# Luminescence Behavior and Light Absorption of Some Fluoro Complexes of Tervalent Chromium

By HANS LUDWIG SCHLÄFER, HANS GAUSMANN, and HANS-UWE ZANDER

Together with spectroscopic data ligand field parameters, $Dq$, $B_{55}$, and $B_{35}$ obtained from reflectance spectra of the compounds (NH$_4$)$_3$[CrF$_6$], K$_2$[CrF$_5$(H$_2$O)], [CrF$_3$(H$_2$O)$_3$], [CrF(H$_2$O)$_5$][SiF$_6$], [Cr(H$_2$O)$_6$]F$_3$, [Cr(H$_2$O)$_6$]Cl$_3$, and NH$_4$[CrF$_4$en] are reported. The crystalline compounds show at liquid air temperature a broad-band fluorescence, which can be assigned assuming approximately octahedral microsymmetry to a transition $^4T_{2g}(d\epsilon^2 d\gamma) \rightarrow {}^4A_{2g}(d\epsilon^3)$. NH$_4$[CrF$_4$en] exhibits besides fluorescence a narrow-band phosphorescence $^2E_g(d\epsilon^3) \rightarrow {}^4A_{2g}(d\epsilon^3)$ at shorter wavelengths compared to the fluorescence. [Cr(H$_2$O)$_6$]Cl$_3$ yields phosphorescence only; [Cr(H$_2$O)$_6$]F$_3$ both types of luminescence. These findings are in agreement with a rule for the correlation between ligand field strength and the type of luminescence observed. The lifetime of the doublet state from which phosphorescence originates is, for NH$_4$[CrF$_4$en], $2 \times 10^{-7}$ sec at liquid air temperature.

Chromium(III) complexes in crystalline form or in rigid solutions at low temperatures show when excited by irradiation in the d→d ligand field, the charge-transfer, or the inner ligand bands a characteristic luminescence.[1-3] Sometimes the emission takes place from the first excited quartet state as a broad-band fluorescence. In a great number of compounds the emission occurs from the lowest doublet state as a narrow-band phosphorescence, often with typical vibrational structure.[1,4,5] A majority of complexes yield phosphorescence only, a few give both types of luminescence simultaneously, and others are known where fluorescence only can be detected. In the case of [CrA$_6$] or [Cr(AA)$_3$] complexes (A stands for a mono- and AA for a bidentate ligand) with octahedral microsymmetry, we have found a rule[6] which allows one to predict the type of luminescence for a certain compound. Complexes with ligands like Br$^-$, Cl$^-$, and F$^-$, which have small values of the ligand field strength parameter $Dq$, exhibit fluorescence only. Compounds where the coordinating atom is oxygen show both fluorescence and phosphorescence or phosphorescence only. For complexes where nitrogen or carbon is coordinated around chromium, where greater values of $Dq$ are obtained, only phosphorescence can be observed.

We discussed elsewhere[6] this empirical rule in terms of the shape and intersection of the potential-energy surfaces of the respective electronic states. Particularly of importance is the energy difference between the first excited quartet $^4T_{2g}$ and the lowest doublet state $^2E_g$. This quantity is closely related to the measurable difference $\Delta E$ between the wavenumber $\bar{\nu}_{max}(I)$ of the absorption maximum of the long-wavelength spin-allowed band $^4A_{2g} \rightarrow {}^4T_{2g}$ and $\bar{\nu}_{max}(J)$ the wavenumber of the maximum of the intercombination band $^4A_{2g} \rightarrow {}^2E_g$; $\Delta E = \bar{\nu}_{max}(I) - \bar{\nu}_{max}(J)$ (cm$^{-1}$).

It is of interest to consider the luminescence behavior of mixed chromium(III) complexes [CrA$_{6-n}$B$_n$], $n = 1$–5. To be sure that for such compounds the concept of approximate octahedral microsymmetry will still hold, the ligands A and B should be sufficiently close together in the spectrochemical series. Then it is to be expected that the deviation from regular octahedral symmetry, which is present in [CrA$_6$] or [CrB$_6$], is not detectable in the absorption spectra by a splitting of the spin-allowed d→d bands. Thus it is possible to obtain an average $Dq$ value from the maximum of the long-wavelength spin-allowed band. Such $Dq$ values can be calculated approximately from the $Dq$ values for A and B using the rule of average environment.[7]

If one is interested in compounds which fluoresce, one has to select the ligand A from the left part of the spectrochemical series (small $Dq$ values). That is the

increasing $Dq$ →

| Br, Cl, F, | O, | N , C |
|---|---|---|
| fluorescence only | fluorescence and phosphorescence or phosphorescence only | phosphorescence only |

(1) G. B. Porter and H. L. Schläfer, *Z. Physik. Chem.* (Frankfurt), **40**, 280 (1964).

