquation from $[Cr(en)_x(NH_3)_{6-2x}]^{3+}$

compd	$\phi(H^+, 365\ nm)$[a]	$\phi(H^+, 436\ nm)$	% NH_3(365 nm)	% NH_3(436 nm)
$[Cr(en)_3]^{3+}$	0.33 ± 0.01 (5)	0.38 ± 0.02 (2)		
cis-$[Cr(en)_2(NH_3)_2]^{3+}$	0.44_4 ± 0.010 (3)	0.46_5 ± 0.014 (4)	15 ± 3 (2)	19 ± 4 (4)
trans-$[Cr(en)_2(NH_3)_2]^{3+}$	0.45_7 ± 0.010 (3)	0.46_9 ± 0.029 (5)	13 ± 2 (2)	13 ± 4 (4)
$[Cr(en)(NH_3)_4]^{3+}$	0.43_0 ± 0.006 (3)	0.44_1 ± 0.012 (4)	50 ± 1 (2)	59 ± 1 (2)
$[Cr(NH_3)_6]^{3+}$	0.45_5 ± 0.019 (6)	0.48_3 ± 0.012 (5)	102 (2)	105 (2)

[a] The results are in the form $\phi \pm x\ (y)$, where x is the standard deviation and y is the number of experiments. Where $y \leqslant 3$, a better indicator of the probable error would be the pooled standard deviation of 0.022 for the quantum yields and 3.0 for the ammonia percentages.

and possible photophysical complications. Thus, although for ground-state molecules ethylenediamine aquates more readily, for $[Cr(en)_3]^{3+}$ the quantum yield of aquation is 0.37,[8] smaller than for $[Cr(NH_3)_6]^{3+}$ where it is 0.51.[9] Furthermore, the two complexes differ in emission properties and show different degrees of quenching of photoreaction,[9,10] both indicative of different excited-state properties in the two molecules.

As reported earlier, *trans*- and *cis*-$[Cr(en)_2(NH_3)_2]^{3+}$ and $[Cr(en)(NH_3)_4]^{3+}$ have now been prepared.[11] These molecules present an opportunity to compare the competitive loss of ethylenediamine and ammonia from the same excited state. This paper reports a study of their photochemistry, undertaken to shed some light on these questions. A second, equally important reason for the study was to clarify the interpretation of the data on *trans*-$[Cr(en)_2NH_3X]^{2+}$, by removing the uncertainty due to the assumption of equivalent behavior of ethylenediamine and ammonia as leaving groups. In addition, the molecules form a useful fundamental test of the purely spectroscopic theories of Cr(III) photochemistry.

Experimental Section

The compounds were prepared and characterized as previously described.[11]

The photolysis apparatus and procedures were as previously described except that a 1-kW AH-6, water-cooled capillary mercury arc (Illumination Industries) was used as the light source, rendered monochromatic using Balzer's interference filters (Rolyn Corp.) for the appropriate mercury lines.

Light fluxes were measured using ferrioxalate[12] and reineckate[13] actinometry and, as a check, the light intensity was continuously monitored with a Philips 150 CV phototube.

All solutions photolyzed were 10^{-2} M in complex and 10^{-3} M in $HClO_4$ with 0.10 M $KClO_4$ to maintain constant ionic strength.

Total amine release was measured by proton uptake using the ΔpH method,[14] while ammonia was determined by separating free ammonium ion from the complex and its photolysis products using a short (2 cm × 0.8 cm diameter) column of Baker Analyzed CGC 241 cation-exchange resin eluted with 15 mL of 0.8 M sodium chloride solution. The eluent was titrated with bromine coulometrically[15,16] to determine NH_4^+, using a pretitrated buffer to minimize the blank corrections. Blanks and the calibration curve for the method were drawn up using an identical chromatographic procedure and standard additions were used occasionally as a check. That free ethylenediamine did not interfere in the method was proved experimentally by standard addition. The linear calibration curve had a slope of 1.049 ± 0.0058 times the Faraday's law value of $3 \times 96\,487$ C mol^{-1} and the blank corresponded to about 0.22 μmol of ammonia.

