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Photoaquation Reactions of *Trans*-Chloro(dimethylformamide)tetraamminechromium(III)

PIETRO RICCIERI and EDOARDO ZINATO

Dipartimento di Chimica, Università di Perugia, 06100 Perugia, Italy

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Upon ligand-field irradiation in acidic solution, the trans-$Cr(NH_3)_4(DMF)Cl^{2+}$ *cation undergoes simultaneous loss of DMF, Cl^- and NH_3. Photosolvation of DMF predominates at all excitation energies. From the wavelength dependence of quantum yields, the lower-lying ^4E state and the upper $^4B_2$ state, are inferred to be the main precursors to aquation of the axial ligands and of NH_3, respectively. The results are examined in the light of the current photolytic models. Differential spectrophotometry indicates that DMF and Cl^- replacement takes place with complete* trans → cis *isomerization. Comparison with the photochemical behavior of* trans-$Cr(NH_3)_4(H_2O)Cl^{2+}$ *suggests that photoisomerization of the latter occurs entirely through water exchange. Charge-transfer irradiation destabilizes the coordinated groups less selectively than ligand-field photolysis.*

Introduction

The ligand-field (LF) photochemistry of CrN_5X^{2+} and *trans*-CrN_4XY^+ complex ions (N = ammonia or amines; X,Y = anionic groups) has been widely investigated [1]. A well-established pattern of photoreactivity is that, whenever the bonds are cleaved along the N–X [2–4] and X–Y [5–13] axes, ligand aquation occurs with stereorearrangement; *i.e.*, the photoproducts are *cis*-$CrN_4(H_2O)X^{2+}$ and *cis*-$CrN_4(H_2O)Y^{2+}$ [2–13]. It is also known that LF excitation of *trans*-$CrN_4(H_2O)X^{2+}$ (with X^- spectrochemically weaker than N) [11] and *trans*-$CrN_4(H_2O)_2^{3+}$ [11, 14] induces *trans* → *cis* isomerization as the dominant photoprocess. By analogy with the previous systems, such a rearrangement was proposed to proceed via solvent photoexchange [1, 11, 15]. Cr–O bond destabilization upon LF irradiation of these complexes is indeed predicted by all the current photolytic theories [16–21].

Some insight into this occurrence may be gained through the study of model compounds having oxygen-coordinated ligands, such as N,N′-dimethylformamide (DMF), in place of H_2O. The spectrochemical and bonding properties of DMF are fairly similar to those of water [22] and allow comparison between analogous DMF and H_2O systems. Although less strict than oxygen exchange studies, this approach presents the advantage of experimental simplicity.

We have determined the efficiencies of ligand labilization and the photoaquation stereochemistry of *trans*-$Cr(NH_3)_4(DMF)Cl^{2+}$ in aqueous acid solution, in order to draw a parallel with the previously reported behavior of *trans*-$Cr(NH_3)_4(H_2O)Cl^{2+}$ [11]. The chloro(dimethylformamide) complex is *per se* interesting, as it offers the possibility of testing the various photolysis models [16–21] in relation to three simultaneous photoreactions, involving one anionic and two neutral ligands of significantly diverse characteristics.

Experimental

Materials

trans- and *cis*-Chloroaquotetraamminechromium(III) Perchlorates were obtained following reported methods [23]. The wavelengths (nm) and the extinction coefficients (M^{-1} cm^{-1}, in parentheses) of the LF absorption maxima in 10^{-2} *M* $HClO_4$ solution are 555 (20), 468 (18) and 384 (42) for the *trans* compound, and 519 (40) and 384 (33) for the *cis* isomer, in agreement with literature values [23, 24].