(2) G. B. Porter and H. L. Schläfer, *Ber. Bunsenges. Physik. Chem.*, **68**, 316 (1964).

(3) L. S. Forster and K. DeArmond, *J. Chem. Phys.*, **34**, 2193 (1961); *Spectrochim. Acta*, **19**, 1687 (1963).

(4) G. B. Porter and H. L. Schläfer, *Z. Physik. Chem.* (Frankfurt), **38**, 227 (1963).

(5) H. L. Schläfer, H. Gausmann, F. Wasgestian, and H. U. Zander, *ibid.*, **51**, 274 (1966).

(6) H. L. Schläfer, H. Gausmann, and H. Witzke, *J. Chem. Phys.*, **46**, 1423 (1967).

(7) See C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962, p 109.

TABLE I

POSITION OF LIGAND FIELD BANDS, VALUES OF THE LIGAND FIELD STRENGTH PARAMETER $\Delta \equiv 10Dq$, AND THE RACAH PARAMETERS $B_{55}$ AND $B_{35}$ FOR INTERELECTRONIC REPULSION[a]

| | Maxima of bands, cm⁻¹ | | | | | |
| | J | I | II | III | $B_{55}$, | $B_{35}$, |
| Compound | $\bar{\nu}_{max}$ (⁴A₂g → ²Eg) | $\bar{\nu}_{max}$ (⁴A₂g → ⁴T₂g) = Δ ≡ 10Dq | $\bar{\nu}_{max}$ (⁴A₂g → a⁴T₁g) | $\bar{\nu}_{max}$ (⁴A₂g → b⁴T₁g) | cm⁻¹ | cm⁻¹ |
|---|---|---|---|---|---|---|
| (NH₄)₃[CrF₆] | 15,670 | 15,060 | 22,780 | 35,100 | 746 | 643 |
| K₂[CrF₅(H₂O)] | 15,130 | 15,850 | 23,310 | 35,490 | 720 | 621 |
| [CrF₃(H₂O)₃] | 14,930 | 16,420 | 23,420 | 37,100 | 710 | 583 |
| | (14,970) | (16,230) | (23,420) | (36,360) | | |
| [CrF₃(H₂O)₃]·0.5H₂O | 15,080 | 16,400 | 23,410 | 38,000 | 718 | 582 |
| [CrF₃(H₂O)₃]·H₂O | 15,040 | 16,340 | 23,470 | 36,500 | 716 | 594 |
| [CrF₃(H₂O)₃]·2H₂O | 14,990 | 16,420 | 23,410 | 36,420 | 713 | 582 |
| [CrF(H₂O)₅][SiF₆] | 14,930 | 16,080 | 22,940 | 38,000 | 710 | 571 |
| | (14,860) | (16,690) | (23,700) | | | |
| [Cr(H₂O)₆]F₃ | 15,150 | 17,270 | 24,100 | 38,000 | 721 | 569 |
| [Cr(H₂O)₆]Cl₃ | 14,810 | 17,450 | 24,570 | 38,150 | 705 | 593 |
| NH₄[CrF₄en] | 14,970 | 17,270 | 23,870 | 37,580 | 712 | 550 |
| | (14,970, 15,050) | (17,450) | (24,390) | (37,310) | | |

[a] In columns 2, 3, 4, and 5 the wavenumbers of the maxima of the intercombination band J and of the three spin-allowed bands I, II, III are given. Values in parentheses refer to solution spectra, the other data to reflectance measurements. $\bar{\nu}_{max}$(I) gives $\Delta \equiv 10Dq$. In columns 6 and 7 the Racah parameters for interelectronic repulsion are seen. They have been deduced using strong field matrix elements, with $C = 4B$, without taking into account off-diagonal elements. $B_{55} = \bar{\nu}_{max}(^4A_{2g} \rightarrow {}^2E_g)/21$; $B_{35} = (\bar{\nu}_{max}(^4A_{2g} \rightarrow a^4T_{1g}) - \bar{\nu}_{max}(^4A_{2g} \rightarrow {}^4T_{2g}))/12$.

reason why we chose F⁻. As the second ligand B H₂O has been taken, which is close to F⁻ in the spectrochemical series. In one case [CrF₄en]⁻ we used ethylenediamine as ligand B.

