bonds. A similar effect has been observed on two compounds in acetonitrile solutions also investigated during this study. The reflectance spectra of $(C_5H_6N)_3[TiCl_6]$ and $(C_5H_6N)_2[TiCl_5CH_3CN]$ have strong maxima at 12,900 and 14,000 cm^{-1}, respectively. In solution these bands appear at higher energies at 13,700 cm^{-1} (+800

cm^{-1}) for the hexachloro complex and at 15,200 cm^{-1} (+1200 cm^{-1}) for the pentachloroacetonitrile complex. Thus, acetonitrile has the opposite effect of methanol.

Excitation Energy Transfer from Chromium in the Cation to Chromium in the Anion in Some Crystalline Compounds: $[CrA_6][Cr(CN)_6]\cdot xH_2O$

BY HANS L. SCHLÄFER, HANS GAUSMANN, AND CHRISTIAN H. MÖBIUS

Luminescence measurements indicate, in a series of double complex salts $[CrA_6][Cr(CN)_6]\cdot xH_2O$ and $[Cr(A-A)_3][Cr(CN)_6]\cdot xH_2O$, where A and (A-A) are mono- or bidentate neutral ligands with oxygen or nitrogen as coordinating atoms, an excitation energy transfer from chromium in the cation (donor, D) to chromium in the anion (acceptor, A). Relative emission intensities and lifetimes of the phosphorescence $^2E_g \rightarrow {}^4A_{2g}$ of the acceptor are reported. It is suggested that a doublet–doublet transfer D*(doublet) + A(quartet) → D(quartet) + A*(doublet) is operating. Possible types of mechanism are discussed.

A. Introduction

In a previous paper[1] we reported an excitation energy transfer from the cation to the anion in the double complex salt $[Cr(OC(NH_2)_2)_6][Cr(CN)_6]\cdot 3H_2O$. This was concluded on the basis of luminescence measurements from the fact that excitation of the cationic component, *i.e.*, absorption in a spectral region where only the hexaureachromium(III) entity absorbed, yielded a phosphorescence emission $^2E_g(an) \rightarrow {}^4A_{2g}(an)$ located in the hexacyano part. The corresponding phosphorescence emission of the cation $^2E_g(ct) \rightarrow {}^4A_{2g}(ct)$ and also the fluorescence $^4T_{2g}(ct) \rightarrow {}^4A_{2g}(ct)$ which are seen in $[Cr(ur)_6]Cl_3\cdot H_2O$ or $[Cr(ur)_6](ClO_4)_3$ were both totally quenched in the double salt. The emission of the $Cr(CN)_6{}^{3-}$ part in the double salt was greatly increased compared to the emission of $K_3[Cr(CN)_6]$.

The present work has been undertaken to clarify the luminescence behavior of similar double complex salts of the type $[CrA_6][Cr(CN)_6]\cdot xH_2O$ or $[Cr(A-A)_3][Cr(CN)_6]\cdot xH_2O$, where A is a monodentate and (A-A) a bidentate neutral molecule. Compounds with oxygen or nitrogen coordination of the cationic Cr^{3+} and with different distances $Cr^{3+}(ct)-Cr^{3+}(an)$ have been investigated in the hope of obtaining information about the relationships between the efficiency of energy transfer, the cation–anion distance, and the nature of the coordinating atom of the cation. These double salts have been selected to fulfill the following conditions. (1) The absorption spectra of the double salts should be very nearly a superposition of the spectra of the indi-

vidual constituent ions. (2) A spectral region should exist where only the cationic part of the double salts absorbs. At an appropriate wavelength, excitation of only the cation is then possible. (3) The lowest doublet state $^2E_g(an)$ of $Cr(CN)_6{}^{3-}$ from which the emission originates should be located at somewhat lower energy than the lowest doublet $^2E_g(ct)$ of the cationic component.

On mixing aqueous solutions of $Cr(CN)_6{}^{3-}$ with $CrA_6{}^{3+}$ or $Cr(A-A)_3{}^{3+}$ [A = urea (ur), antipyrine (atp), imidazolone (imid), or ammonia; (A-A) = ethylenediamine (en), propylenediamine (pn), or trimethylenediamine (tn), respectively], one easily obtains crystalline precipitates of the corresponding double complex salts.

B. Results and Discussion

The reflectance spectra of the double salts are very nearly a superposition of the individual spectra of the cation and the anion (Figures 1–7), indicating little or no coupling between the two chromium(III) centers. Therefore it is possible to discuss the energy states of the double complex salts from the point of view of two Cr^{3+} entities, each of which consists of a chromium(III) metal ion surrounded octahedrally by six identical ligands A or CN^- or by three equal bidentate ligands (A-A). Also it seems reasonable to regard the electronic excitation of the double complex salts as at least temporarily completely localized in the cation or the anion part.