trans-Chloro(dimethylformamide)tetraamminechromium(III) Perchlorate was synthesized by heating a solution of *trans*-$[Cr(NH_3)_4(H_2O)Cl](ClO_4)_2$ in DMF at 60 °C for 15 min, as already described [25]. The LF spectral maxima in aqueous solution (Fig. 1) occur at 559 (37), 470 (18) and 387 nm (46). *cis*-Aquo(dimethylformamide)tetraamminechromium(III) Perchlorate was prepared by controlled aquation of *cis*-$[Cr(NH_3)_4(DMF)_2](ClO_4)_3$ which, in turn, was obtained by exchange of coordinated water of *cis*-$[Cr(NH_3)_4(H_2O)_2](ClO_4)_3$ with DMF (1 h at 60 °C). The preparation of the bis(dimethylformamide) complex was similar to that reported by other authors [26] when this work was in progress. A *ca.* 10^{-2} *M* solution of *cis*-$Cr(NH_3)_4(DMF)_2^{3+}$ in 10^{-3} *M*

$HClO_4$ was kept at 50 °C for 30 min. The pH was then adjusted to *ca.* 10 (NaOH), so as to deprotonate *cis*-$Cr(NH_3)_4(DMF)(H_2O)^{3+}$. The reaction mixture was quickly eluted through a 2 cm × 1 cm column of Sephadex cationic exchanger (*vide infra*) with 0.15 *M* $NaClO_4$ at pH 10. After discarding the first fraction consisting of minor amounts of *cis*-$Cr(NH_3)_4(OH)_2^+$, the 2+ hydroxo(dimethylformamide) ion was collected in an ice-cold beaker containing 10^{-2} *M* $HClO_4$, in order to immediately restore protonation. The tripositive parent compound was retained by the resin. The temperature of alkaline solutions was kept below 10 °C to suppress the decomposition that hydroxoammine complexes usually undergo at a much faster rate than their aquo analogs. The red aquo(dimethylformamide) product was characterized in solution by Cr, NH_3 and DMF analysis (1:4.02: 1.05). The LF spectral features are: 498 (52, max), 421 (7, min) and 370 nm (34, max).

An independent preparation of this compound has appeared in the literature and consists of Hg^{2+}-promoted chloride aquation of *cis*-$Cr(NH_3)_4(DMF)Cl^{2+}$ [26]. While the positions of the absorption maxima given for that product are in fair agreement with our data, the extinction coefficient of the first LF band is by 15% lower (and the minimum is more intense) than the present one. The discrepancy may be due to the complexity of the reported synthesis and separation procedure [26].

All the complex salts were recrystallized at least twice. Other chemicals were of reagent grade.

Analytical Procedures

Uncoordinated DMF in photolyzed samples was determined spectrophotometrically at 225 nm (ϵ 472 M^{-1} cm^{-1}), after removing all chromium(III) complexes, which are strongly absorbing in this region. Aliquots were adsorbed on 3 cm × 1 cm columns of Sephadex SP-C25 cationic resin in the proton form, which had been previously washed with 0.5 *M* $HClO_4$ until the eluate was spectrophotometrically pure at 225 nm, and then conditioned with 1 × 10^{-2} *M* $HClO_4$. Elution with 1 × 10^{-2} *M* $HClO_4$ displaced only DMF, while any chromium(III) species was retained. Known quantities of DMF were put through the same procedure to obtain standardization plots. A 15 ml volume of eluate was required for complete recovery of DMF. By this technique, only solutions with an ionic strength lower than 2 × 10^{-2} *M* could be employed in order to avoid displacement of the complex cations from the resin. The reproducibility allowed by this elaborate method was ±8%.

Photoreleased chloride was either titrated potentiometrically with $AgNO_3$, or monitored by an Amel Model 201-Cl Sens-Ion electrode. In the former case a silver electrode and a Radiometer TTT 1c automatic titrator were used while in the latter the chloride-sensitive electrode was connected to an Orion Model 801 digital potentiometer. In order to minimize thermal reaction effects, the aliquots of 2 to 3 ml volume, were chilled in an ice bath. Blank experiments showed that the presence of complexes did not affect the results.