**Light Absorption.**—The results of measurements of reflectance spectra on crystal powders of the complexes $[CrF_{6-n}(H_2O)_n]^{-3+n}$ ($n = 1, 3, 5, 6$) and of [CrF₄en]⁻ are collected in Table I. Also the ligand field strength parameter $\Delta \equiv 10Dq$ and the Racah parameters of interelectronic repulsion $B_{55}$ and $B_{35}$[8] are reported.

As $[CrF_6]^{3-}$ and $[CrF_5(H_2O)]^{2-}$ undergo aquation to $[CrF_3(H_2O)_3]$ in aqueous solution only the reflectance spectra of crystal powders have been measured. [Cr(H₂O)₆]F₃ and [Cr(H₂O)₆]Cl₃ in aqueous solution show substitution of H₂O by F⁻ or Cl⁻. This can also occur in crystals of [Cr(H₂O)₆]F₃ by irradiation. Therefore reflectance spectra of these complexes have been taken. In the case of the other compounds absorption spectra of solutions have been measured in addition.

All complexes show the three parity-forbidden, spin-allowed quartet → quartet bands indicated by I, II, and III according to increasing energy. They can be classified assuming approximately octahedral microsymmetry as electronic transitions: I, ⁴A₂g → ⁴T₂g; II, ⁴A₂g → a⁴T₁g; III, ⁴A₂g → b⁴T₁g. The assumption of octahedral microsymmetry for the compounds mentioned above is obviously correct, as no splitting of the bands in the case of mixed complexes can be detected. In addition an intercombination band J normally located on the long-wavelength tail of band I is to be seen. It corresponds to a transition ⁴A₂g → ²Eg and usually has a smaller intensity compared to the spin-allowed bands (cf. Figure 2). The intensity of this intercombination band J increases with decreasing

distance $\Delta E$ between the maxima of the long-wavelength spin-allowed band I and the intercombination band J. The reason is that the intercombination band borrows its intensity by way of spin–orbit[9,10] coupling from the nearest quartet → quartet band I. In the case of $[CrF_6]^{3-}$ (cf. Figure 1) its intensity is about the same as the intensity of band I. The intercombination band is located 610 cm⁻¹ at shorter wavelength than band I, $\Delta E = -610$ cm⁻¹. All other compounds in Table I have J at longer wavelengths than I. Also in $[CrF_5(H_2O)]^{2-}$ J and I have intensities of comparable magnitude ($\Delta E = +720$ cm⁻¹). As typical examples Figures 1 and 2 give the reflectance spectra of (NH₄)₃[CrF₆] and NH₄[CrF₄en].

**Luminescence Spectra.**—As is shown in Table II all crystalline compounds investigated (with the exception of [Cr(H₂O)₆]Cl₃) yield fluorescence ⁴T₂g → ⁴A₂g as a broad band without structure. NH₄[CrF₄en] and [Cr(H₂O)₆]F₃ exhibit in addition at shorter wavelengths a narrow-band phosphorescence ²Eg → ⁴A₂g which has in the case of NH₄[CrF₄en] a characteristic vibrational structure (cf. Figure 4). [Cr(H₂O)₆]Cl₃ shows only a weak phosphorescence. Substitution of D₂O for H₂O leads—as Forster[11] has demonstrated—to an increase of luminescence intensity. Therefore besides phosphorescence fluorescence also can be seen in [Cr(D₂O)₆]³⁺. Table II contains the compounds investigated arranged in increasing values of the energy difference $\Delta E$ (column 4). $\Delta E$ goes approximately parallel with $\Delta \equiv 10Dq$ (column 2). The type of luminescence which occurs can be seen in columns 5 and 6. Figures 3 and 4 give as typical examples the luminescence spectra of (NH₄)₃[CrF₆] (fluorescence only)

(8) As to the significance of $B_{55}$ and $B_{35}$, compare, e.g., C. K. Jørgensen, *Advan. Chem. Phys.*, **5**, 67 (1963), and "Structure and Bonding," Vol. 1, 3, Springer, Berlin, 1966.

(9) S. Sugano and Y. Tanabe, *J. Phys. Soc. Japan*, **13**, 880 (1958); Y. Tanabe, *Progr. Theoret. Phys.* (Kyoto), *Suppl.*, **14**, 17 (1960).

(10) K. K. Chatterjee, G. B. Porter, and H. Witzke, Proceedings of the 9th International Conference on Coordination Chemistry, 1966, p 116.