Figures 8 and 9 show the term diagrams for the different compounds, obtained using the spectral data of Figures 1–7. On the right the electronic energy states

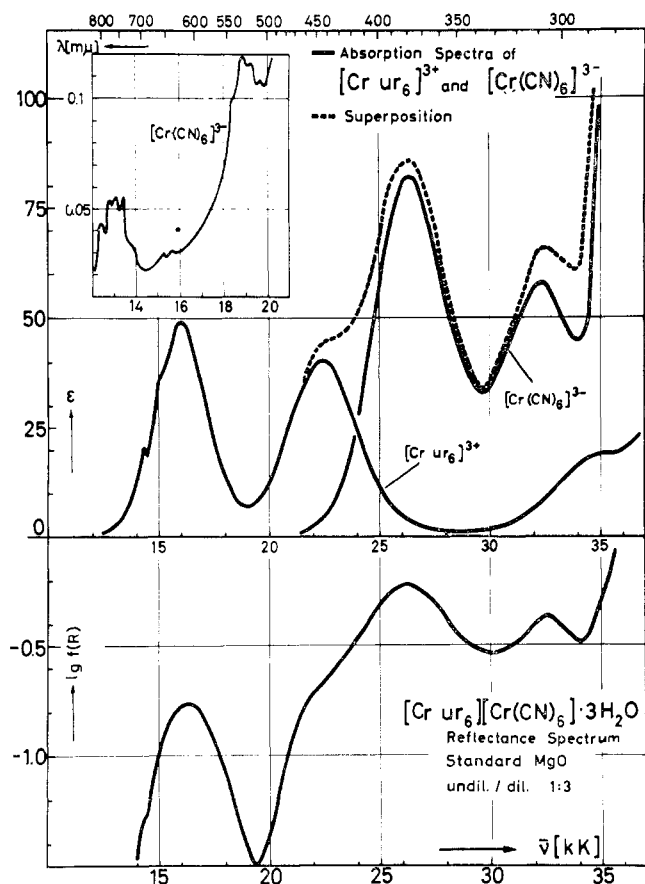(1) H. L. Schläfer, H. Gausmann, and H. Witzke, *J. Chem. Phys.*, **46**, 1423 (1967).

Figure 1.—Light absorption of $Cr(ur)_6{}^{3+}$ and $Cr(CN)_6{}^{3-}$ and of $[Cr(ur)_6][Cr(CN)_6]\cdot 3H_2O$. (All spectra in Figures 1–7 were run at room temperature.)

Figure 2.—Light absorption of $Cr(imid)_6{}^{3+}$ and $Cr(CN)_6{}^{3-}$ and of $[Cr(imid)_6][Cr(CN)_6]$.

of the hexacyano part are shown and on the left are seen the energy states of the different cation components. Dashed lines indicate positions of the doublet states derived from the respective intercombination bands in absorption. These lines roughly represent the energy of the zero vibrational level of the corresponding electronic state, because the electronic transitions take place between states which have potential energy surfaces with minima at approximately the same values of the corresponding normal coordinates. The ground state and the doublet states arise in the strong ligand field approximation from the one-electron configurations $t_{2g}{}^3$ if electron repulsion is taken into account. Only those doublets are shown whose positions can be taken from the corresponding intercombination bands. For most of the cations the higher doublets $^2T_{1g}$ and $^2T_{2g}$ cannot be located experimentally because the respective intercombination bands are hidden under the tail of the broad $^4A_{2g} \rightarrow {}^4T_{2g}$ band.

Solid lines give the energies of the quartet states derived from the maxima of the respective broad spin-allowed absorption bands. Because the excitation on absorption in these cases goes to higher vibrational levels (potential energy surfaces with different values of the internuclear coordinates for the minima) the zero vibrational level lies always at lower energy, at least ~2000 cm⁻¹, the half-width of the bands, which is indicated by the hatched areas. Ground state and excited

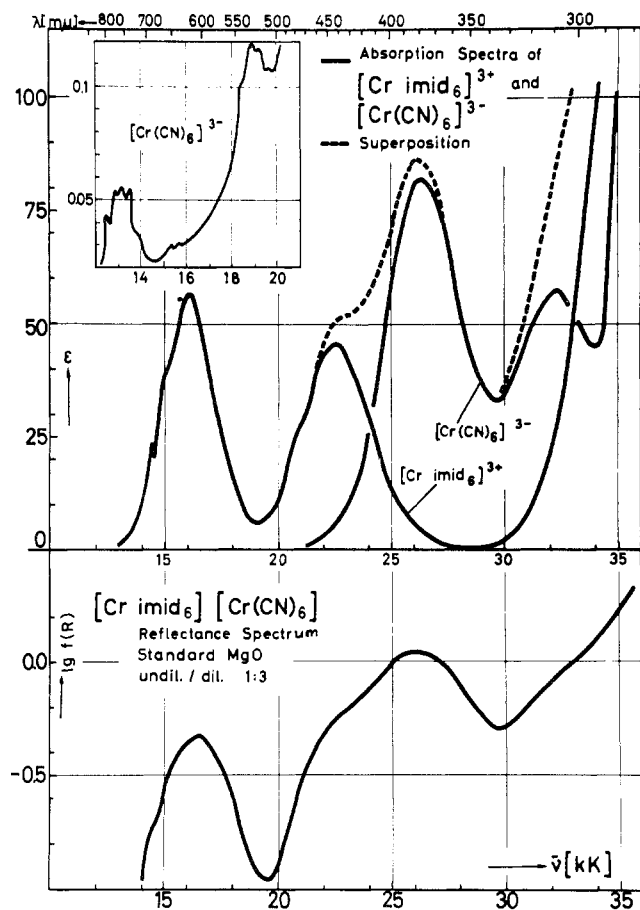quartet states arise from different one-electron configurations $t_{2g}{}^3$ and $t_{2g}{}^2e_g$ or $t_{2g}e_g{}^2$. The three wavelengths which were used for the energy-transfer experiments are indicated by arrows on the left of the diagrams in Figures 8 and 9.