Free ammonia was determined as proton uptake, according to a published procedure [27]. pH differences between dark and irradiated samples were measured by a glass microelectrode, coupled with the above-mentioned pH meter. The ionic strength was kept constant at 0.2 *M* by addition of sodium perchlorate. Calibration plots of ΔpH *vs.* $[NH_3]$ were obtained by introducing known amounts of ammonia in solutions of the complex, having the same concentrations and initial pH (10^{-3} *M* $HClO_4$) as in the actual photolytic runs. As the photoaquated chromium(III) cations are weak acids themselves, the possible buffering action of these species was considered in evaluating the concentrations of uncoordinated NH_3. At these pH levels however, deprotonation of the aquo complexes ($pK_a \sim 5$) [24] is limited to a few units percent and the error incurred by neglecting this effect was estimated to be in any case well within the uncertainty introduced by secondary NH_3 photoaquation (*vide infra*).

Absorbances at specific wavelengths were measured with a Beckman DU spectrophotometer, while electronic absorption spectra were recorded with either a Shimadzu UV 200S or a Cary 17 instrument.

Photolysis Procedures

The general equipment has been described elsewhere [11]. Irradiation wavelengths were isolated by means of either interference filters or a Bausch & Lomb high-intensity, grating monochromator. Incident light intensities were about 10^{-8} einstein s^{-1} and were determined either by a thermopile [11] or by reineckate [28] and ferrioxalate [29] actinometry. Aliquots of 2.5 ml volume, *ca.* 10^{-2} *M* in complex, in 10^{-1} to 10^{-3} *M* $HClO_4$, were photolyzed in spectrophotometer cells of 1 cm pathlength, held in a thermostatted compartment at 20.0 ± 0.5 °C. Continuous magnetic stirring was applied. Photolyses were generally carried out under conditions of partial light absorption and the absorbed energy was evaluated as previously reported [30]. Irradiation times ranged between 10 and 40 min and were such that the contribution of dark reactions was generally very small. In all cases, dark samples were analyzed in parallel with the irradiated ones, in order to allow for any possible thermal process.

Total conversion was usually less than 10%. When the ligands to be analyzed were either DMF or Cl^-, inner filter absorption, hence secondary photolysis,

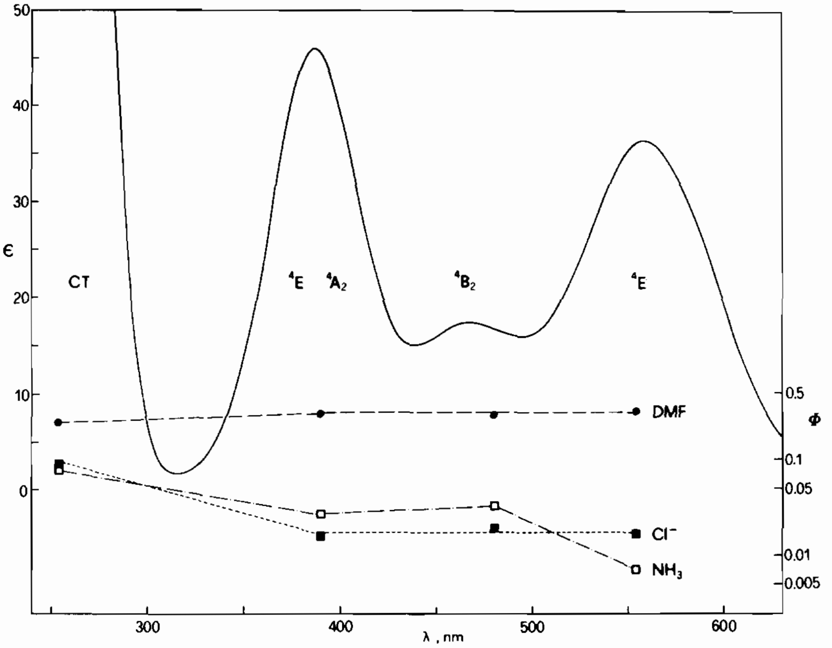

Fig. 1. Electronic absorption spectrum of *trans*-$Cr(NH_3)_4(DMF)Cl^{2+}$ in 10^{-2} *M* $HClO_4$ (ϵ on the left), and wavelength dependence of the photoaquation quantum yields (logarithmic scale on the right).

