

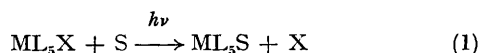
## Solvent Control of the Photolabilization Pathways from the Ligand Field Excitation of $[\text{Rh}(\text{NH}_3)_5\text{Cl}]^{2+}$

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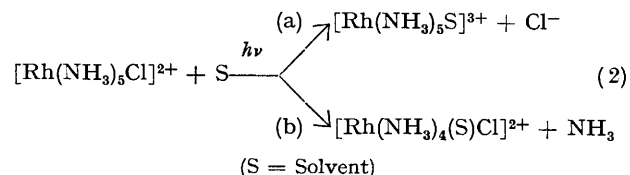
**Summary** It is demonstrated that the identity of the ligand labilized from the ligand field excited states of  $[\text{Rh}(\text{NH}_3)_5\text{Cl}]^{2+}$  is a function of the solvent medium, with  $\text{Cl}^-$  substitution predominating in water and formamide solutions but  $\text{NH}_3$  substitution predominating in dimethylformamide, methanol, and dimethyl sulphoxide solutions.

PHOTOSUBSTITUTION of a ligand by a solvent molecule (equation 1) is the most common (and most studied) chemical consequence of the ligand field (LF) excitation of  $d^6$  metal complexes.<sup>1</sup> Despite this, the potentially crucial



role of solvent in the reactions of LF excited states (e.s.) has been little explored for a system where a reactive LF state is well characterized as the lowest energy e.s. Here we report that for one such complex,  $[\text{Rh}(\text{NH}_3)_5\text{Cl}]^{2+}$ , both the photosubstitution quantum yields and, more importantly, the nature of the predominant photosubstitution pathway are functions of the solvent medium.

In aqueous solution, LF excitation of  $[\text{Rh}(\text{NH}_3)_5\text{Cl}]^{2+}$  leads principally to the photosubstitution of  $\text{Cl}^-$  (equation 2a),<sup>2,3</sup> although solution pH changes indicate small quantum



yields for  $\text{NH}_3$  labilization<sup>3</sup> (Table). In formamide (fma) solution,  $\text{Cl}^-$  photosubstitution again predominates to give  $[\text{Rh}(\text{NH}_3)_5(\text{fma})]^{3+}$  as the rhodium(III) product. However, a marked reversal of behaviour is noted in dimethylformamide (dmf), methanol, and dimethylsulphoxide (dmsO) solutions where  $\text{NH}_3$  photosubstitution (equation 2b) predominates to give *trans*- $[\text{Rh}(\text{NH}_3)_4(\text{S})\text{Cl}]^{2+}$  in each case. (These products were identified by comparing their u.v.-vis. spectra with those of authentic, thermally prepared complexes.<sup>4</sup>) Quantum yields are listed in the Table.

The reactive LF e.s. of  $[\text{Rh}(\text{NH}_3)_5\text{Cl}]^{2+}$  is the  $^3E$  state.<sup>3</sup> This can be viewed as having the excitation concentrated along the weak field  $\text{NH}_3 \cdots \text{Cl}^-$  axis,<sup>5</sup> a view which predicts labilization of *trans*- $\text{NH}_3$  or  $\text{Cl}^-$ . Various rationales including the relative  $\sigma$  and  $\pi$  donor strengths of the ligands<sup>5,6</sup> have been offered to explain the relative importance of these two pathways in water and the analogues of

TABLE. Photosubstitution quantum yields for the photolyses of  $[\text{Rh}(\text{NH}_3)_5\text{Cl}]^{2+}$  in various solvents

Solvent	DN <sup>a</sup>	AN <sup>b</sup>	$\epsilon^c$	$\Phi(\text{Cl}^-)^d$	$\Phi(\text{NH}_3)^d$	$R^e$
H <sub>2</sub> O(l)	33	54.9	78.5	0.18	0.02	9.0
fma	23	39.8	109.5	0.058	<0.01	>5
dmsO	29.8	19.3	46.7	<0.006	0.029 <sub>4</sub>	<0.2
dmf	26.6	16.0	36.7	0.004	0.070	0.06
MeOH	19	41.3	32.6	0.008	0.11	0.07

<sup>a</sup> Gutmann donor number, ref. 10. <sup>b</sup> Gutmann acceptor number, ref. 10. <sup>c</sup> Dielectric constant, ref. 11. <sup>d</sup> Quantum yields in mol einstein<sup>-1</sup>, measured at 25 °C; irradiation wavelength 366 nm. <sup>e</sup> The quantum yield ratio for Cl<sup>-</sup> and NH<sub>3</sub> photosubstitutions,  $\Phi(\text{Cl}^-)/\Phi(\text{NH}_3)$ .

equations 2a and 2b for other  $[\text{ML}_5\text{X}]^{n+}$  complexes. However, the LF spectra of  $[\text{Rh}(\text{NH}_3)_5\text{Cl}]^{2+}$  and similar complexes are generally insensitive to the solvent medium.<sup>7</sup> Thus, there is no spectroscopic information regarding the electronic redistribution in going from the ground state to the reactive e.s. that explains the solvent induced variations in the dominant photoreaction pathway as reflected by the  $\Phi(\text{Cl}^-)/\Phi(\text{NH}_3)$  ratios ( $R$ , Table).

Unlike the total quantum yield  $[\Phi(\text{Cl}^-) + \Phi(\text{NH}_3)]$ , variations in selectivity  $R$  cannot be rationalized by the sensitivity of nonradiative deactivation rates to the medium.<sup>8,9</sup> Thus, changes in  $R$  must reflect different influences by solvent on the activation free energies of competitive Cl<sup>-</sup> and NH<sub>3</sub> labilization from the same e.s. Of the solvent parameters listed in the Table,<sup>10,11</sup> the only systematic correlation with  $R$  appears to be for the dielectric constant. This suggests that the solvents' abilities to stabilize charge separation developing during Cl<sup>-</sup> labilization may be the controlling factor given that NH<sub>3</sub> loss should be accompanied by little charge separation and that NH<sub>3</sub> solvation energies are relatively small.<sup>12</sup>

Cusumano and Langford<sup>13</sup> have recently reported the direct dependence of  $[\text{Cr}(\text{en})_2(\text{NCS})_2]^+$  (en = ethylenedi-

amine) quantum yields on the DN (donor number) values<sup>10</sup> of various solvent media and have argued for an associative mechanism on the basis of these results; however, this argument depends on the assumption that deactivation rates are medium independent. We do not consider the present data for the  $d^6$  Rh<sup>III</sup> complexes to differentiate between an associative mechanism for ligand substitution from the LF e.s. and the more commonly assumed<sup>5</sup> dissociative mechanism. Either mechanism may require considerable solvation of the  $(\text{NH}_3)_5\text{Rh}^{2+} \cdots \text{Cl}^-$  charge separation at the transition state. We expect that better insight into the associative or dissociative nature of the substitution mechanism will result from pulse laser measurements of the rate constants for the reactive, nonradiative and radiative deactivation processes from the lowest LF e.s. which are now in progress.

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