As can be seen from Figures 8 and 9 the first excited quartet state of the cation $^4T_{2g}(ct)$ lies in all of the double complex salts below that of the anion $^4T_{2g}(an)$, but the lowest doublet level of the cation $^2E_g(ct)$ lies above that of the anion $^2E_g(an)$. Therefore it is possible using radiation of appropriate wavelength to excite selectively only the cation (absorption in the very weak intercombination bands $^2A_{2g} \rightarrow {}^2E_g$, $^2T_{1g}$ of cation and anion is negligible). Thus all of these compounds fulfill the conditions mentioned in the Introduction.

All of the double complex salts exhibit luminescence behavior paralleling that of $[Cr(ur)_6][Cr(CN)_6]\cdot 3H_2O$ and clearly indicative of an excitation energy transfer from Cr^{3+} of the cation (donor) to Cr^{3+} of the anion (acceptor). (See Figures 10–16.) In the following discussion the luminescence properties of a typical example, the antipyrine double salt $[Cr(atp)_6][Cr(CN)_6]$, are discussed in some detail. The other compounds show, with the minor exceptions mentioned below, a similar behavior. [In Figures 10–16 λ_{exc} is the wavelength of the exciting light. In the case of $[Cr(en)_3]$-$[Cr(CN)_6]\cdot 2H_2O$, $[Cr(tn)_3][Cr(CN)_6]\cdot 2H_2O$, and $[Cr(pn)_3][Cr(CN)_6]\cdot 4H_2O$, the structure of the phos-
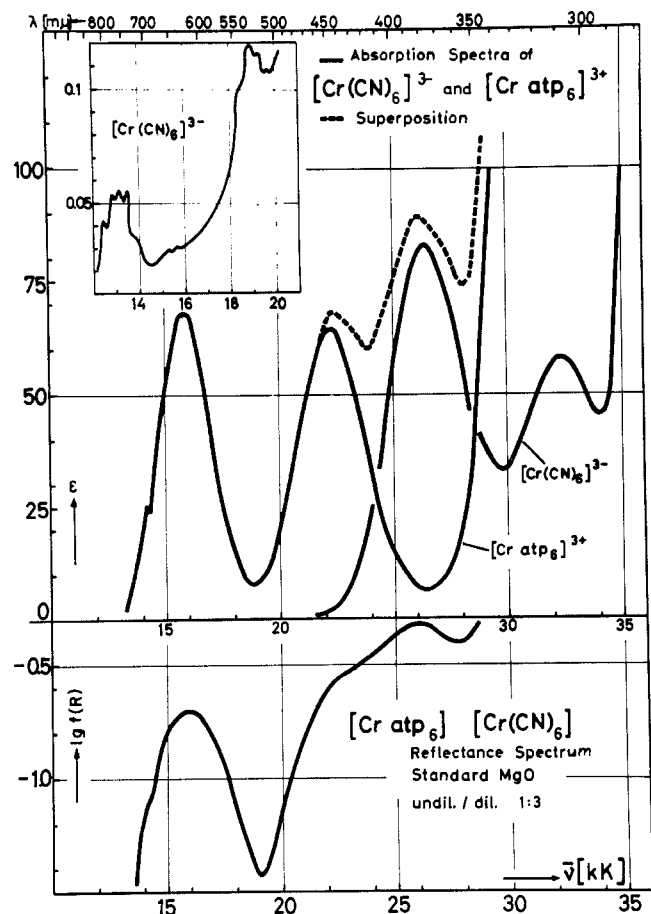
Figure 3.—Light absorption of $Cr(atp)_6^{3+}$ and $Cr(CN)_6^{3-}$ and of $[Cr(atp)_6][Cr(CN)_6]$.

Figure 4.—Light absorption of $Cr(NH_3)_6^{3+}$ and $Cr(CN)_6^{3-}$ and of $[Cr(NH_3)_6][Cr(CN)_6]$.

phorescence depends on the wavelength of the exciting light; therefore two luminescence spectra for different wavelengths of the exciting radiation are given.]

When $K_3[Cr(CN)_6]$ in crystalline form at 77°K is excited by irradiation with light of wavelengths corresponding to absorption in the spin-allowed, parity-forbidden d → d bands, or in the ultraviolet charge-transfer band, it emits a narrow-band phosphorescence ^2E_g → $^4A_{2g}$ with characteristic vibrational structure at 11,389–12,561 cm^{-1} (Figure 12). However, irradiation with light of 580 mμ (~17.5 kK) gives no emission since there is no appreciable absorption in this spectral region (Figure 3). Similarly irradiation of $[Cr(atp)_6](ClO_4)_3$ in the d → d bands or the ultraviolet charge-transfer band at 77°K gives rise to a phosphorescence ^2E_g → $^4A_{2g}$ at 13,405–14,065 cm^{-1}, in addition to a broad-band fluorescence $^4T_{2g}$ → $^4A_{2g}$ at 12,500 cm^{-1} (Figure 12).