Results

Photolyses were carried out at 365 and 436 nm and at a temperature of 10 °C to minimize thermal reactions. It was noted that, whereas $[Cr(en)(NH_3)_4]^{3+}$ was quite stable thermally, *cis*-$[Cr(en)_2(NH_3)_2]^{3+}$ and particularly *trans*-$[Cr(en)_2(NH_3)_2]^{3+}$ lost ammonia much more rapidly. Approximate rate constants at 10 °C were 3.4×10^{-6} and 1.6×10^{-5} s^{-1}, respectively. In the last example the rate constant was also measured by direct ammonia analysis, giving a value of 1.38×10^{-5} s^{-1}, suggesting that 90% of the aquation is due to loss of ammonia. Both the differences in lability between the bis- and mono(ethylenediamine) complexes and the readier ammonia labilization we found surprising, but we have not pursued the results further. Thermal corrections were applied by monitoring pH continuously and measuring ΔpH for photolysis from the extrapolated pH value for thermal reaction alone. This is an acceptable procedure for the small conversions of 2–6% conversion maintained throughout the work, and significant correction occurred only for *trans*-$[Cr(en)_2(NH_3)_2]^{3+}$. Since low conversions were used, corrections for secondary photolysis were negligible for the photolysis wavelengths used.

As a check on the procedures and precision of the determinations, data were also obtained for $[Cr(en)_3]^{3+}$ and $[Cr(NH_3)_6]^{3+}$ and are included along with the other data in Table I. The results for $[Cr(en)_3]^{3+}$ and $[Cr(NH_3)_6]^{3+}$ are in good agreement with the literature[8,9] although our results for the former complex differ somewhat from the published value of 0.37 at both wavelengths. The results for $[Cr(NH_3)_6]^{3+}$ are a good test of the precision of the data since the pH method and direct ammonia analysis should give the same quantum yield. The figures of 102 and 105% ammonia aquation at 366 and 436 nm show that the ammonia determination may overestimate by a few percent but the agreement is otherwise good. We have earlier noted[2] that the coulometric method tends to give high results as a result of slight contamination by oxidizable impurities. The data for the intermediate complexes show that, within experimental error, there is no difference in overall quantum yield for the three compounds and no variation with wavelength of the overall quantum yield. For $[Cr(en)_2(NH_3)_2]^{3+}$ the observed variation of percent ammonia with wavelength is on the margin of significance and may not be real. Our efforts to reduce the variability further to explore any possible wavelength dependence of quantum yield ratios were not successful.

Discussion

From the spectroscopic point of view ethylenediamine and ammonia are extremely similar ligands; Perumareddi[4] gives Dq(en) = 2185 cm^{-1} and $Dq(NH_3)$ = 2155 cm^{-1}, only a 1.5% difference, while Vanquickenborne and Ceulemans[5] set both ligands at $Dq = 2188$, $\epsilon_\pi = 0$ and $\epsilon_\sigma = 7183$ cm^{-1}. This approximation will be accepted for now and the changes expected if it is not valid will be discussed later.

On this basis the spectroscopically based theories of Cr(III) photochemistry predict that $[Cr(en)(NH_3)_4]^{3+}$ will lose 67% ammonia and *cis*- and *trans*-$[Cr(en)_2(NH_3)_2]^{3+}$ will lose 33% ammonia. The data reveal this not to be so; the former complex loses only about 55% ammonia while the latter complexes lose about 15% ammonia, being equal within experimental error. Note also that despite the higher quantum yields of the ammonia-containing compounds, it is the ammonia yield that is depressed compared to that of theory.

These departures from theory almost certainly reflect enhanced yields of ethylenediamine rather than depressed yields of ammonia. Also they do not arise from the assumption of equal σ- and π-donor strengths for ethylenediamine and ammonia. Taking account of the slightly larger ϵ_σ value for ethylenediamine would, according to theory, lead to greater than 67% ammonia aquation for $[Cr(en)(NH_3)_4]^{3+}$, greater than 33% ammonia for *trans*-$[Cr(en)_2(NH_3)_2]^{3+}$, and less than 33% ammonia for *cis*-$[Cr(en)_2(NH_3)_2]^{3+}$. The first two predictions are in the opposite sense to the observations, and the sequence for *cis*- and *trans*-$[Cr(en)_2(NH_3)_2]^{3+}$ is reversed. The observed preferences for ethylenediamine loss therefore do not seem in any way related to the small difference in σ-donor ability of the two ligands.