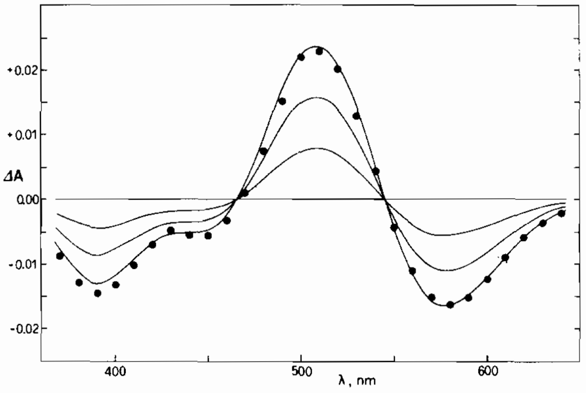

Fig. 2. Differential absorption spectra during the 546 nm photolysis of a 2.5 ml sample of *trans*-$Cr(NH_3)_4(DMF)Cl^{2+}$ in 10^{-2} *M* $HClO_4$. The traces correspond to irradiation times of 180, 360, and 540 s, with an absorbed light-intensity of 1.38×10^{-8} einstein s^{-1}. Circles represent the spectral changes expected on the basis of the conccentrations of *cis*-$Cr(NH_3)_4(H_2O)Cl^{2+}$ and *cis*-$Cr(NH_3)_4(DMF(H_2O)^{3+}$ obtained by a least-squares analysis of the experimental curves (see text).

could be ignored. Ammonia determination instead required that these effects be taken into account, because of the high efficiency of NH_3 photorelease from the principal photoproduct (*vide infra*). Ammonia photoaquation quantum yields were then evaluated from the total NH_3 concentrations, by a mathematical treatment already applied to analogous *trans*-diacidotetraammines [11].

Results

The ground-state behavior of *trans*-$Cr(NH_3)_4(DMF)Cl^{2+}$ in aqueous solution has been characterized previously [25]. The complex undergoes simultaneous replacement of the apical groups with complete retention of configuration. The aquation rate is larger for DMF than for Cl^- by a factor of 5 and is pH independent for both ligands. Under the photolysis conditions the two processes are slow enough ($k_{DMF} = 5.0 \times 10^{-6}$ s^{-1}; $k_{Cl^-} = 1.0 \times 10^{-6}$ s^{-1} at 20 °C) that their contribution to the over-all reactivity is practically negligible.

The absorption spectrum of the *trans*-chloro-(dimethylformamide) cation is illustrated in Fig. 1. The three LF bands, typical of *trans*-disubstituted amines, are attributed to the $^4B_1 \rightarrow {}^4E$, $^4B_1 \rightarrow {}^4B_2$ and $^4B_1 \rightarrow {}^4A_2$, ^4E transitions, in order of increasing energy. The first two maxima are originated by the splitting of the octahedral $^4T_{2g}$ energy level in C_{4v} symmetry [31, 32].

The absorption changes induced by LF irradiation, are of the same type at all excitation wavelengths. Between 545 and 465 nm the optical density increases, while it decreases in the other LF regions. The persistence of isosbestic points at the above wavelengths, up to at least 15% total conversion,

TABLE I. Photolysis Quantum Yields[a] in Acidic Aqueous Solution at 20 °C.

Irradiation wavelength nm; transition		*trans*-$Cr(NH_3)_4(DMF)Cl^{2+}$			*trans*-$Cr(NH_3)_4(H_2O)Cl^{2+}$ [b]		
		ϕ_{DMF}	ϕ_{Cl^-}	ϕ_{NH_3}	ϕ_{cis} [c]	ϕ_{Cl^-}	ϕ_{NH_3}
546	${}^4B_1 \rightarrow {}^4E({}^4T_{2g})$	0.31 ± 0.03 (7)	0.017 ± 0.003 (3)	0.007 ± 0.003 (7)	0.42 ± 0.02	<0.004	0.023 ± 0.002
480	${}^4B_1 \rightarrow {}^4B_2$	0.29 ± 0.02 (8)	0.019 ± 0.003 (4)	0.032 ± 0.006 (5)	0.40 ± 0.02	<0.005	0.065 ± 0.003
390	${}^4B_1 \rightarrow {}^4A_2, {}^4E({}^4T_{1g})$	0.30 ± 0.03 (12)	0.016 ±0.003 (4)	0.027 ± 0.002 (5)	0.43 ± 0.01	<0.005	0.050 ± 0.005
254	C.T.	0.25 ± 0.01 (4)	0.087 ± 0.005 (5)	0.081 ± 0.007 (3)		0.21 ± 0.01	0.29 ± 0.02