If one now irradiates the double salt $[Cr(atp)_6][Cr(CN)_6]$ with 580-mμ light, the phosphorescence $^2E_g(ct)$ → $^4A_{2g}(ct)$ and also the fluorescence $^4T_{2g}(ct)$ → $^4A_{2g}(ct)$ of the cation part are totally quenched, whereas for the phosphorescence of the anion part $^2E_g(an)$ → $^4A_{2g}(an)$ a strong signal is seen. The same happens if the irradiation is done with light of 435 mμ (Figure 12), where both cation and anion absorb. Since irradiation with 580 (or 610) mμ excites the compound to $^4T_{2g}(ct)$ localized within the cation (donor) (Figure 8), then clearly an energy transfer to $^2E_g(an)$ localized within

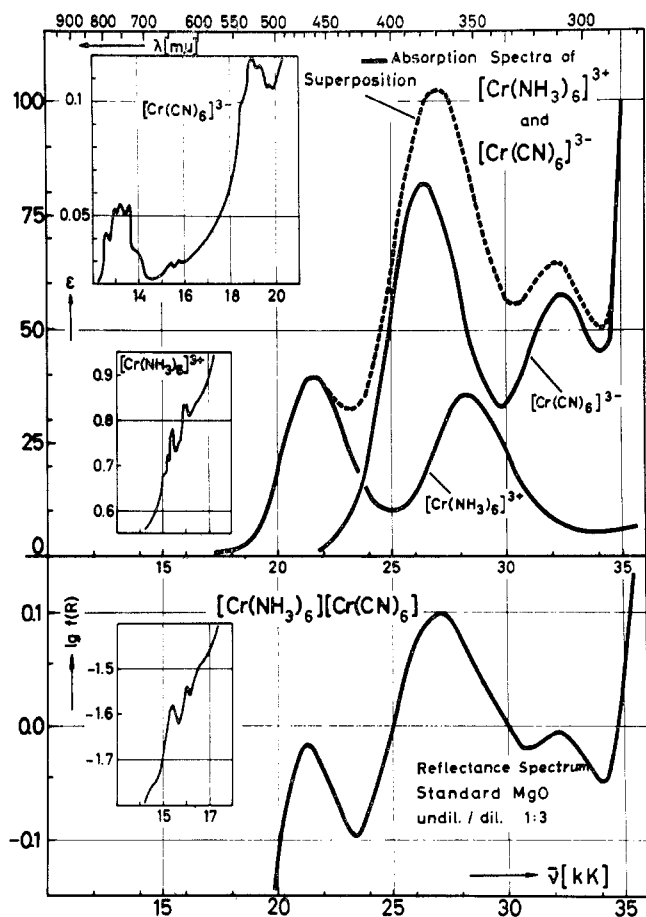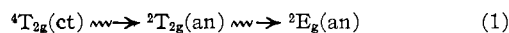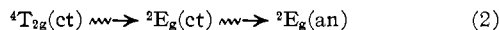the anion (acceptor) takes place, followed by the phosphorescence emission $^2E_g(an)$ → $^4A_{2g}(an)$. In principle, this energy transfer can take place directly from $^4T_{2g}(ct)$

$$^4T_{2g}(ct) \rightsquigarrow ^2T_{2g}(an) \rightsquigarrow ^2E_g(an) \qquad (1)$$

or from $^2E_g(ct)$

$$^4T_{2g}(ct) \rightsquigarrow ^2E_g(ct) \rightsquigarrow ^2E_g(an) \qquad (2)$$

[Quartet–quartet transfer is unlikely because of the energetic positions of $^4T_{2g}(ct)$ and $^4T_{2g}(an)$ (cf. Figures 8 and 9).] In the case of irradiation with 435 mμ the donor is excited to a$^4T_{1g}(ct)$ (Figure 8). The absorption curves of the pure components (Figure 3) show that part of the molecules are expected directly to populate $^4T_{2g}(an)$. Excitation energy transfer to $^2E_g(an)$ from a$^4T_{1g}(ct)$ is then expected to occur by internal conversion from a$^4T_{1g}$ to $^4T_{2g}(ct)$ followed by process 1 or 2.

Because of its relatively long lifetime, the doublet state is in general a more likely candidate to participate in energy-transfer processes than the relatively short-lived quartet state. Consequently we believe that an excitation energy transfer proceeds by way of $^2E_g(ct)$ $\rightsquigarrow$ $^2E_g(an)$, which means a doublet–doublet transfer

D*(doublet) + A(quartet) ⟶ D(quartet) + A*(doublet)
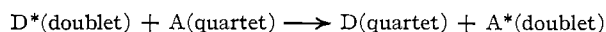
is operating, where D and A are the abbreviations for donor and acceptor. This process obeys the Wigner

