

Wavelength Dependence over the Envelope of a Single Electronic Band in the Photochemistry of the Penta-amminechlorocobalt(III) Ion

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The quantum yields for the aquation of the title ion with loss of chloride or ammonia decrease monotonically across the envelope of the first spin allowed ligand field electronic band indicating competition of intersystem crossing or reactive processes with vibrational relaxation; since the curves for chloride loss and ammonia loss intersect, three potential surfaces are invoked in the interpretation.

Several recent reports have presented evidence that the photochemistry of transition metal complexes may be determined by 'prompt' processes which occur in competition with vibrational relaxation.¹ The present communication extends the evidence to ligand substitution photochemistry of a Co^{III} complex. It may be of interest to comment on the reason why such 'prompt' processes are so common in transition metal photochemistry in sharp contrast with organic photochemistry in the near u.v. or visible regions. The most obvious difference is the distribution of excited states. In the title ion there are two spin allowed bands in the visible which may be assigned to the states ${}^1\text{T}_{1g}$ and ${}^1\text{T}_{2g}$ in octahedral symmetry. Each has a corresponding triplet and these four states split to eight in the C_{4v} symmetry of the title ion. These eight closely spaced states arise from promotion of a single electron from the ground state ${}^1\text{A}_{1g}$ of the low spin d^6 configuration. The promotion of two electrons leads to a quintet which is also close. Thus, nine first-order electronic potential surfaces probably interact in a fairly narrow region and, in addition, the Laporte forbidden ligand field transitions gain intensity by vibronic mechanisms. The nuclei are set in motion by the primary photon absorption.²

The title ion, $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$, was prepared as the nitrate and purified by well-known methods.³ Its extinction coefficient at 532 nm is $51.7 \text{ l mol}^{-1} \text{ cm}^{-1}$. Irradiations were carried out in solutions at pH 2 prepared with perchloric acid and distilled deionized water. Ammonia yields were estimated by the ' ΔpH ' method⁴ and Cl^- release was followed by titration with $\text{Hg}(\text{NO}_3)_2$ after passing through a cation exchange column. Conversions were $<5\%$. The study of quantum yield variation over narrow wavelength ranges depends on the high resolution of laser sources. The source at 488 and 514 nm was a Coherent Radiation 6W Ar-ion laser. For experiments at 570–620 nm a Coherent 590 dye laser was used with rhodamine 6G pumped by the Ar-ion laser. Laser power was measured with a Coherent power meter calibrated against the Reineckate chemical actinometer as described recently.⁵ The absorbed light intensity was obtained by making readings before and after the 10 cm path absorption cell, which was thermostatted at 25°C , and comparing the readings for the reaction solution with those for the same cell filled with pure water. Calibration of the actinometry is given in detail elsewhere.⁵ Results of a number of runs at each wavelength are given in Table 1 and represented in Figure 1. The results at 488

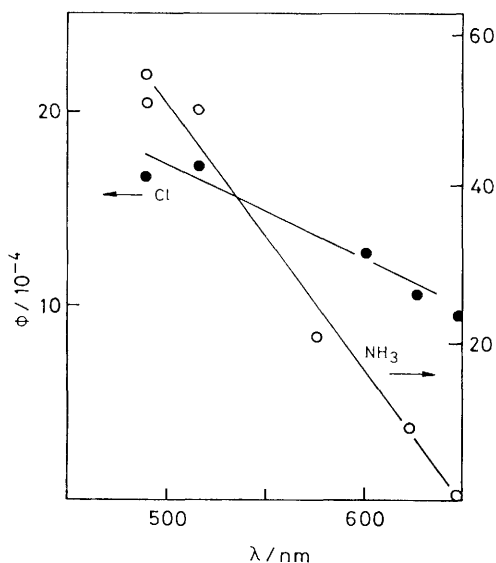


Figure 1. Quantum yields for photochemical ligand substitution vs. wavelength. Left axis and filled circles refer to chloride loss; right axis and open circles refer to ammonia loss.

Table 1. Quantum yields for photochemical ligand substitution of $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ at 25 °C.^a

Wavelength/ nm	Ligand substituted	Laser power/ mW ^b	Quantum yield/ 10 ⁻⁴
488	Cl ⁻	200	16.7 ± 0.5
	NH ₃		17.1 ± 1.2 ⁷
514	Cl ⁻	200	55 ± 2.6
	NH ₃		51 ± 1.3 ⁷
573	Cl ⁻	200	17.2 ± 1.0 ⁶
600	NH ₃	125	20.9 ± 2.4
	Cl ⁻		12.8 ± 0.9
622	NH ₃	80	23.6 ± 0.9
	Cl ⁻		10.9 ± 1.0
647	NH ₃	80	9.1 ± 0.6
	Cl ⁻		9.6 ⁹
	NH ₃		1.3 ⁹

^a Each number reported is the average of 3–4 runs using a complex concentration of 4.2×10^{-3} M. Concentrations of complex up to 7×10^{-3} M were studied and revealed no concentration dependence. ^b Power dissipated in the cell by absorption and losses.

and 514 nm are in good agreement with earlier reports.^{6,7} The results extrapolate satisfactorily to those reported for 647 nm from Kr-ion laser irradiation.⁷

The wavelength 647 nm was associated in ref. 7 with the triplet absorption region. We see that neither reaction can be exclusively associated with intersystem crossing to the triplet state which absorbs at 647 nm since absorption into the singlet gives a higher yield for both reactions. Moreover, the path for ammonia aquation cannot be entirely the same as that for chloride aquation since the yield for chloride aquation is lower in the singlet region but higher in the triplet region. This implies the involvement of a minimum of one other state in addition to the singlet and triplet. Candidates include the ground state surface (hot ground state reaction) and the quintet. The wavelength dependence reported here shows that the crossing processes among these states in the case of both reactions are prompt and occur *in competition with vibrational relaxation in the original singlet manifold*. Once this dependence on the initial degree of vibronic excitation is realized, it is clear that there is nothing in the results to exclude production of primary products with varying efficiency as a function of initial vibronic state. This is known as state specific chemistry.

The results presented here are the first example of two reaction pathways whose yields vary across a single absorption band in a way which may be differentiated. This emphasizes the role of processes in competition with vibrational relaxation with an insistence beyond that of previous examples.

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