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# Correspondence

## Photochemistry of $Cr(NH_3)_5F^{2+}$, $trans$-$Cr(en)_2(NH_3)F^{2+}$, and $trans$-$Cr(en)_2F_2^+$

*Sir:*

The development of ligand field photochemistry in coordination complexes[1,2] has been stimulated to a great extent by the formulation of Adamson's empirical rules[3] in 1967. Later on, these rules have been generalized and modified; moreover, they have been related to a theoretical understanding of the electronic structure of transition-metal complexes.[1,4]

Recently, Adamson[5] and Kirk[6] independently reported on the photolysis of fluoropentaamminechromium(III); their papers apparently intended to fill an important gap in Cr(III) photochemistry. It is well to stress that the importance of this gap is particularly obvious from the viewpoint of several theoretical models.[4,7–9]

However, the experimental data, reported for $trans$-$Cr(en)_2(NH_3)F^{2+}$ and $Cr(NH_3)_5F^{2+}$, are claimed[6] to be in complete disagreement with the theoretical predictions; it was suggested that the strong ionic character of the Cr(III)–F bond is responsible for this anomaly.[6] It is the purpose of the present paper to show that the new experimental data, on the contrary, contribute significantly to the corroboration of a ligand field model. At the same time, several theoretical features of the model will be discussed in more detail.

Let us briefly summarize the experimental results. It has been shown[6] that irradiation of $trans$-$Cr(en)_2(NH_3)F^{2+}$ in its lowest quartet band liberates $NH_3$:

$$trans\text{-}Cr(en)_2(NH_3)F^{2+} + H_2O \xrightarrow[\text{546 nm}]{h\nu}$$
$$cis\text{-}Cr(en)_2(H_2O)F^{2+} + NH_3$$
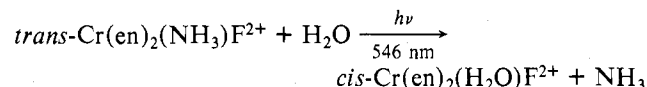
This experiment clearly demonstrates a strong preferential labilization effect of the heteroaxis $NH_3$–Cr–F over the equatorial ethylenediamine axes. Indeed, since the ground-state bond strengths should be nearly identical for the axial amine ligand and for the equatorial ethylenediamine ligands, the observed aquation directly reflects a specific, oriented destabilization effect of the absorbed photon energy.

$Cr(NH_3)_5F^{2+}$ also predominantly photoaquates $NH_3$, resulting in a cis product; in this case, the axial character of the labilization has not been proven unambiguously, but it is considered quite probable.[5]

It is interesting to compare these results to the photoaquation of $trans$-$Cr(en)_2F_2^+$, where the leaving ligand has been shown to be predominantly the equatorial amine.[10,11] Here, axial and equatorial labilizations necessarily result in chemically *different* leaving ligands ($F^-$ and en, respectively). Therefore, in this case, the ground-state bond strengths are different to begin

with, and the photochemical labilization will not be the *only* factor determining the dominant aquation mode.[4]

**Application of the Ligand Field Model.** Despite an earlier erroneous treatment by Rowley,[12] the energy ordering of the five d orbitals in $Cr(NH_3)_2F^{2+}$ and $trans$-$Cr(en)_2F_2^+$ seems quite well established by now.[6,13,14] If the heteroaxis containing the fluoride ligand(s) is taken to be the z axis, the relative ordering is given by the sequence

$$d_{xy} < d_{xz}, d_{yz} \ll d_{x^2-y^2} < d_{z^2}$$

the three lowest orbitals being singly occupied. It reflects the stronger σ- and π-donor properties of fluoride relative to amine:

$$\sigma_F > \sigma_N \quad \text{and} \quad \pi_F > \pi_N$$

From this energy level ordering, it does *not* follow that the lowest excited quartet state should correspond to the $(xz, yz) \rightarrow (x^2 - y^2)$ excitation. Figure 1 shows the relevant state energies and their octahedral parentage.[15–17] In deriving the orbital composition of Figure 1, use was made of the matrix equation