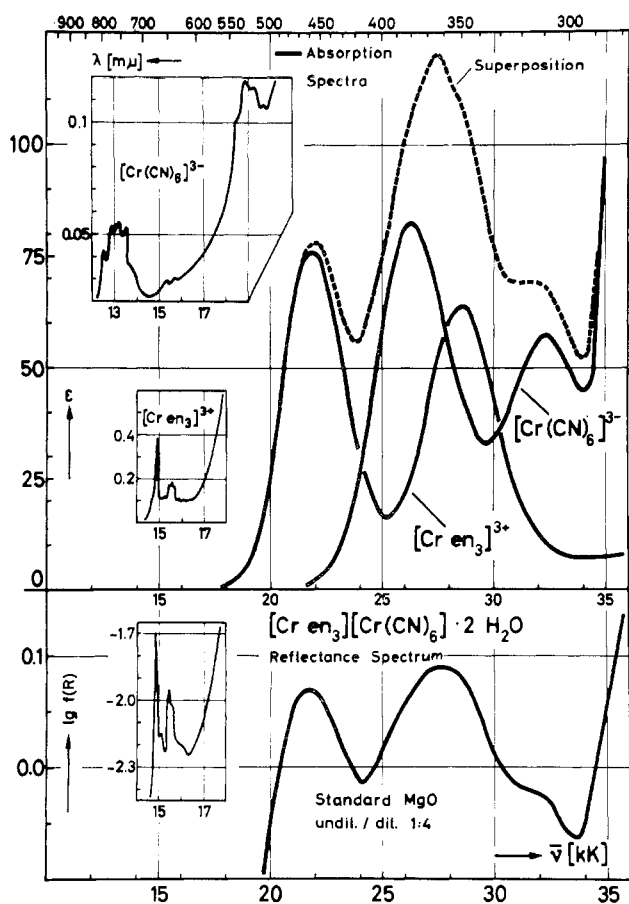Figure 5.—Light absorption of $Cr(en)_3{}^{3+}$ and $Cr(CN)_6{}^{3-}$ and of $[Cr(en)_3][Cr(CN)_6] \cdot 2H_2O$.
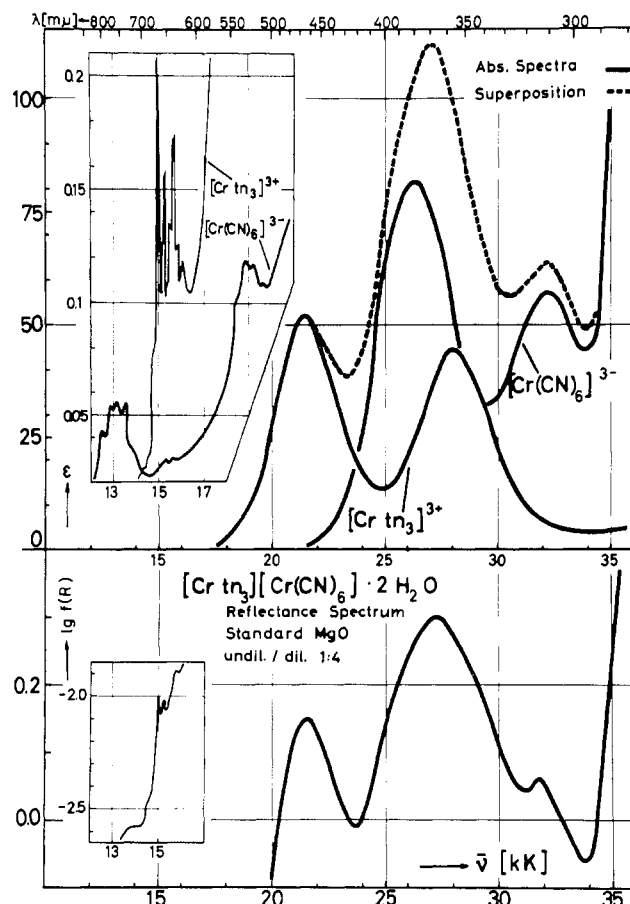
Figure 6.—Light absorption of $Cr(tn)_3{}^{3+}$ and $Cr(CN)_6{}^{3-}$ and of $[Cr(tn)_3][Cr(CN)_6] \cdot 2H_2O$.

spin-conservation rule, whereas a quartet–doublet transfer

$$D^*(\text{quartet}) + A(\text{quartet}) \longrightarrow D(\text{quartet}) + A^*(\text{doublet})$$
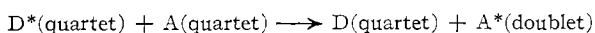
violates the rule and therefore is less likely.

It is seen from Figure 12 that the vibrational structure which is observed in the emission spectrum of K_3-$[Cr(CN)_6]$ is smeared out to a considerable extent in the spectrum of the double salt. Also it is remarkable that the intensity of the acceptor phosphorescence $^2E_g(\text{an}) \rightarrow$ $^4A_{2g}(\text{an})$ taken from the current of the photomultiplier at the wavelength of the most intense band is about 10 times greater than the phosphorescence intensity of K_3-$[Cr(CN)_6]$ (see the Experimental Section).

The behavior of the other double complex salts is very nearly the same as that of $[Cr(atp)_6][Cr(CN)_6]$. Irradiation with light which is only absorbed by the donor component gives in all of the compounds the characteristic phosphorescence of the acceptor part. The donor emission is completely quenched (Figures 10–16). The vibrational structure of the phosphorescence to be seen in $K_3[Cr(CN)_6]$ more or less disappears in all of the double salts, but the effect is particularly strongly marked in $[Cr(atp)_6][Cr(CN)_6]$ (Figure 12), $[Cr-(imid)_6][Cr(CN)_6]$ (Figure 11), and $[Cr(pn)_3][Cr(CN)_6] \cdot 4H_2O$ (Figure 16).