[a] Number of runs in parentheses. [b] Data from ref. 11. [c] Quantum yield for formation of *cis*-$Cr(NH_3)_4(H_2O)Cl^{2+}$.

implies formation of constant ratios of products. Expanded-scale, difference spectra (Fig. 2) show that, at constant light intensity, the variations in absorbance follow zero-order kinetics. Postirradiation effects are ruled out by the spectral stability of photolyzed samples.

Determination of uncoordinated ligands indicates that DMF, Cl^- and NH_3 are released in parallel. Dimethylformamide loss largely predominates over the other photoreaction modes. Plots of [DMF] and [Cl^-] *vs.* the absorbed energy are linear throughout photolysis (generally less than 10%). On the contrary, [NH_3] does not exhibit such a dependence. An upward curvature, even in the early photolysis stages, reveals the occurrence of efficient secondary photoprocesses. This complication arises from the following factors. Ammonia photoaquation represents a minor fraction of total photoreaction (only about 2% at 546 nm). The quantum yield for secondary NH_3 loss from the main photoproduct, *cis*-$Cr(NH_3)_4(H_2O)Cl^{2+}$, is larger than that of primary NH_3 release by one order of magnitude ($\phi = 0.30 \pm 0.02$) [11], so that even small percentages of light intercepted by the product(s) generate relatively large concentrations of secondary NH_3. After correcting the experimental values according to a previously developed procedure [11], also the NH_3 quantum yields result to be independent of the photolysis extent.

The efficiencies of photoaquation of the three ligands at various LF wavelengths are reported in Table I. Each entry is the average of at least three independent runs.

Isomeric assignment of the photolysis products was accomplished by spectrophotometric analysis. Even on qualitative grounds, the spectral variations suggest that the major product (*i.e.* that related to DMF aquation) is *cis*-$Cr(NH_3)_4(H_2O)Cl^{2+}$. The isosbestic points are very close to the wavelengths (545 and 470 nm) at which the spectra of the *cis*-chloroaquo and the *trans*-chloro(dimethylformamide) complexes are expected to cross. Moreover, had the product been *trans*, the absorbance would have decreased in the entire LF range, and no crossing points (at the most a tangency around 470 nm) would have been observed (*cf.* the spectral features in the Experimental Section).

The differential absorption curves (Fig. 2) allow quantitative characterization of both products of axial photosolvation. In the 546 nm photolysis, the spectral changes may be entirely attributed to DMF and Cl^- substitution, as the contribution of NH_3 release is minimal. Thus, at a given wavelength, the difference in optical density between a photolyzed and a dark solution is

$$\Delta A_i = (\epsilon_I - \epsilon_o)_i [I] + (\epsilon_{II} - \epsilon_o)_i [II] \tag{1}$$

where ϵ_o, ϵ_I and ϵ_{II} are the extinction coefficients of the reactant and of the DMF and Cl^- photoaquation products, and [I] and [II] are the unknown concentrations of the latter. A least-squares fit, over numerous wavelengths leads to the equations:

$$\Sigma_i\{(\epsilon_I - \epsilon_o)_i^2[I] + (\epsilon_I - \epsilon_o)_i(\epsilon_{II} - \epsilon_o)_i[II] - \Delta A_i(\epsilon_I - \epsilon_o)_i\} = 0 \qquad (2)$$

$$\Sigma_i\{(\epsilon_{II} - \epsilon_o)_i^2[II] + (\epsilon_I - \epsilon_o)_i(\epsilon_{II} - \epsilon_o)_i[I] - \Delta A_i(\epsilon_{II} - \epsilon_o)_i\} = 0 \qquad (3)$$