The kinetic evidence for more facile ethylenediamine aquation cited in the Introduction is indicative that the enhanced ethylenediamine aquation may involve steric effects. Consistent with this is the observation that the enhancement of ethylenediamine loss is greater in the bis complexes than in the mono(ethylenediamine) complex. For these two types of complex, respectively, $\phi_{NH_3}/\phi_{total} = k_{NH_3}/(k_{NH_3} + 2k_{en})$ and $\phi_{NH_3}/\phi_{total} = 2k'_{NH_3}/(2k'_{NH_3} + k'_{en})$. Here the k_i represent the rate constants for photoaquation of the ligand i from the excited state of *cis*- or *trans*-$[Cr(en)_2(NH_3)_2]^{3+}$ and k'_i are the analogous constants for $[Cr(en)(NH_3)_4]^{3+}$. Thus $k_{en} = 2.83k_{NH_3}$ and $k'_{en} = 1.64k'_{NH_3}$, respectively. These rate constant ratios reveal an almost threefold increase in k_{en} in the bis complexes in contrast to a 65% increase in the mono(ethylenediamine) complex. This is the type of result to be expected if the ethylenediamine chelate ring "bite" is such as to distort the chromium(III) octahedral environment and if the strain of two such rings is multiplicative in nature.

These results imply important consequences for the purely spectroscopic/theoretical models of photochemistry of complex ions. It must be emphasized that the observed results cannot be consistently related to any differences in the spectroscopic parameters for ethylenediamine and ammonia nor to any uncertainties in the σ- and π-donor strengths or the ligand field parameters. The absence of significant wavelength dependence also eliminates complications due to participation of different excited states yielding different percentages of ammonia. The results reflect pure differences in the relative leaving-group tendencies of ethylenediamine and ammonia from the respective participating excited states and are nonspectroscopic in origin. The results are therefore a clear experimental demonstration of the usual caution[5] that a number of other factors, in this case probably steric effects, which may not show up to any great extent in the ligand field spectra or their derived parameters, can have an important role in determining the detail of quantum yields for a given complex or series of complexes.

While the authors remain convinced that the spectroscopically based theories are an extremely useful and helpful guide for the experimental photochemist and also have played and are still playing a crucial role in stimulating important experimental work, this study demonstrates the need to take the cautionary warnings seriously and avoid being misled by theoretical predictions.

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Registry No. $[Cr(en)_3]^{3+}$, 15276-13-8; *cis*-$[Cr(en)_2(NH_3)_2]^{3+}$, 66008-05-7; *trans*-$[Cr(en)_2(NH_3)_2]^{3+}$, 65982-64-1; $[Cr(en)(NH_3)_4]^{3+}$, 65982-66-3; $[Cr(NH_3)_6]^{3+}$, 14695-96-6.

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Photoinduced Oxygenation of *trans*-Aquohydridotetraamminerhodium(III). Evidence for a Transition-Metal Chain Carrier[1a]

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Ultraviolet excitations of aerated, acidic aqueous solutions of $Rh(NH_3)_4(OH_2)H^{2+}$ result in the efficient formation of $Rh(NH_3)_4(OH_2)O_2H^{2+}$. The rate of formation of hydroperoxide was found to be zero order in O_2 but first order in both substrate concentration and incident light intensity. The photoinitiated thermal reaction appears to be a chain reaction with $Rh(NH_3)_4{}^{2+}(aq)$ acting as a chain carrier which "activates" O_2 by coordination. The hydroperoxo complex decomposes very slowly, even in the presence of excess $Rh(NH_3)_4(OH_2)H^{2+}$, to form a colored, paramagnetic species identified as a superoxo complex.

Introduction

Complexes between hydrogen and transition-metal complexes have been of long and continuing interest. Early interest in these systems originated from the search for effective homogeneous hydrogenation catalysts.[2] Some of the more current interest derives from suggestions that hydrido complexes would be useful in cycles involving the photochemical cleavage of water.[3-5]

Hydridocobalamin[6-8] and hydridopentacyanocobaltates[9] are known but are very reactive species. These and some related hydrido complexes of cobalt(III) tend to be very labile substrates, unstable toward H^+ [6,10,11] and O_2.[6,12] As a consequence, it is very difficult to characterize them or to quantitatively investigate their solution behavior.[10]

The hydrido complexes of rhodium have been reported to be much less reactive than their cobalt analogues and they have