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# Solvent Influence on Ligand Field Strength in Fluoro Complexes of Chromium(III)

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The uv–visible absorption and emission spectra of coordination complexes of Cr(III) and other transition metal ions have generally been considered to be solvent independent once ion-pairing and similar effects have been accounted for. Exceptions are the reported medium effects on molar absorptivity for $[Cr(byp)_3]^{3+}$ [1] and $[Cr(CN)_6]^{3-}$ [2]. Only for the latter [2] has any appreciable change in transition energy been observed, and this was ascribed to a solvatochromic effect and correlated with solvent polarity. We wish to report here our observations of previously unreported solvent effects on transition energies and intensities which appear to be unique to fluoride-containing mixed ligand complexes, in this study of Cr(III), both in absorption and emission. In this communication only the absorption effects will be described. The more complex emission behaviour will be described elsehwere [3].

The largest spectral changes are observed between water and solvents such as dimethyl formamide (DMF), tetrahydrofuran (THF), pyridine, acetonitrile and acetone. Figure 1 shows representative spectra for *trans*-$[Cr(en)_2F_2]^+$ (A), *trans*-$[Cr(en)_2NCSF]^+$ (B) and $[Cr(NH_3)_5F]^+$ (C) in water and in DMF. Similar results are obtained for *trans*-$[Cr(en)_2NH_3F]^{2+}$, *trans*-$[Cr(en)_2H_2OF]^{2+}$ and *trans*-$[Cr(NH_3)_4H_2OF]^{2+}$.

In contrast only small or zero spectral changes are observed for these molecules between water and other hydroxylic solvents such as methanol, ethanol, iso-propanol and ethylene glycol. Experiments with *trans*-$[Cr(en)_2X_2]^+$, X≡$Br^-$, $-NCS^-$ showed no spectral changes with any solvent suggesting the effect was specifically associated with the fluoride ligand. This was further supported by data on $[Cr(en)_3]^{3+}$ which, despite a 25% increase in molar absorptivity, showed no change in transition energy, on changing from water to DMF. That the effects were not due to ion-pairing or association was established both by varying the concentration of the complex in DMF and $H_2O$ over a factor of five and by the addition in acetone of a five-fold excess of the tetraphenylborate counter ion, neither of which exerted any influence on the results.

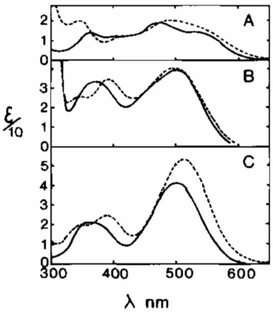

Fig. 1. Absorption spectra of fluoro amine Cr(III) complexes in water and dimethylformamide. A) *trans*-$[Cr(en)_2F_2)^+$, B) *trans*-$[Cr(en)_2NCSF]^+$,. C) $[Cr(NH_3)_5F]^{2+}$. Solutins were $1.0 \times 10^{-2}$ *M* either of the perchlorate or tetraphenylborate salts.

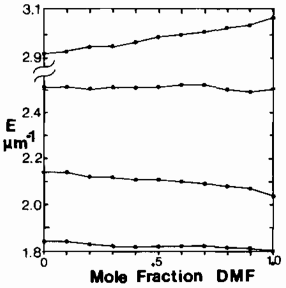

Fig. 2. *trans*$[Cr(en)_2F_2]^+$ transition energies as a function of composition in water/DMF solvent. The bands, in order of increasing energy, are ${}^4E_g$ $\{d_{zx(y)} \rightarrow d_{z^2-x^2(y^2)}\}$, ${}^4B_{2g}$ $\{d_{xy} \rightarrow d_{x^2-y^2}\}$, $4E_g$ $\{d_{zx(y)} \rightarrow d_{y^2(x^2)}\}$, ${}^4A_{2g}$ $\{d_{xy} \rightarrow d_{z^2}\}$ where the parenthetical identifiers indicate the approximate single electron transitions.

In all instances the fluoride-containing compounds show a noticeable change in the spectral splitting patterns in DMF. The bands in question are theoretically four [4, 5] in number (most clearly resolved, Fig. 1, for *trans*-$[Cr(en)_2F_2]^+$ in water) and correspond respectively to the split components ${}^4E_g(a)$, ${}^4B_{2g}$ and ${}^4A_{2g}$, ${}^4E_g(b)$ in $D_{4h}$ symmetry of the ${}^4T_{2g}$ and ${}^4T_{1g}$ bands in octahedral symmetry. The spectral changes appear to be consistent with a decrease in the splitting of the two lower energy components and an increase in the splitting of the higher energy components.

To study the nature of the effects more precisely the spectrum of *trans*-$[Cr(en)_2F_2]^+$ was recorded in a series of $H_2O$/DMF and $H_2O$/THF mixtures at mol fraction intervals of 0.1. The choice of this compound for detailed analysis was based on the clearer splittings and the fact that a detailed study of the bands by polarized crystal absorption spectra exists [6]. The spectra were digitized, converted to

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a wavenumber scale and then resolved into four Gaussian components using a least squares computer program to fit the band energies, intensities and halfwidths; the results for the band energies are shown in Fig. 2. In all examples convergence to the same values was obtained using quite different input values showing that local minima were not a problem. The residual errors were typically $< 1\%$ per point on average.

