Solid-state Photochemical and Energy-transfer Processes in Some Hexa-amminechromium(III) Salts

By **C. D. Flint,* P. Greenough, and A. P. Matthews,** Department of Chemistry, Birkbeck College, Malet Street, London WC1E 7HX

Irradiation of $Cr(NH_3)_6ZnCl_4,X$ ($X = NO_3^-$ and Cl^-) and $Cr(NH_3)_6X_3$ ($X = NO_3^-$, Cl^-, Br^-, and I^-) at 366, 404, and 436 nm resulted in their partial conversion into the penta-ammine species $Cr(NH_3)_5X^{3+}$. Rise-time and decay-curve measurements indicate that efficient non-radiative energy transfer from the hexa-ammine to the penta-ammine ion occurs.

HEXA-AMMINECHROMIUM(III) salts show a variety of luminescence and photochemical behaviour. Of the salts studied,[1] the perchlorate and hexafluorophosphate are most resistant to photodecomposition and, since the Cr^{3+} ions occupy sites of O_h symmetry, these compounds give readily assignable luminescence spectra.[1,2] Other salts [*e.g.*, $Co(CN)_6^{3-}$ and $CdCl_5^{3-}$] have comparable photochemical stability but the lower symmetry of the Cr^{3+} sites result in more complex luminescence spectra.[3] With salts of smaller anions which are better ligands towards class A metals, photochemically induced replacement of one of the ammine groups by the anion occurs. In general, the weaker average ligand field, the ligand field asymmetry, and the greater reduction of the effective electron–electron repulsion parameters in the penta-ammine photoproducts result in their having ^2E (O) states several hundred wavenumbers lower than the ^2E state of the hexa-ammine. The overlap of the $^2E \rightarrow {}^4A$ emission of the hexa-ammine and of the $^4A \rightarrow {}^2E$ absorption spectra of the penta-ammine[4,5] allows efficient non-radiative energy transfer.[6] Thus a small quantity of the photoproduct may dominate the observed luminescence from partly decomposed hexa-amminechromium(III) salts. We now report the photodecomposition and reactant-to-product energy transfer in six compounds where the rates of the photochemical and photophysical processes are convenient for study.

EXPERIMENTAL

Materials.—$Cr(NH_3)_6X_3$ ($X = NO_3^-$, Cl^-, Br^-, and I^-) were prepared by standard methods.[7] $Cr(NH_3)_6ZnCl_4,X$ ($X = Cl^-$ and NO_3^-) were prepared by methods similar to those used for the analogous Co^{III} compounds.[8] All *salts* were prepared in subdued light below 300 K. [Found for $Cr(NH_3)_6ZnCl_4,Cl$: H, 4·6; N, 21·25; Cl, 44·6. $H_{18}N_6Cl_5$-CrZn requires H, 4·6; N, 21·20; Cl, 44·6%. Found for $Cr(NH_3)ZnCl_4,NO_3$: H, 4·30; N, 23·2; Cl, 33·5; Cr, 12·35. $H_{18}N_7O_3Cl_4CrZn$ requires H, 4·30; N, 23·2; Cl, 33·5; Cr, 12·3%].

Instrumental.—Luminescence spectra and some of the rise and decay curves were measured on microcrystalline samples with the apparatus described[9] but fitted with an EMI 9558 QA photomultiplier (S20). For the other rise–decay curves the xenon flash tube was replaced by the 530 nm radiation from a high repetition rate, *Q*-switched, frequency-doubled Nd–YAG laser (Laser Associates Model 252A). The much higher output of the laser (up to 20 mJ per pulse at 20 Hz) greatly facilitated the measurements. The relative output in quantum units of the HBO arc–monochromator–filter combination as measured by a thermopile was 1·0 at 366 nm and 1·5 at 436 nm.