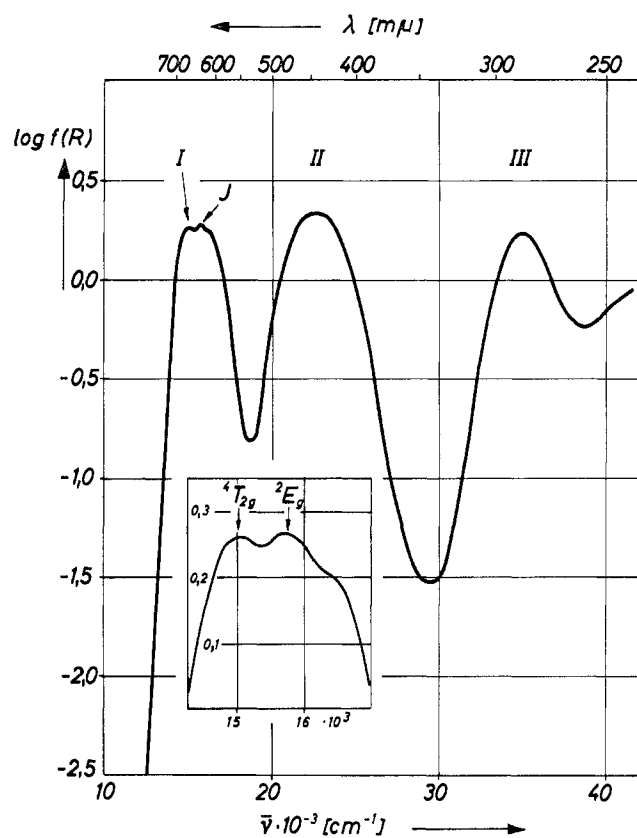(11) K. K. Chatterjee and L. S. Forster, *Spectrochim. Acta*, **20**, 1603 (1964).

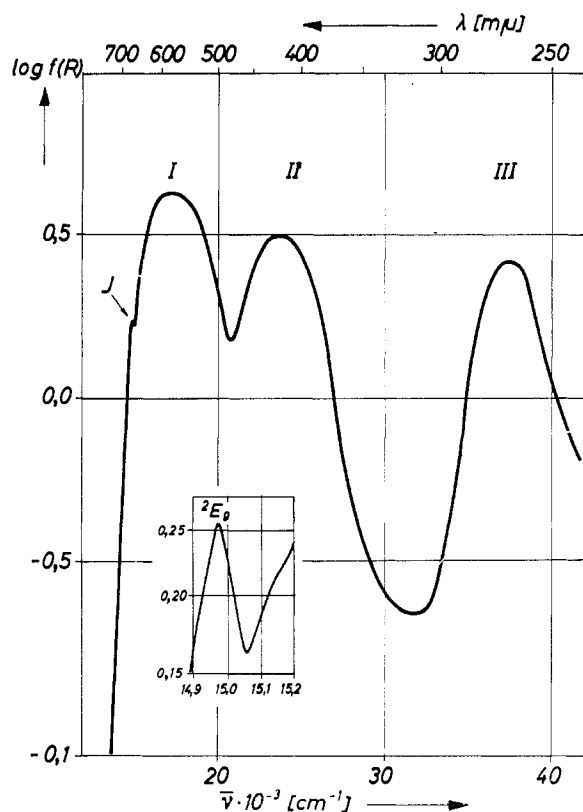Figure 1.—Reflectance spectrum of $(NH_4)_3[CrF_6]$ (standard $BaSO_4$, undiluted sample, room temperature).



Figure 2.—Reflectance spectrum of $NH_4[CrF_4en]$ (standard $BaSO_4$, undiluted sample, room temperature).

TABLE II

LUMINESCENCE BEHAVIOR OF THE COMPOUNDS[a]

