The 2537Å Photolysis of Co(NH₃)₅Cl²⁺ in Aqueous Solution: Products

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Balzani and his co-workers[1] have reported that u.v. photolysis of acidified solutions of $Co(NH_3)_5Cl^{2+}$ quantitatively releases into solution 5·0 moles of co-ordinated NH_3 for every g.-ion of Co^{2+} formed. They have also tentatively identified $Co(NH_3)_4(OH_2)Cl^{2+}$ by spectrophotometric methods as a minor photolysis product. Two of us[2] found earlier that Cl^- and Co^{2+} are quantitatively recovered after photolysis. Because the oxidation product has never been reported, we have re-examined the reaction.

We have confirmed the previous observation[2] that Co^{2+} and Cl^- are produced in a 1 : 1 ratio (see Table 1) indicating that photoaquation of Cl^- is not an important process and that oxidation of Cl^- does not occur. After complete photolysis, NH_4^+ was the only other product detected in solution.

G.l.c. and mass spectrometric analysis of the evolved gases showed N_2 and N_2O to be products of the photolysis. Quantitative analysis on a 5Å molecular-sieve column gave

the results in Table 2. The yield of N_2O was low and near the limits of detection. By the use of $^{15}NH_4Cl$ or co-ordinated $^{15}NH_3$, we have identified the origin of the N_2 as

TABLE 1

Co²⁺ yield (10⁻³ M)	Cl⁻ yield (10⁻³ M)
1·17 (±0·02)	1·10 (±0·02)
1·80	1·65
2·42	2·25
3·08	3·14
5·20ᵃ	5·29ᵃ

ᵃ Complete photodecomposition when $[Co(NH_3)_5Cl^{2+}] = 5·28 \times 10^{-3}$ M.

being primarily from the NH_4^+ in the bulk solution whereas the N_2O arises primarily from the co-ordinated NH_3. The use of $^{36}Cl^-$ in the bulk solution has shown that photolysis

TABLE 2

Contents of solution[a]			N$_2$ Yield[b]	N$_2$O Yield[c]
0·1M-HClO$_4$	..	..	..	0·2	0·03—0·05
0·1M-HClO$_4$, 0·1M-NH$_4$ClO$_4$	..	0·2	0·03—0·05
0·1M-HClO$_4$, 0·1M-KCl ..	..	0·4	0·03—0·05
0·1M-HClO$_4$, 0·1M-NH$_4$Cl	..	0·8	0·03—0·05
0·01M-HClO$_4$	..	..	..	0·1	0·1

[a] $[Co(NH_3)_5Cl^{2+}] = 5·0 \times 10^{-3}$ M.

[b] In equivalents relative to Co^{2+} yield; 1 mole N$_2$ = 6 equivalents.

[c] In equivalents relative to Co^{2+} yield; 1 mole N$_2$O = 4 equivalents.

results in no appreciable inclusion of radioactivity in the substrate Co(NH$_3$)$_5$Cl^{2+}.

The apparent discrepency between our results and those of Balzani[1] is easily reconciled when it is realized that even quantitative formation of N$_2$ would account for only 6·7% of the NH$_3$ bound to the metal centre. They estimated their accuracy in the NH$_3$ determination to be about 5%. The formation of N$_2$ and N$_2$O must be taken into account in the formulation of the reaction mechanism.

[1] L. Moggi, N. Sabbatini, and V. Balzani, Gazzetta, 1967, 97, 980; V. Balzani, L. Moggi, F. Scandola, and V. Caressiti, Inorg. Chem. Acta Rev., 1967, 1, 7.

[2] J. F. Endicott and M. Z. Hoffman, J. Amer. Chem. Soc., 1965, 87, 3348.