Before going on to discuss the results on relative intensity and half-life of the emissions in the series of

double salts, it is important to recognize that these phenomena can be very sensitive to impurities. Because of the fact that all of the double salts are very insoluble and are prepared as fine precipitates by mixing solutions of the soluble constituent components, it is not possible to purify them by recrystallization. However, the component salts which were used for the preparations were recrystallized several times for purification. Variation of intensity and lifetime values of samples of different preparations of the double salts were in no case more than 20%.

In Table I, column 4, the amplification factors of the phosphorescence are seen, *i.e.*, the relation of the relative intensities of the double salt to the emission of K_3-$[Cr(CN)_6]$ (see the Experimental Section). In case of oxygen coordination of Cr^{3+} in the donor part, the intensity of the emission of the double salts is always considerably increased compared to that of $K_3[Cr(CN)_6]$. This is not observed in case of nitrogen coordination of Cr^{3+} in the donor, where both intensities are of the same magnitude.

By inspection of the radii of the different ions and molecules which build up to double salts, crude values of the distances between the two Cr^{3+} ions can be estimated. They give approximately the distances over which the energy transfer takes place. These distances are given in column 5 of Table I together with the amplification, which increases in case of the oxygen-co-
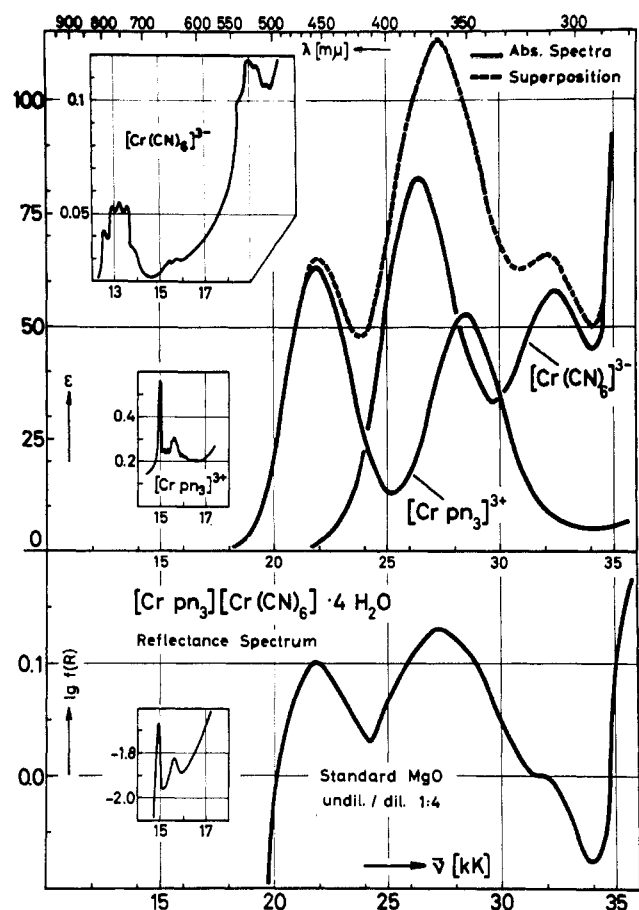
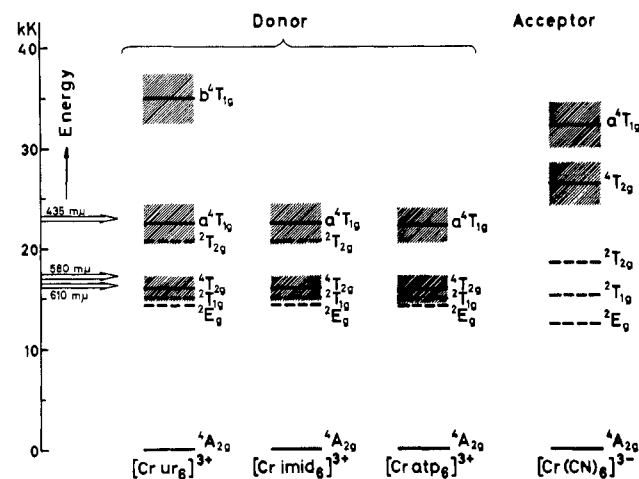Figure 7.—Light absorption of $Cr(pn)_3{}^{3+}$ and $Cr(CN)_6{}^{3-}$ and of $[Cr(pn)_3][Cr(CN)_6]\cdot 4H_2O$.

Figure 8.—Term diagram for discussion of the energy transfer in $[CrA_6][Cr(CN)_6]\cdot xH_2O$ (oxygen coordination of the donor part).

ordinated compounds with decreasing chromium–chromium distance. In case of nitrogen coordination of Cr^{3+} such a relationship does not exist. Also, as mentioned before, the emission intensity is very nearly the same as in $K_3[Cr(CN)_6]$, whereas in the oxygen-coordinated double salts the emission intensity is very much increased compared to that of $K_3[Cr(CN)_6]$.