| Compound | $\bar{\nu}_{max}(I)$, cm$^{-1}$ | $\bar{\nu}_{max}(J)$, cm$^{-1}$ | $\Delta E = \bar{\nu}_{max}(I) - \bar{\nu}_{max}(J)$, cm$^{-1}$ | Luminescence Phosphorescence $\bar{\nu}_{00}$, cm$^{-1}$ | Fluorescence $\bar{\nu}_{max}$, cm$^{-1}$ |
|---|---|---|---|---|---|
| $(NH_4)_3[CrF_6]$ | 15,060 | 15,670 | −610 | ... | 12,820 |
| $K_2[CrF_5(H_2O)]$ | 15,850 | 15,130 | 720 | ... | 12,650 |
| $[CrF_3(H_2O)_3] \cdot H_2O$ | 16,340 | 15,040 | 1300 | ... | 12,800 |
| $[CrF_3(H_2O)_3] \cdot 0.5H_2O$ | 16,420 | 15,080 | 1340 | ... | 12,800 |
| $[CrF_3(H_2O)_3] \cdot 2H_2O$ | 16,420 | 14,990 | 1430 | ... | 12,800 |
| $[CrF_3(H_2O)_3]$ | 16,420 | 14,930 | 1490 | ... | 12,500 |
| $[CrF(H_2O)_5][SiF_6]$ | 16,690 | 14,860 | 1830 | ... | 11,200 |
| $[Cr(H_2O)_6]F_3$ | 17,270 | 15,150 | 2120 | 14,550 | 13,100 |
| $NH_4[CrF_4en]$ | 17,270 | 14,970 | 2300 | 15,010 | 13,430 |
| $[Cr(H_2O)_6]Cl_3$ | 17,450 | 14,810 | 2640 | 14,520 | ... |

[a] In columns 2 and 3 the maxima of the long-wavelength spin-allowed band I and the intercombination band J at room temperature are given. Column 4 shows the difference $\Delta E$ between both maxima. From columns 5 and 6 can be seen which type of luminescence occurs and at what wavenumber. The phosphorescence is referred to $\bar{\nu}_{00}$ the maximum of the 0–0 band, the fluorescence to the maximum of the broad-band fluorescence, both at liquid air temperature.
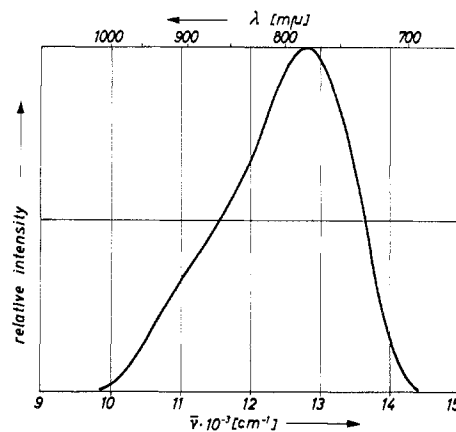


Figure 3.—Fluorescence spectrum ($^4T_{2g} \rightarrow {}^4A_{2g}$) of $(NH_4)_3[CrF_6]$ (−186°).
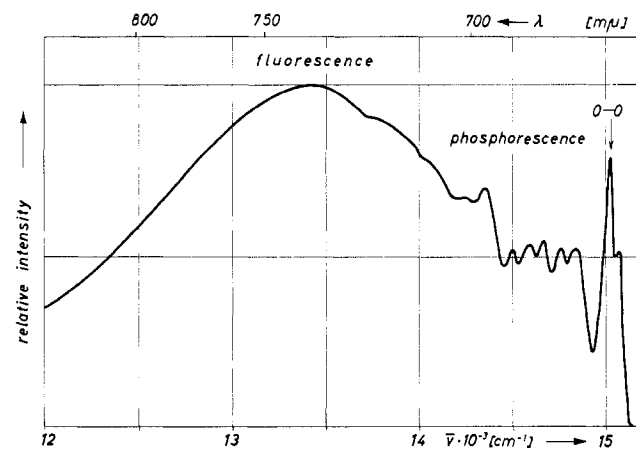


Figure 4.—Luminescence spectrum (phosphorescence and fluorescence) of $NH_4[CrF_4en]$ (−186°).

and $NH_4[CrF_4en]$ (fluorescence and phosphorescence). The maximum of the 0–0 band of the phosphorescence at liquid air temperature lies at 15,010 cm$^{-1}$. The maximum of the intercombination band at room tem-

perature is located at 14,970 cm$^{-1}$. Both maxima coincide within experimental error. An antistokes band of small intensity is seen at 15,070 cm$^{-1}$. It has a different temperature dependence of intensity than the main part of the phosphorescence ($\bar{\nu} \leqslant$ 15,010 cm$^{-1}$), which consists of stokes bands. From Figure 4 it can be seen that part of the vibrational structure of the phosphorescence is superposed on the broad-band fluorescence. Table III gives in column 1 the observed band maxima of the phosphorescence, the relative intensity in column 2, and the difference between the band maxima and the 0–0 band $\Delta\bar{\nu} = \bar{\nu}_{00} - \bar{\nu}$ in column 3. In Table IV the measured infrared frequencies of NH$_4$[CrF$_4$en] which are of interest with respect to the vibrational structure of the phosphorescence are summarized. Some of them correspond to $\Delta\bar{\nu}$ values of Table III, column 3 (*cf.* column 4).