The extent to which the mixture of I and II consists of *cis*-$Cr(NH_3)_4(H_2O)Cl^{2+}$ and *cis*-$Cr(NH_3)_4(DMF)(H_2O)^{3+}$ may be verified by solving eqns. (2) and (3), after introduction of the known ϵ of the two *cis* complexes. The concentrations of I and II, obtained by extending the calculation to 25 wavelengths under actinometric conditions, correspond to the following quantum yields: $\phi_I = 0.33 \pm 0.02$; $\phi_{II} = 0.018 \pm 0.002$. These coincide, within error limits, with the ϕ_{DMF} and ϕ_{Cl^-} values independently determined at 546 nm by analysis of the released ligands (Table I). Both this agreement and the quality of the fitting, illustrated by the circles in Fig. 2, indicate that at least the product of DMF aquation is mostly, if not exclusively, in the *cis* configuration. Since ϕ_{II} is much smaller than ϕ_I, the chloride aquation product has a scant influence on the spectra. Hence, the curve-fitting may not be taken as definite stereochemical proof for the $Cr(NH_3)_4(DMF)(H_2O)^{3+}$ ion. However, previous experience with *trans*-$Cr(NH_3)_4XY^+$ systems [11] suggests that also this product should be totally *cis*.

That the main product is *cis* may be also inferred from the occurrence of efficient secondary NH_3 photoaquation. *Cis*-diacidotetraamminechromium(III) ions are, in fact, predicted, [16–21] and found, [11, 33, 34] to preferentially photolyze NH_3.

The thermal (20 °C) [25] and photochemical (546 nm) reactivities of the *trans*-$Cr(NH_3)_4(DMF)Cl^{2+}$ ion are summarized by the following Scheme:

Charge-transfer (CT) excitation gives rise to qualitatively similar optical density changes, with three (instead of two) isosbestic points at 545, 455 and 377 nm. The ligand preferentially aquated is still DMF. The major difference from LF irradiation is that the fractions of photoreleased Cl^- and NH_3 are now much larger (see Table I). Due to its higher quantum yield, NH_3 loss exhibits zero-order behavior, at least for low percentages of photoconversion. Therefore, correction for secondary NH_3 photolysis may be initially neglected. The presence of relatively large amounts of the NH_3 aquation product (the configuration and the spectrum of which are unknown) now hinders quantitative isomeric analysis. However, also in this case the spectrophotometric evolution is qualitatively consistent with the prevalence of a *cis* product for DMF photoaquation.

Discussion

This system affords one more clear-cut example of intrinsically different substitutional chemistries in the ground state and in the excited states of chromium(III). The wavelength dependence of the quantum yields, shown in Fig. 1, provides information as to the number and the nature of the photoactive states.

ϕ_{DMF} and ϕ_{Cl^-} present only small variations throughout the LF region. ϕ_{NH_3} instead exhibits different trends. From these profiles it may be inferred that most, if not all of DMF and Cl^- are labilized in the same excited state and that this state is the lowest of a spin multiplicity. The importance of the lowest quartet has been widely proven [1], although recent studies have demonstrated that the lowest doublet may be also involved in photoreactions [35]. Owing to the lower spectrochemical strength of both apical ligands with respect to the equatorial ones, the tetragonal splitting of the parent $^4T_{2g}$ level is such that the lowest spin-allowed excited quartet is ^4E [31, 32]. The antibonding electron density of ^4E is predominantly axial (86.8% d_{z^2} character) [20] and clearly relates to the cleavage of the Cr–DMF and Cr–Cl bonds.