$$(x^2 \quad y^2 \quad x^2-z^2 \quad y^2-z^2) =$$
$$(z^2 \quad x^2-y^2)\begin{pmatrix} -1/2 & -1/2 & -3^{1/2}/2 & -3^{1/2}/2 \\ 3^{1/2}/2 & -3^{1/2}/2 & 1/2 & -1/2 \end{pmatrix} \quad (1)$$

where $z^2$ stands for $d_{z^2}$, etc. The $d_{x^2}$ orbital has the same functional form as $d_{z^2}$, but it is characterized by a rotational symmetry around the x axis; the $d_{x^2-z^2}$ orbital has the same functional form as $d_{x^2-y^2}$ and can be obtained from the latter by a rotation over 90° around the x axis.

The notation of eq 1 has the advantage that it shows immediately why the octahedral $^4T_{2g}$ wave functions are characterized by the same energy: each one of the three functions corresponds to an orbital excitation $pq \rightarrow p^2 - q^2$ (where p or q stand for x, y, or z). Both orbitals $pq$ and $p^2 - q^2$ have their largest probability density in the same coordinate plane, perpendicular to the third coordinate axis r (z, x, or y); they can be transformed into each other by a rotation of 45° around the r axis. This explains why the $^4T_{2g}$ state is characterized by the same interelectronic repulsion energy as the ground state. Indeed, the $pq \rightarrow p^2 - q^2$ excitation leaves the $pr$ and $qr$ orbitals singly occupied; the electron density $[(pr)^2 + (qr)^2]$ exhibits axial symmetry around the r axis. Therefore the excitation—corresponding to the rotation of the remaining singly occupied orbital $pq$ around the r axis—does not modify the interelectronic interactions, and $E(^4T_{2g}) - E(^4A_{2g}) = E(e_g) - E(t_{2g}) = 10Dq = 3\sigma - 4\pi$.

The $^4T_{1g}$ functions on the other hand are of the general type $pq \rightarrow r^2$; therefore, this excitation concentrates one electron
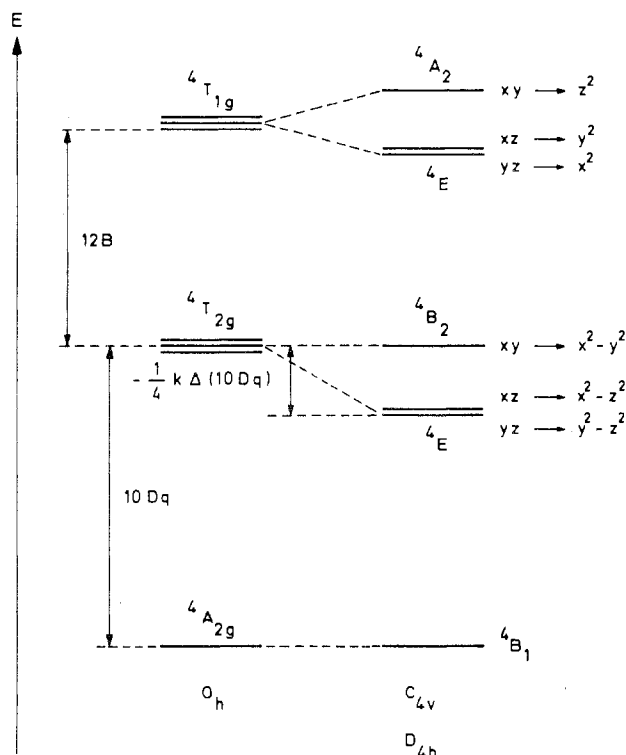
**Figure 1.** Schematic state energy level diagram (not drawn to scale) for $Cr(NH_3)_5F^{2+}$ and *trans*-$Cr(en)_2F_2^+$. For each state, the octahedral parentage and the zero-order orbital composition are also included; $B$ is the Racah parameter; $k$ equals the number of $F^-$ ligands.

along the $r$ axis, while leaving the $pr$ and $qr$ orbitals occupied. Since the electron density $[(pr)^2 + (qr)^2]$ also has axial symmetry about the same axis (albeit at a larger distance), the electron repulsion of $^4T_{1g}$ will be considerably larger than in $^4T_{2g}$. Crystal field calculations show that the energy difference $E(^4T_{1g}) - E(^4T_{2g}) = 12B \approx 1$ eV.