### TABLE III
#### LUMINESCENCE OF SOLID NH$_4$[CrF$_4$en] ($-186°$)$^d$

| $\bar{\nu}_{max}$, cm$^{-1}$ | Rel intens | $\bar{\nu}_{00} - \bar{\nu}_{max} = \Delta\bar{\nu}$, cm$^{-1}$ | $\bar{\nu}_{ir}$, cm$^{-1}$ |
|---|---|---|---|
| | | Phosphorescence | |
| 15,070$^a$ | 50.4 | −60 | |
| 15,010$^b$ | 79.9 | 0 | |
| 14,830 | 51.3 | 180 | |
| 14,760 | 51.3 | 250 | 250 |
| 14,680 | 53.4 | 330 | 330 |
| 14,580 | 52.7 | 430 | 434 |
| 14,520 | 51.3 | 490 | 489 |
| 14,345 | 66.6 | 665 | 650 |
| 14,270 | 63.8 | 740 | 728 |
| ∼14,100$^c$ | ∼78.9$^c$ | 910 | |
| ∼13,750$^c$ | ∼91.9$^c$ | 1260 | 1280 |
| | | Fluorescence | |
| 13,430 | 100.0 | | |

$^a$ Antistokes band. $^b$ 0–0 band. $^c$ These bands can be seen only as inflections on the short-wavelength tail of the broad-band fluorescence. $^d$ In columns 1 and 2 the maxima of the observed bands and the relative intensities are reported referred to the fluorescence maximum at 13,430 cm$^{-1}$ taken as 100. Column 3 shows the differences between the wavenumber of the 0–0 band and the wavenumbers of the other band maxima of the phosphorescence. Column 4 gives infrared frequencies (*cf.* Table IV) which correspond to $\Delta\bar{\nu}$.

The interesting temperature dependence of the intensity of fluorescence and phosphorescence and the characteristic differences between the crystalline compound and the rigid solution (solvent glycerin–H$_2$O 1:1) will be discussed elsewhere. The lifetime obtained from the experimental decay of the phosphorescence for NH$_4$[CrF$_4$en] is 2 × 10$^{-7}$ sec at liquid air temperature.

### Discussion

As is expected by the rule[6] for those chromium(III) compounds which have $\Delta E < $ ∼1700–1800 cm$^{-1}$, the mixed complexes [CrF$_{6-n}$(H$_2$O)$_n$]$^{-3+n}$ ($n$ = 1, 3, 5) and the hexafluoro complex ($n$ = 0) fluoresce. [Cr-(H$_2$O)$_6$]F$_3$ as well as NH$_4$[CrF$_4$en] show both types of emission, fluorescence and phosphorescence, as predicted for complexes which have ∼1700–1800 < $\Delta E <$ ∼2400 cm$^{-1}$. Also [Cr(urea)$_6$]$^{3+}$ ($\Delta E$ =

### TABLE IV
#### INFRARED FREQUENCIES OF NH$_4$[CrF$_4$en]$^a$

| $\bar{\nu}_{ir}$, cm$^{-1}$ | | | Assignment |
|---|---|---|---|
| 205 | | s | |
| 225 | | s | |
| 250 | + | s | |
| 280 | | m | |
| 312 | | m | |
| 330 | + | m | |
| 360 | | m | |
| 404 | | m | |
| 434 | + | s | |
| 489 | + | vs (broad) | st Cr–F |
| 526 | | vs | st Cr–N |
| 550 | | vs | st Cr–N |
| 632 | | m | ot (312) |
| 650 | + | m | |
| 728 | + | s | r CH$_2$ |
| 870 | | w | ot (434) |
| 886 | | w | |
| 977 | | m | |
| 1005 | | w | |
| 1046 | | vs | st C–N |
| 1088 | | m | |
| 1119 | | s | st C–N |
| 1170 | | m | |

$^a$ vs, very strong; s, strong; m, medium; w, weak; st, stretching; r, rocking; ot, overtone. + Corresponds to vibrational frequencies $\Delta\bar{\nu} = \bar{\nu}_{00} - \bar{\nu}_{max}$ in the phosphorescence spectrum (*cf.* Table III, columns 3 and 4).