RESULTS AND DISCUSSION

The 366, 404, and 436 nm excited luminescence spectra of $Cr(NH_3)_6X_3$ ($X = NO_3^-$, Cl^-, Br^-, and I^-) and $Cr(NH_3)_6ZnCl_4,X$ ($X = NO_3^-$ and Cl^-) at 300 and 80 K were initially similar to those of salts containing the $Cr(NH_3)_6^{3+}$ ion in cubic environments.[2] However in each of these compounds the O'–O line is stronger, owing to the lack of inversion symmetry at the Cr^{3+} sites[10] permitting the transitions to become electric dipole-allowed. For each compound the intensity of the luminescence slowly decreased during excitation at 300 K but no new band appeared. Excitation at 80 K resulted in a similar decrease in the intensities of the hexa-ammine bands but new bands appeared which steadily increased in intensity (Figures 1 and 2). The positions and relative intensities of these new bands correspond to those of the most intense emission maxima of the penta-ammine ion, $Cr(NH_3)_5X^{2+}$. The 300 K luminescence of compounds containing the $Cr(NH_3)_5X^{2+}$ ion is very weak[5,6] and observation of luminescence from the penta-ammine photoproduct is not expected at this temperature. For the $Cr(NH_3)_6X_3$ salts the rates of growth of the penta-ammine bands increased along the series $NO_3^- < I^- < Br^- < Cl^-$. The rate of photodecomposition is expected to depend on the metal–ligand bond strength and the mobility of the anion, the latter quantity being inversely related to the size of the anion.[10] Both factors suggest the experimentally observed order. This agreement is, however, partly fortuitous since the apparent rate of product of the penta-ammine depends on the efficiency of energy transfer and the relative luminescence efficiency of the hexa-ammine and penta-ammine ions in the compounds in

---

[1] C. D. Flint and P. Greenough, *J.C.S. Faraday II*, 1972, **68**, 897.

[2] C. D. Flint, *J. Mol. Spectroscopy*, 1971, **37**, 414.

[3] C. D. Flint, P. Greenough, and A. P. Matthews, *J.C.S. Faraday II*, 1973, **69**, 23.

[4] W. N. Shepard and L. S. Forster, *Theoret. Chim. Acta*, 1971, **20**, 135.

[5] C. D. Flint and A. P. Matthews, *J.C.S. Faraday II*, in the press.

[6] C. D. Flint and A. P. Matthews, *Chem. Comm.*, 1971, 954.

[7] A. L. Oppegard and J. C. Bailar, jun., *Inorg. Synth.*, 1950, **3**, 153.

[8] M. Mori, Y. Saito, and T. Watanabe, *Bull. Chem. Soc. Japan*, 1961, **34**, 295.

[9] C. D. Flint and P. Greenough, *J. Chem. Phys.*, 1972, **56**, 5771.

[10] D. Klein, C. W. Moeller, R. Ward, *J. Amer. Chem. Soc.*, 1958, **80**, 265.

addition to the rate of photosubstitution. With 436 nm irradiation the penta-ammine emission appears more rapidly for $Cr(NH_3)_6ZnCl_4,NO_3$ than for $Cr(NH_3)_6ZnCl_4,Cl$. The latter compound is also unusual in that the rate of substitution is more rapid with 366 nm irradiation than with 436 nm irradiation, although both wavelengths are *ca.* 80% absorbed by the compounds and the intensity of the 366 nm source is lower than that of the 436 nm source (see Experimental section). The relative rates of photosubstitution of the other compounds with 436 and 366 nm radiation are approximately proportional to the intensities of the sources as expected if the reaction occurs from the ^2E state.

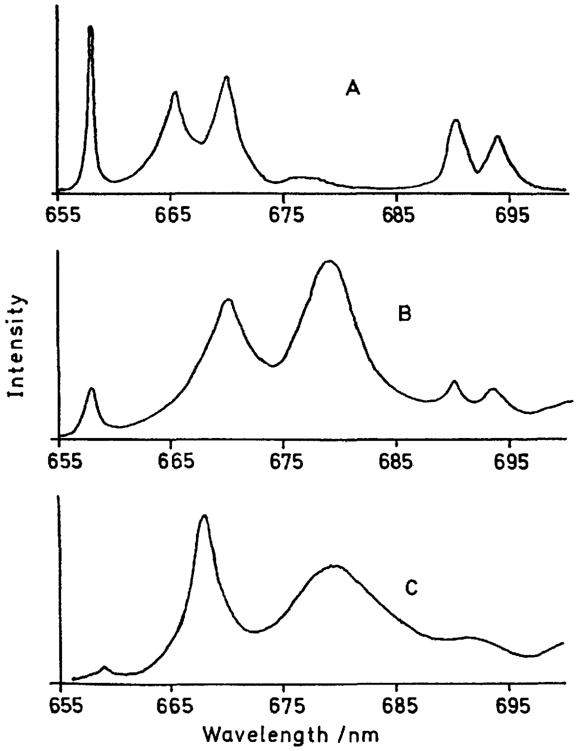

FIGURE 1 Emission spectra at 80 K of A, $Cr(NH_3)_6(NO_3)_3$; B, partially photodecomposed $Cr(NH_3)_6(NO_3)_3$; and C, $[Cr(NH_3)_5ONO_2](NO_3)_2$

The 530 nm excited 80 K luminescence decay curves of the pure compounds were approximately exponential and independent of the wavelength of observation (Table).