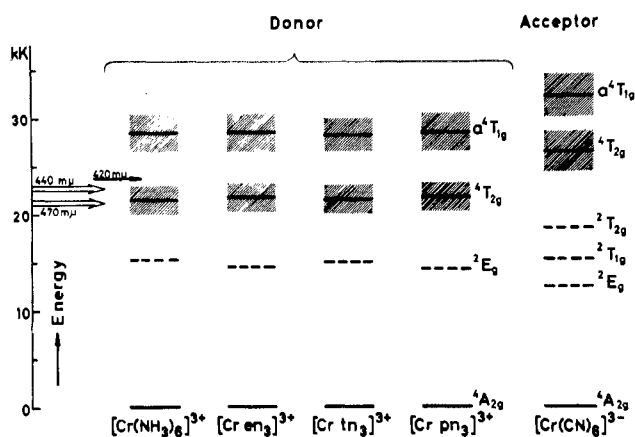This increase is observed in those compounds whose pure cationic components of oxygen-coordinated ligands

Figure 9.—Term diagram for discussion of the energy transfer in $[CrA_6][Cr(CN)_6]$ and $[Cr(A\text{-}A)_3][Cr(CN)_6]\cdot xH_2O$ (nitrogen coordination of the donor part).
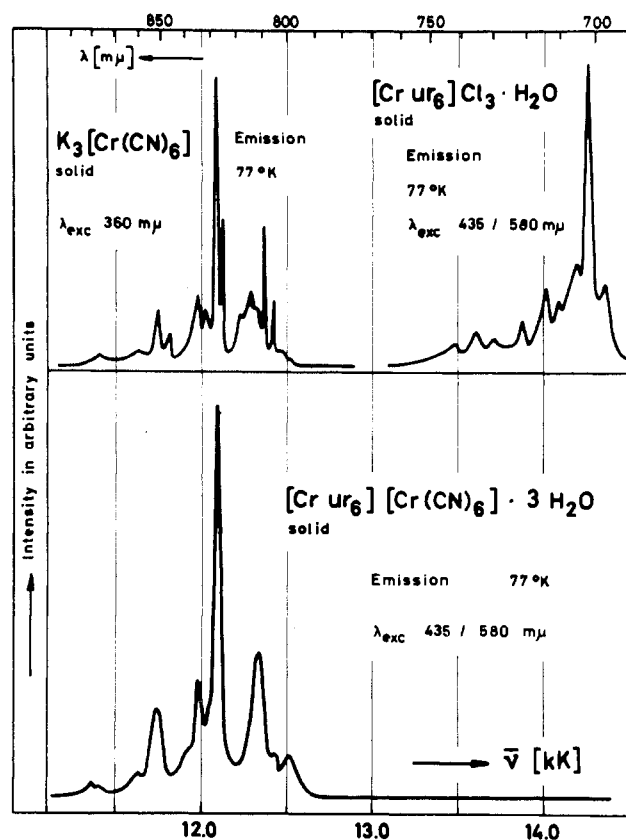
Figure 10.—Luminescence spectra of $K_3[Cr(CN)_6]$ and $[Cr(ur)_6]Cl_3\cdot H_2O$ and of $[Cr(ur)_6][Cr(CN)_6]\cdot 3H_2O$.

exhibit fluorescence as well as phosphorescence (dashed curves, Figures 11 and 12). $[Cr(ur)_6]Cl_3\cdot H_2O$ shows the broad-band fluorescence only at higher temperatures; at 77°K (Figure 10) only the phosphorescence emission is seen. [A change of Cl^- against $ClO_4{}^-$ gives in $[Cr(ur)_6](ClO_4)_3$ both types of emission already at 77°K.] The pure cationic components of the nitrogen-coordinated ligands yield only phosphorescence.