1770 cm$^{-1}$), [Cr(antipyrine)$_6$]$^{3+}$ ($\Delta E$ = 1800 cm$^{-1}$), and [CrCl$_3$(py)$_3$] ($\Delta E$ = 2100 cm$^{-1}$) belong to the group of compounds which exhibit fluorescence and phosphorescence.

Figure 5 gives potential-energy curves for the case of fluorescence only (left side) and for the case of fluorescence and phosphorescence (right side). The curves represent schematically a cut through the potential energy surfaces of the respective electronic states in the direction of a totally symmetric internuclear displacement coordinate. The type of luminescence observed depends on the position of the intersection point P of the curves for $^4T_{2g}$ and $^2E_g$ and on the energies of the minima of both curves.

Fluorescence only occurs if the minimum of the $^4T_{2g}$ curve is sufficiently lower in energy than the minimum of the $^2E_g$ curve and point P is located near the bottom of this curve (that means within a few thousand wavenumbers). Thus most of the complexes after irradiation will finally be in $^4T_{2g}$, where they can emit fluorescence $^4T_{2g} \rightarrow {}^4A_{2g}$ or undergo radiationless transition to the ground state.

If both minima occur at about equal energies and if the intersection point P has about equal distances to both minima a distribution of the complex ions in both states $^4T_{2g}$ and $^2E_g$ takes place. Thus simultaneous fluorescence and phosphorescence ($^2E_g \rightarrow {}^4A_{2g}$) can be observed. The distances of P to the minima of the two curves for $^4T_{2g}$ and $^2E_g$ should be small, not more than a few thousand wavenumbers. As discussed elsewhere[6] the energy difference between the minima of both curves depends on the ligand field strength parameter $Dq$. Increasing values of $Dq$ give increasing energy
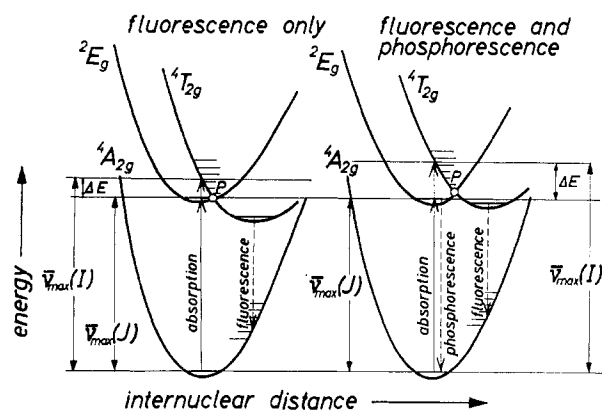
Figure 5.—Schematic potential energy curves of chromium(III) complexes for the case of fluorescence only and for the case of simultaneous fluorescence and phosphorescence (octahedral microsymmetry).

differences between the minima and also approximately increasing values of the experimentally available quantity $\Delta E$. Also the intersection point P is assumed to appear the higher above the minimum of $^2E_g$ the greater $Dq$. The reason is that the energy of $^2E_g$, considering the strong-field approximation and neglecting off-diagonal elements, is independent of $Dq$.

The lifetime of the doublet state $\tau = 2 \times 10^{-7}$ sec of $NH_4[CrF_4en]$ determined from the decay of the emission at 15,010 cm$^{-1}$ is remarkably short for a phosphorescence. Most of the measured lifetimes are in the range $\sim 3 \times 10^{-3}$ to $\sim 3 \times 10^{-5}$ sec,[11] but refer to substances which only phosphoresce, that means with greater $Dq$ and $\Delta E$. As far as data are available the lifetimes of the doublet state seem to increase approximately with increasing $\Delta E$. Therefore one should expect in the case of comparatively small $\Delta E$, as in $NH_4[CrF_4en]$, a short lifetime for this electronic state.

### Experimental Section[12]

(1) **Preparations.**—All preparations of fluoro complexes have been done in polyethylene vessels. The suction filters for filtrations were covered with paraffin. Except for $(NH_4)_3$-$[CrF_6]$ the preparations were done as described in the literature cited below.

$(NH_4)_3[CrF_6]$.[13]—A solution of 80 g of $NH_4F$ in 200 ml of $H_2O$ was heated to 90°. Into this solution a concentrated solution of 20 g of $[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$ in 40 ml of $H_2O$ was dripped under vigorous stirring. Instantaneously dark green crystals separated which were removed by suction. The crystals consist of a mixture of $(NH_4)_3[CrF_6]$ and $(NH_4)_2[CrF_5(H_2O)]$. Washing of the product with water yielded $[CrF_5(H_2O)]^{2-}$. Therefore the crystals were dried at 110° without washing. Then after mixing with one-fifth of their weight with $NH_4F$, the mixture was held for 24 hr at 140° under oil pump vacuum in order to displace all the complex bound water. Also in the course of this procedure the excess of $NH_4F$ was eliminated by sublimation. The latter operation has been repeated until constant weight was obtained. The complex crystallizes in small slight green octahedrons. *Anal.* Calcd: Cr, 23.63; F, 51.79; $NH_4$, 24.48. Found: Cr, 23.5; F, 51.9; $NH_4$, 24.5.