Decay half-lives ($t_{\frac{1}{2}}$) of the $^2E \rightarrow {}^4A$ emission from hexa-ammine salts at 80 K

Compound	$t_{\frac{1}{2}}/\mu s$
$Cr(NH_3)_6ZnCl_4,Cl$	50
$Cr(NH_3)_6ZnCl_4,NO_3$	50
$Cr(NH_3)_6I_3$	38
$Cr(NH_3)_6Br_3$	34
$Cr(NH_3)_6Cl_3$	24
$Cr(NH_3)_6(NO_3)_3$	22

After photodecomposition the half-life of the hexa-ammine emission is reduced to about two-thirds of its initial value and becomes non-exponential. The emission of the penta-ammine photoproduct has a slow rise-time and a non-exponential decay. The rise-times are at least one order of magnitude longer than the rise-time of the pure penta-ammine and indicate that the ^2E state of the penta-ammine is populated from the ^2E state of the hexa-ammine ion, this being the only available state with a sufficiently long lifetime. If it is assumed that the processes populating the ^2E state of the hexa-ammine ions are fast, the intensity of the penta-ammine emission from a given hexa-ammine–penta-ammine pair is given by equation (1) and that of the

$$I_p = I' [\exp(-k_2t) - \exp(-k_1t)] \qquad (1)$$

hexa-ammine emission by equation (2), where k_1 is the

$$I_h = I_0 \exp(-k_1t) \qquad (2)$$

sum of the rate constants governing relaxation of the hexa-ammine species (including the hexa-ammine to penta-ammine energy transfer constant) and k_2 is the sum of the rate constants describing relaxation of the penta-ammine species. The non-exponential decay of the hexa-ammine and penta-ammine emissions, the difficulty of choosing wavelengths of observation where the two emissions can be measured separately, and the probability that k_1 will vary from pair to pair prevents the evaluation of rate constants for the various photophysical processes. Moreover the rate constants are

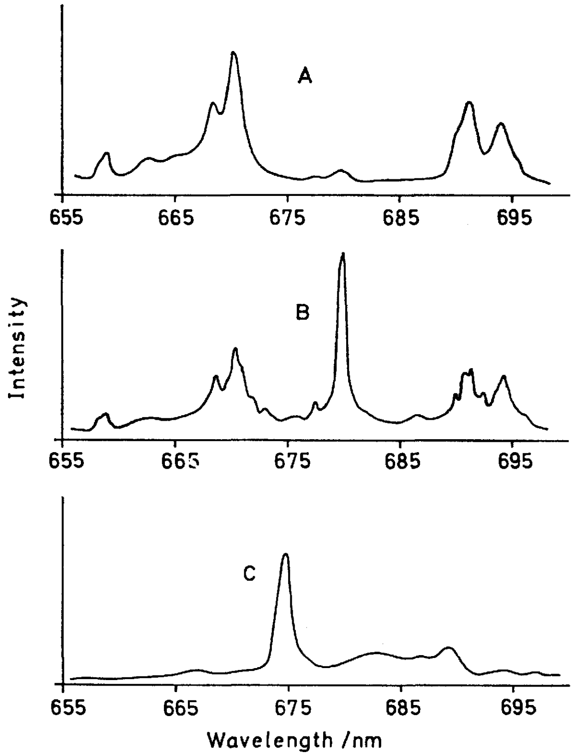

FIGURE 2 Emission spectra at 80 K of A, $Cr(NH_3)_6ZnCl_4,Cl$; B, partially photodecomposed $Cr(NH_3)_6ZnCl_4,Cl$; and C, $[Cr(NH_3)_5Cl]Cl_2$. The displacement of the penta-ammine emission maxima in C relative to B is due to the different anion