If one or two amines on the $z$ axis are replaced by fluoride ligands, the threefold degeneracies are destroyed. In the $^4T_{2g}$ state for instance, the energy of the $xy \rightarrow x^2 - y^2$ excitation ($^4B_2$) remains unaffected, while the $^4E$ state is lowered with respect to the octahedral case. Indeed, to first order in perturbation theory, one obtains[4]

$$E(^4E; {}^4T_{2g}) - E(^4B_2) = \frac{1}{4}k[10Dq(F) - 10Dq(NH_3)]$$
$$= \frac{1}{4}k\Delta(10Dq) \qquad (2)$$

where $k$ is again the number of F ligands. The relative spectrochemical strength of $NH_3$ and $F^-$ is known with certainty: $\Delta(10Dq)$ is negative.

Therefore, the lowest excited state is $^4E(^4T_{2g})$ in both the mono- and difluoro compounds. To first order in perturbation theory, this state corresponds to the pure ($xz \rightarrow x^2 - z^2$) and ($yz \rightarrow y^2 - z^2$) excitations. Let us now examine the corresponding labilizations. In the transition $d_{xz} \rightarrow d_{x^2-z^2}$ for instance, the total excitation energy $10Dq(NH_3) + \frac{1}{4}k\Delta(10Dq)$ will be distributed over the four ligands along the $x$ and $z$ axes *only*.[4] The metal–ligand bond weakening is simply proportional to the spectrochemical strength of the interaction: for each individual ligand,[18] the resulting bond labilization is given by $\frac{1}{4}[10Dq(L)]$. The same type of reasoning also applies to the $yz \rightarrow y^2 - z^2$ transition. Since the $^4E$ state is described to an equal extent by both functions, the total labilization due to the electronic excitation amounts to $\frac{1}{4}[10Dq(L)]$ for an axial ligand (along the $z$ axis) and $\frac{1}{8}[10Dq(L)]$ for an equatorial ligand.

As a consequence, in $Cr(NH_3)_5F^{2+}$ or *trans*-$Cr(en)_2$-$(NH_3)F^{2+}$ the axial amine is labilized *twice as much* as any

of the equatorial ligands. Moreover, the axial metal–amine bond absorbs more excitation energy than the trans fluoride, since $Dq(NH_3) > Dq(F)$. The ligand field model therefore predicts quite unambiguously the experimental results of Adamson[5] and Kirk.[6] This conclusion will not be modified significantly by second-order interactions between $^4E(T_{2g})$ and $^4E(T_{1g})$. The latter will indeed decrease somewhat the difference in labilization energy between axial and equatorial bonds, but a numerical calculation shows that the axial amine will still absorb 1.9 times as much energy as an equatorial amine.

In *trans*-$Cr(en)_2F_2^+$, the Cr–F bonds will be weakened more than the Cr–N bonds, namely, to the extent $\frac{1}{4}[10Dq(F)]$ vs. $\frac{1}{8}[10Dq(N)]$ for the amine ligands. Why en release is observed is thus *not* due to the population of $x^2 - y^2$ but to the fact that the *ground-state* bond strength of Cr–F is much larger than Cr–N; a numerical calculation[4] bears this out quite clearly.

The same argument can be rephrased in a different way so as to make a closer connection with the previous literature on the subject. The $x^2 - z^2$ and $y^2 - z^2$ orbitals that are populated in the photoactive $^4E$ state are both 75% $z^2$ and 25% $x^2 - y^2$ in character (eq 1). The latter orbitals are more obviously adequate in the description of tetragonal systems characterized by a unique $z$ axis.

By second-order interactions between the two $^4E$ states, the $z^2$ character decreases slightly[4,19] whenever $E(z^2) > E(x^2 - y^2)$. Accounting for the numerical value of $\Delta\sigma$ in the fluoro–amine complexes, one calculates[4] the $z^2$ character at about 73% for $Cr(NH_3)_5F^{2+}$ and at 71% for $Cr(en)_2F_2^+$. Decreasing the $z^2$ character from 75% to 71% does indeed repartition the labilization to a slightly greater extent toward the equatorial plane. The point is however that this shift is not nearly sufficient to favor equatorial over axial labilization!