$K_2[CrF_5(H_2O)]$.[14]—Fine pale green crystals were obtained. *Anal.* Calcd: K, 32.15; Cr, 21.38; F, 39.06. Found: K, 32.0; Cr, 20.8; F, 38.7.

$[CrF_3(H_2O)_3]$.[15]—The product obtained according to the method of Talipov and Antipov[15] was recrystallized from hot water by adding an equal amount of $CH_3OH$. A fine olive-green powder was obtained. *Anal.* Calcd: Cr, 31.95; F, 34.95. Found: Cr, 31.8; F, 35.0.

$[CrF_3(H_2O)_3] \cdot xH_2O$, $x = \frac{1}{2}$, 1, 2.[16,17]—The compounds which have been prepared by Werner and Costachescu[16] and later by Birk[17] were formulated originally as $[Cr(H_2O)_6][CrF_6] \cdot xH_2O$, $x = 1, 2, 4$. We believe that the appropriate formulation is $[CrF_3(H_2O)_3] \cdot xH_2O$, $x = \frac{1}{2}$, 1, 2. The absorption spectra of the compounds cannot be obtained by a superposition of the spectra of $[CrF_6]^{3-}$ and $[Cr(H_2O)_6]^{3+}$. They agree closely with the spectrum of $[CrF_3(H_2O)_3]$ prepared according to Talipov and Antipov.[15]

$[CrF(H_2O)_5][SiF_6]$.[18]—Green hygroscopic crystals were formed, which decompose easily under normal pressure by loss of $SiF_4$. *Anal.* Calcd: Cr, 17.15; F, 6.27; $SiF_6$, 46.86. Found: Cr, 18.0; F, 6.6; $SiF_6$, 45.2.

$[Cr(H_2O)_6]F_3$.[18]—Violet crystals were obtained, which are not stable at room temperature as an exchange of $H_2O$ by $F^-$ occurs. At 0° this process runs slowly. The exchange can be seen by a change in the color of the crystals from violet to green. Also irradiation causes this ligand exchange.

$[Cr(H_2O)_6]Cl_3$.[19]—Gray-blue crystals were obtained. A slow ligand exchange of $H_2O$ by $Cl^-$ occurs in the crystals at room temperature.

$NH_4[CrF_4en]$.[20]—Dark blue crystals were obtained. *Anal.* Calcd: Cr, 25.23; F, 36.86; C, 11.65; H, 5.86; N, 20.37. Found: Cr, 24.6; F, 36.7; C, 11.8; H, 5.9; N, 20.4.

(2) **Absorption and Reflectance Spectra.**—Spectra of finely powdered samples of the complexes have been measured with a Cary Model 14 spectrophotometer with reflectance attachment 1411. In the spectral region <310 m$\mu$ a Zeiss PMQ II with a special equipment RA2 and a photomultiplier RCA 1 P 28 has been used for the reflectance measurements. In Figures 1 and 2 the logarithm of the Kubelka–Munk function $f(R)$[21] is plotted vs. wavenumbers. The spectra were measured against $BaSO_4$ or MgO as standards. Those substances which are hygroscopic were handled in a glove box under a dry atmosphere. The bowls for containing the powders during the measurements were covered with quartz disks, which are attached by stopcock grease. The solution spectra were measured with a Cary Model 14.

(3) **Infrared Spectra.**—Perkin-Elmer instruments, Type 521 or 225, have been used. Samples in KBr pellets or in Nujol between CsI windows were investigated.

(4) **Luminescence Measurements.**—Luminescence spectra have been obtained at liquid air temperature with an apparatus constructed in this laboratory which is described in detail elsewhere.[22] Powdered samples of the compounds in special cuvettes were measured. In Figures 3 and 4 relative luminescence intensites are plotted vs. wavenumbers.

(5) **Lifetime Measurements.**—The oscillographic method for the determination of lifetimes was used. Excitation was done with a ruby laser, using the second harmonics. Photographs of the decay curves on the screen of the oscillograph were taken and analyzed.

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