The derived transition energies yielded by the computer program for the spectrum in water, 1.84, 2.14, 2.51 and 2.87 $\mu m^{-1}$ are in close agreement with the published values based on the single crystal polarized absorption spectrum [6], namely 1.85 ($^4F_g$), 2.17 ($^4B_{2g}$), 2.53 ($^4F_g$) and 2.93 ($^4A_{2g}$) $\mu m^{-1}$. This lends credence to the assumption of Gaussian band shapes and further demonstrates the validity of the computer fits.

We find a monotonic change in the band energies and splittings in going from $H_2O$ to DMF as shown in Fig. 2. No particular effects on intensities and bandwidths were discernable. This detailed analysis confirms that the direction of the change in transition energies is such as to increase the higher energy splitting and decrease the lower, but also reveals some shifts in the position of the average energy of the two components in each pair. In pure DMF the bands have moved to 1.80, 2.04, 2.50, and 3.02 $\mu m^{-1}$.

The angular overlap model of the spectra of tetragonal complexes, *trans*$[CrL_4X_2]$, relates the $^4E_g/{}^4B_{2g}$ splitting to $2\Delta\pi - 3/2\Delta\sigma$, and the $^4A_{2g}/{}^4E_g$ splitting to $2\Delta\pi + 3/2\Delta\sigma$ where $\Delta\pi = \epsilon'\pi_X - \epsilon'\pi_L$ and $\Delta\sigma = \epsilon'\sigma_X - \epsilon'\sigma_L$, the $\epsilon'$ values being the single ligand contributions to the orbital energies [4]. From the data in water one may calculate ($\mu m^{-1}$) $\Delta\sigma_{H_2O} = 0.020$ and $\Delta\pi_{H_2O} = 0.165$, altering to $\Delta\sigma_{DMF} = 0.093$ and $\Delta\pi_{DMF} = 0.190$ in DMF. For intermediate mixtures of water/DMF there is a monotonic change in the derived values.

These simple calculations suggest that the observed changes have their origin in an increase in the $\sigma$ and $\pi$ donor strength of the fluoride ligand and possibly a decrease in the $\sigma$ donor strength of nitrogen in DMF and other non-hydroxylic solvents. The latter is suggested by the decrease in $^4B_{2g}$ transition energy ($d_{xy} \rightarrow d_{x^2-y^2}$) from 21.4 ($H_2O$) → 20.4 (DMF). That this is a small, and probably secondary effect, is confirmed by more detailed calculations. Using the published equations for the single ligand contributions to the energy of the four excited states and the ground state [4], the changes with solvent in sigma donor strength of nitrogen and the sigma and $\pi$ donor strengths of fluoride can be uniquely calculated. Thus the change in nitrogen sigma donor strength, $\Delta\epsilon'\sigma_N = -0.033$ $\mu m^{-1}$, a decrease in DMF of about 5%, while $\Delta\epsilon'\sigma_F = 0.092$ and $\Delta\epsilon'\pi_F = 0.032$ $\mu m^{-1}$, that is increased about 10 and 30%, respectively [7].

An explanation of these changes in ligand field strength, consistent with the observation that they appear to occur only with fluoro complexes in non-hydroxylic solvents, lies in the influence of strong hydrogen bonding from solvent on the donor strength of the fluoro ligand. In water and other hydroxylic solvents the competition by strong solvent hydrogen bonding can reduce both the $\sigma$ and $\pi$ donor strength of the fluoride ligand while in non hydrogen bonding solvents fluoride achieves its full donor capacity. It also seems reasonable to expect some concomitant compensatory change in the donor strength of the nitrogen ligands consistent with the observed shift in $^4B_{2g}$ energy and the calculated 5% decrease in $\sigma_N$ donor strength in DMF. We emphasize that this type of spectral change is not observed for the non fluoro-complexes we have examined and cannot therefore be ascribed to solvatochromic shifts or other solvent effects of a general nature.

It seems probable that this hydrogen-bonding influence may be fairly unique to the fluoride ligand, although certain oxygenated ligands could be candidates. One might expect to see similar effects in fluoro complexes of other metals. We find for $[Co(NH_3)_5F](NO_3)_2$ in methyl sulphoxide, shifts of the low energy bands analogous to those shown in Fig. 1 for the Cr(III) analogue, but the behaviour of the higher energy pair is observed by shifts in the charge transfer bands.

These solvents effects for fluoro complexes add another dimension to the interpretation of their ligand field spectra and their relationship to ligand donor/acceptor properties. They reveal also some details of the synergistic effects that may occur between ligands, the strengthening of the fluoro interaction is compensated somewhat by a decrease in the nitrogen ligand field strength.

There is a close parallel between the effects described here and the spectral effects of protonation of basic ligands such as hydroxo, carbonato, *etc.* There is also a relationship to the well-known phenomenon of proton assigned solvation of fluoride from its complexes [9]. Also analogous are the many current observations on the spectra of compounds with bridging ligands.

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