The situation can be summarized as follows:

| | | |
|---|---|---|
| $^4B_2(^4T_{2g})$ | $100\% \ x^2 - y^2$ | equatorial labilization |
| $^4E(^4T_{2g})$ | $75\% \ z^2, 25\% \ x^2 - y^2$ | predominantly axial labilization |
| $^4T_{2g}[\frac{1}{3}(^4B_2); \frac{2}{3}(^4E)]$ | $50\% \ z^2, 50\% \ x^2 - y^2$ | |

The latter case, involving *equal* fractions of the two $d\sigma^*$ orbitals, represents the truly isotropic labilization of the cubic complex. The $^4T_{2g}$ wave functions *together* constitute an electron density of cubic symmetry; but even the zero-order individual components ($^4B_2$ and $^4E$) are definitely anisotropic. Therefore, merely separating these components energetically (by the tetragonal perturbation) induces a pronounced equatorial or axial labilization, even when the *same* zero-order "octahedral" wave functions are used as a first approximation.

Two additional comments may be made here.

(1) The transition $(xz, yz) \rightarrow x^2 - y^2$, corresponding to the smallest orbital transition energy, need never be considered. Indeed, it is the predominant configuration of the $^4E(^4T_{1g})$ state, which is pushed up so high by interelectronic repulsion energy that it plays no role in the present context.

(2) In the formalism of our previous work,[4] the photochemistry of both $Cr(N)_5F^{2+}$ and *trans*-$Cr(en)_2F_2^+$ is unique in a certain sense. It is characterized by the following: (a) $\overline{Dq}_{ax} < \overline{Dq}_{eq} = Dq(NH_3)$: $^4E$ is the lowest excited state. (b) $\bar{\sigma}_{ax} > \bar{\sigma}_{eq} = \sigma(NH_3)$: therefore the fraction of $z^2$ is somewhat smaller than $^3/_4$ (usually $\bar{\sigma}_{ax} < \bar{\sigma}_{eq}$ and the $z^2$ fraction increases slightly). (c) In *trans*-$Cr(en)_2F_2^+$, the preferential axial labilization cannot be observed directly because of the large bond strength difference of Cr–F and Cr–N in the ground state; in $Cr(NH_3)_5F^{2+}$ and *trans*-$Cr(en)_2(NH_3)F^{2+}$, the identical or nearly identical Cr–N bond strengths make a direct observation of the axial labilization possible.

**Limitations of the Theoretical Ligand Field Model.** From

the previous considerations, it follows that one always predicts axial ligand release when $\overline{Dq}_{ax} < \overline{Dq}_{eq}$, *except* when the ground-state bond strengths M–L$_{ax}$ and M–L$_{eq}$ are too different. This does not mean that equatorial ligand release is completely impossible in all other cases. Two amendatory remarks are in place here.

(1) All predictions considered so far relate to excitation of the lowest excited $^4E(^4T_{2g})$ state. Direct excitation of the higher lying $^4B_2$ state gives rise—as can be expected—to equatorial labilization and ligand release. This is effectively proven to hold in wavelength-dependent studies of *trans*-Cr(en)$_2$(NCS)Cl$^+$,[20] *trans*-Cr(en)$_2$(NH$_3$)F$^{2+}$,[6] and *trans*-Cr(en)$_2$(NH$_3$)Cl$^{2+}$.[21] However, the equatorial release is always accompanied by reaction modes characteristic of direct $^4E$ excitation, very likely due to photophysical communication between the two states.

(2) Ligand field models cannot be expected to offer more than a prediction of the *dominant* reaction mode. The $^4E(^4T_{2g})$ photoactive state has also a certain fraction of $x^2 - y^2$ character, labilizing the equatorial plane. This, together with the (small) antibonding properties of $z^2$ in the $xy$ plane, might be responsible for a minor amount of equatorial ligand release.