dependent on the extent of the photodecomposition. For these reasons we can quote only typical experimental data. The results obtained for two of the compounds are given in Figures 3 and 4. The behaviour of the other compounds is qualitatively similar. The measurements indicate that the effective rate constant governing the penta-ammine rise is several times greater than the mean rate constant describing the hexa-ammine emission in the photodecomposed compounds. Comparison with equations (1) and (2) indicates that hexa-ammine ions close to penta-ammine ions have k_1 at least several times larger than other hexa-ammine ions, probably owing to the energy-transfer rate constant dominating k_1. The rate of hexa-ammine to hexa-ammine transfer must be slow enough for the differences between the hexa-ammine ions not to be averaged out. This slow hexa-ammine to hexa-ammine transfer is also responsible for the non-exponential hexa-ammine decay in the photodecomposed compounds. Examination of each sample after irradiation indicated the presence of an appreciable concentration of the (red) penta-ammine species in the surface layer.

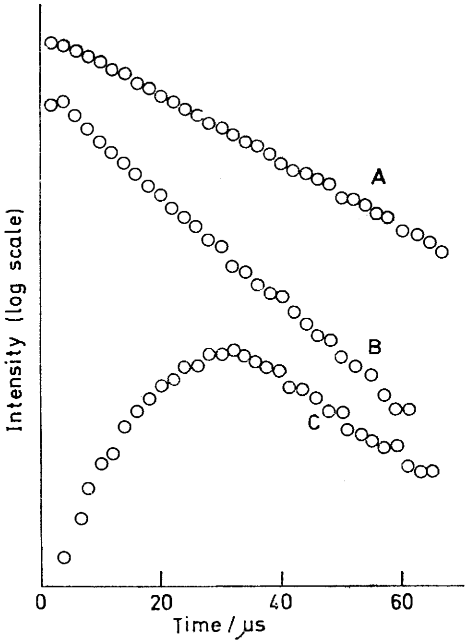

FIGURE 3 Decay curves at 80 K for $Cr(NH_3)(NO_3)_3$; A, pure; B, partially photodecomposed; hexa-ammine emission at 658 nm; and C, partially photodecomposed; penta-amine emission at 679 nm

Comparison for these compounds with the observed hexa-ammine to chloropenta-ammine energy transfer in $Cr(NH_3)_6(ClO_4)_3$ is of interest. In that system the charge inbalance is most probably made up by an anion vacancy. In the compounds studied here, the photoproduced anion vacancy may be occupied, at least initially, by an ammonia molecule. It is probable that photoproduction of the penta-ammine species causes a greater disruption of the lattice than its incorporation by co-precipitation and this may account for the relative inefficiency of hexa-ammine to hexa-ammine transfer in these compounds. Alternatively, the cubic lattice of $Cr(NH_3)_6(ClO_4)_3$ may be particularly favourable for excitation transfer.

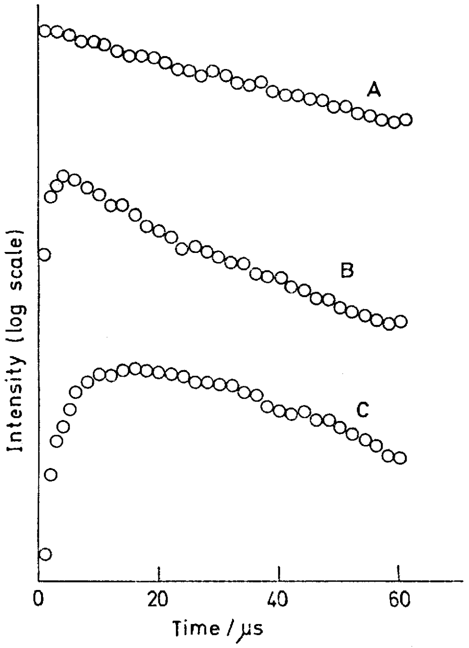

FIGURE 4 Decay curves at 80 K for $Cr(NH_3)ZnCl_4,Cl$; A, pure; B, partially photodecomposed; hexa-ammine emission at 658 nm; C, partially photodecomposed; penta-ammine emission at 680 nm

We thank the S.R.C. and the University of London Central Research Fund for grants, and the S.R.C. for Studentships (to P. G. and A. P. M.).

[2/1375 *Received*, 15*th June*, 1972]