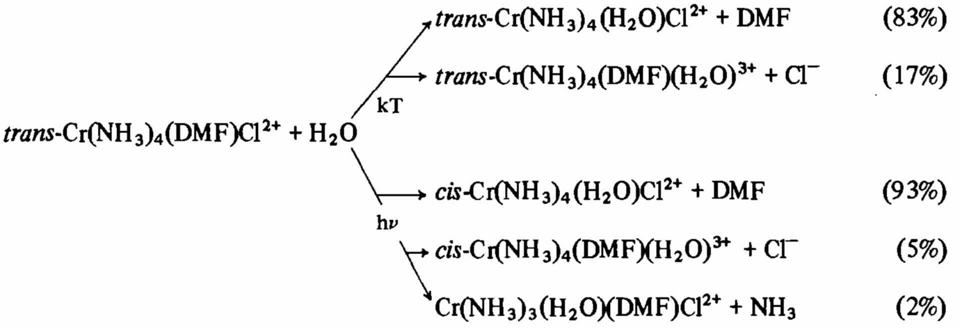

TABLE II. Bond Energies for the Two Lowest Quartet Excited States (cm^{-1}).[a]

Complex	State	I*(Cr–O)	I*(Cr–Cl)	I*(Cr–N)
trans-$Cr(NH_3)_4(DMF)Cl^{2+}$ [b]	^4E	8500	9020	12100
	$^4B_2$	12900	12970	8980
trans-$Cr(NH_3)_4(H_2O)Cl^{2+}$	^4E	8250	9050	12080
	$^4B_2$	12890	12970	8980

[a] Calculated according to the Vanquickenborne-Ceulemans model (ref. 20). [b] Spectrochemical parameters for DMF (σ = 5800 cm^{-1}, π +640 cm^{-1}) from ref. 22.

The wavelength dependence of NH_3 suggests that ammonia loss is largely unconnected to the other two processes and originates mainly in the upper, $^4B_2$ state. The exclusively equatorial antibonding charge distribution of $^4B_2$ (100% $d_{x^2-y^2}$) is also congruent with the observed reaction mode, *i.e.* with 'in-plane' photoaquation.

It may be noticed that the 559 nm and 470 nm maxima are separated enough to allow selective excitation to the corresponding states, possessing diametrically opposite reactivities. The small ϕ_{NH_3} value upon long-wavelength irradiation may be attributed [36] to the $d_{x^2-y^2}$ component (13.2%) [20] of ^4E. An alternative explanation has often been put forward, namely, establishment of thermal equilibrium between ^4E and $^4B_2$. This possibility now seems unlikely, in view of the very short (ps) lifetimes found for the excited quartets of other chromium(III) complexes [37, 38].

The *trans*-$Cr(NH_3)_4(DMF)Cl^{2+}$ cation is one of the few systems in which three different, simultaneous photoreactions have been fully characterized. It is therefore interesting to compare the observed competition in the labilization of the various ligands with the available photolytic theories, following an order of increasing complexity. All the models appear able to rationalize the experimental findings.

Adamson's semi-empirical rules [16] state that the ligand preferentially released is the stronger-field one (DMF) on the weaker average-field axis (DMF–Cl) and that discrimination (over NH_3) is larger at longer irradiation wavelengths.

According to MO–LF σ/π bonding models, [17–19] the $^4B_1 \rightarrow {}^4E$ excitation, $\pi^*(d_{xz}, d_{yz}) \rightarrow \sigma^*$ (predominantly d_{z^2}), weakens the σ bonds in the z (DMF–Cl) direction but, at the same time, increases π donation along this axis. As the π-donor ability is much higher for Cl^- than for DMF, loss of the latter group is expected to dominate. On the contrary, the $^4B_1 \rightarrow {}^4B_2$ transition, $\pi^*(d_{xy}) \rightarrow \sigma^*(d_{x^2-y^2})$, destabilizes σ bonding on the equatorial $(NH_3)_4$ plane. Since ammonia is σ donor only, π effects need not be considered in this case.

A more quantitative prediction is given by the recent additive angular overlap approach [20]. The bond energies for the two lowest quartet excited states, evaluated using the available σ and π spectrochemical parameters [20, 22] are collected in Table II. The most destabilized ligand again results to be DMF for the ^4E state, and NH_3 for $^4B_2$.