More generally, it should be stressed that the validity of the present treatment is subject to two main limitations.

(1) It is assumed throughout that the photochemistry is related to the excited quartet states only. This does not mean that, in actual fact, the doublet states are photoinert; indeed, recent work[22] seems to indicate the simultaneous existence of a specific doublet reactivity; we do not attempt to account for these observations.

(2) The influence of an associative reaction mechanism is not considered. It is very possible that a purely dissociative reaction path is an oversimplification. However, in our opinion, the present status of the theory does not allow a satisfactory treatment of solvation effects. Moreover, any successful model that rationalizes Adamson's rules pays major attention to excited-state bond strength and bond labilization. This suggests very strongly that the dissociation of the leaving ligand is a capital factor in the photomechanism.

**Registry No.** Cr(NH$_3$)$_5$F$^{2+}$, 19443-25-5; *trans*-Cr(en)$_2$(NH$_3$)F$^{2+}$, 58410-71-2; *trans*-Cr(en)$_2$F$_2$$^+$, 24407-74-7.

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(16) Certain state functions cited in ref 4 and 17 contain a typographical sign error.
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## McConnell's Model vs. the HPO$_4$ → CO$_3$ Model for Carbonate Apatite

*Sir:*

McConnell and Foreman[1] have raised some objections on our model for carbonate apatite.[2] Actually, these objections can be regarded as a defense for the McConnell model[3,4] rather than as a true criticism to our model. In fact, while most of ref 1 is devoted to supporting McConnell's proposal, only inappropriate arguments are dedicated to question the foundations for HPO$_4$ → CO$_3$.

The McConnell and Foreman proposal that 3PO$_4$ → 4CO$_3$ "to preserve the oxygen lattice essentially intact" is unnecessary. For example, no OH or H$_2$O librational bands are present in the infrared spectrum of carbonate apatite. These librational bands actually result from the equivalence between the three oxygens surrounding one OH or one water molecule in the lattice[5] and would have to appear if the McConnell model should hold.

The internal hydrogen motion in nonstoichiometric hydroxylapatite is shown as a stabilizing mechanism allowing the existence of these compounds. If the geometrical or electronic characteristics of the unit cell should not permit such a mechanism to act, nonstoichiometric hydroxylapatite could not exist. This is the case for Sr, Ba, and Pb apatites[6] which never contain HPO$_4$ ions whatever the initial conditions for their syntheses are. These compounds, when synthesized under conditions other than required by the apatitic stoichiometry, take atmospheric CO$_2$ to form the stoichiometric carbonate apatite of the corresponding cation. The only possible explanation for this phenomenon is that CO$_3$ replaces the HPO$_4$ formed because of the initial conditions of synthesis. Since the crystallographic structure of Sr, Ba, and Pb apatite is close to that of Ca apatite, it seems reasonable that the mechanism of CO$_3$ inclusion into the Ca apatite is also through HPO$_4$ → CO$_3$. Moreover, when nearly HPO$_4$-free carbonate apatite is heated at around 800 °C, it converts into stoichiometric hydroxylapatite plus a certain amount of more or less hydrated calcium oxide. It does not seem at all clear how the McConnell model could justify this transformation. Nevertheless, it is readily shown that, from formula 4 or 5 of our paper,[2] the products of calcination of nearly HPO$_4$-free carbonate apatite are completely justified. One would get

$$((4 - x)/4)Ca_{10}(PO_4)_6(OH)_2 + (3x/2)CaO$$
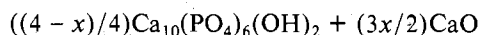
in agreement with that observed.

The strongest criticism made by McConnell and Foreman of our model is of the interpretation of the infrared data. Since they state that our interpretations are "highly speculative", we are obliged to present our interpretations in a more detailed form. CO$_3$ ions, which belong to the $D_{3h}$ point group as free ions, possess lower symmetries when included into the apatitic lattice. The $\nu_2$ mode is assigned to the species A$_2$, to which T$_z$ belongs, and therefore gives rise to one active infrared band when one CO$_3$ ion is placed on a single site. The possibility