The main point of interest is the stereochemistry of DMF photoaquation. The results indicate that complete *trans* → *cis* isomerization accompanies replacement of the axial ligands, in line with a general characteristic of chromium(III) LF photochemistry [1–13]. Specifically, the quantum yield for DMF aquation upon excitation to ^4E, equals that for appearance of *cis*-$Cr(NH_3)_4(H_2O)Cl^{2+}$, independently determined.

Analogy between *trans*-$Cr(NH_3)_4(H_2O)Cl^{2+}$ and *trans*-$Cr(NH_3)_4(DMF)Cl^{2+}$ appears reasonable on the basis of the parallelism of the quantum yields for the various reaction modes of the two systems (Table I). Several factors ensure a sufficient degree of similarity between the DMF and H_2O ligands, so as to make dimethylformamide complexes comparable with their aquo homologues. (i) Both these oxygen-bound groups are uncharged and exert little π interaction. (ii) Their spectrochemical positions are fairly close, as indicated by the proximity of the absorption maxima for analogous DMF and H_2O species [22, 25]. Also the two-dimensional bonding parameters [22] are quite similar. (iii) The rates of DMF aquation and of H_2O exchange in the ground state (the only available, homogeneous data pertain to $Cr(NH_3)_5(DMF)^{3+}$ [25] and $Cr(NH_3)_5(H_2O)^{3+}$ [39]) are of the same order of magnitude, and the respective activation energies are not very different.

From comparison of the two sets of data, it may be inferred that in the chloroaquo complex, as in the chloro(dimethylformamide) one, each molecule undergoing isomerization also undergoes photolytic Cr–O bond cleavage, *i.e.*, the quantum yield for stereorearrangement of *trans*-$Cr(NH_3)_4(H_2O)X^{2+}$ species may be taken as a measure of the efficiency of water photoexchange. Such an inference is also supported by the theoretical predictions of Table II. It may be noticed that the differences between the excited-state energies of the axial bonds are in agreement with the observed higher preference for Cr–O, over Cr–Cl, bond weakening in *trans*-$Cr(NH_3)_4(H_2O)Cl^{2+}$, with respect to *trans*-$Cr(NH_3)_4(DMF)Cl^{2+}$.

The present results may be combined with those relative to other ligands, in order to place DMF in a scale of photoinduced leaving ability. Rather than comparing single quantum yield values, even within a series of similar compounds (*e.g.*, ϕ_{X^-} in various $Cr(NH_3)_5X^{2+}$ systems), it is more significant to consider *ratios* of quantum yields for loss of pairs of different ligands, each pair within the same complex and in the same excited state. The data for competitive axial photoaquation in *trans*-$Cr(NH_3)_4XY^{z+}$ [2, 11] and *trans*-$Cr(en)_2XY^{z+}$ species [3, 4, 6, 7, 10, 13, 40] lead to the following order of preferential photolabilization: $F^- < Cl^- < NCS^- <$ DMF $< H_2O < NH_3$. The sequence roughly parallels (with the exception of NCS^-) an order of decreasing π donation, as expressed by the spectrochemical π parameters [20, 22].

Finally, in the 254 nm photolysis the ligands are labilized with less selectivity than upon LF irradiation. The substantial increment of ϕ_{Cl^-} and ϕ_{NH_3} relatively to the visible region suggests the participation of another reactive (CT) excited state, possibly inclined to primary homolytic bond rupture [11]. Table I shows that, despite the similar LF reactivities of the DMF and H_2O systems, the above increase is less pronounced for the DMF complex. A possible explanation for this difference is related to the fact that light absorption at 254 nm is, at least in part, due to a transition within the DMF group. This absorption is present also in uncoordinated dimethylformamide and, upon coordination, obscures the CT (ligand-to-metal) band to some extent. Consequently, DMF-localized vibrations may dissipate a considerable fraction of the excitation energy, in competition with conversion to the photoactive CT state. The behavior may be quite similar to that observed upon uv irradiation of analogous NCS^- complexes [11].

Acknowledgement

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