Table II shows the phosphorescence lifetimes at room temperature and at $-193°$ of the double complex salts and of pure $K_3[Cr(CN)_6]$. The latter compound gives a nonexponential decay curve, an analysis of which
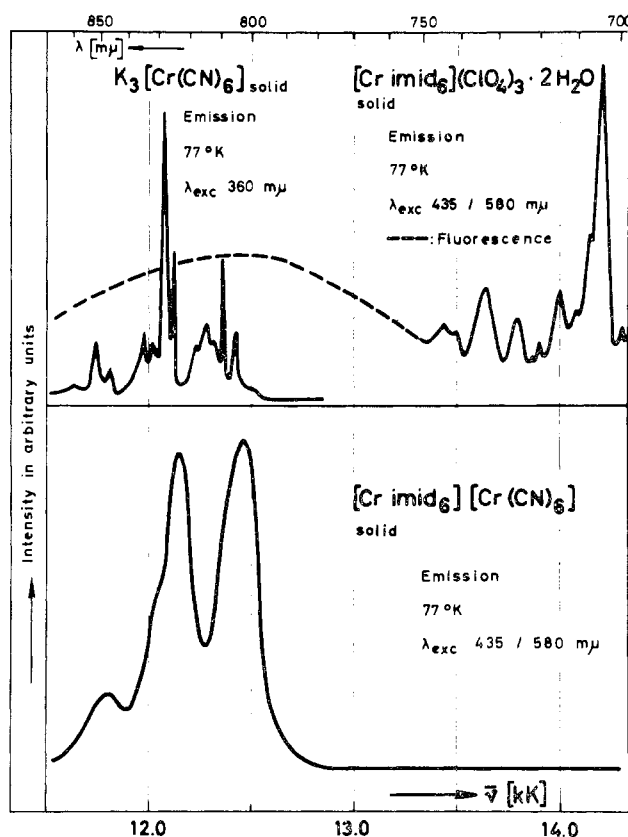
Figure 11.—Luminescence spectra of $K_3[Cr(CN)_6]$ and $[Cr(imid)_6](ClO_4)_3 \cdot 2H_2O$ and of $[Cr(imid)_6][Cr(CN)_6]$.
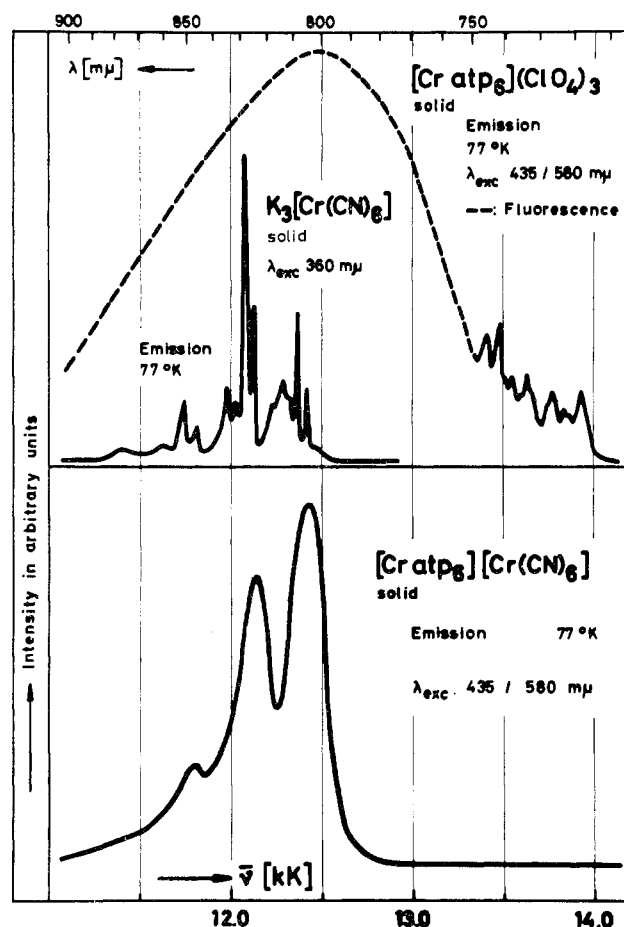

Figure 12.—Luminescence spectra of $K_3[Cr(CN)_6]$ and $[Cr(atp)_6](ClO_4)_3$ and of $[Cr(atp)_6][Cr(CN)_6]$.

TABLE I

PHOSPHORESCENCE INTENSITY *vs.* Cr–Cr DISTANCE[a]

Compound	Coordinated atom in the cation part	Wavelength of excitation, mμ	Amplification of phosphorescence intensity compared to that of K$_3$[Cr-(CN)$_6$]	Cr–Cr, Å
[Cr(ur)$_6$][Cr(CN)$_6$]$\cdot$3H$_2$O	O	580	20–40	6
[Cr(imid)$_6$][Cr(CN)$_6$]	O	580	10–15	7
[Cr(atp)$_6$][Cr(CN)$_6$]	O	580	8–15	8.5
[Cr(NH$_3$)$_6$][Cr(CN)$_6$]	N	440	0.3–0.5	3.5
[Cr(en)$_3$][Cr(CN)$_6$]$\cdot$2H$_2$O	N	470	1–1.3	4.5
[Cr(tn)$_3$][Cr(CN)$_6$]$\cdot$2H$_2$O	N	470	3.5–4.2	5
[Cr(pn)$_3$][Cr(CN)$_6$]$\cdot$4H$_2$O	N	470	2	5.5

[a] Column 4 gives the relation of the phosphorescence intensity of the double salt to the intensity of pure $K_3[Cr(CN)_6]$ at 77°K, when excitation is done with light of the wavelength indicated in column 3. It should be mentioned that this relation, which measures the amplification of the emission compared to that of $K_3[Cr(CN)_6]$, depends to a certain degree on the wavelength of excitation. For example, for $[Cr(ur)_6][Cr(CN)_6]\cdot3H_2O$ the following data have been obtained [λ_{exc} (mμ), amplification factor]: 435, 10–14; 580, 20–40; 610, 20–30.

yields two lifetime values since it is a superposition of two exponential decay curves. It is seen from Table II that, apart from $K_3[Cr(CN)_6]$, $[Cr(NH_3)_6][Cr(CN)_6]$, $[Cr(en)_3][Cr(CN)_6]\cdot2H_2O$, and $[Cr(tn)_3][Cr(CN)_6]\cdot2H_2O$, the lifetimes show a significant temperature dependence. The greatest lifetime of 2.2 msec was found for $[Cr(atp)_6][Cr(CN)_6]$ at $-193°$.

TABLE II

LIFETIMES OF THE PHOSPHORESCENCE OF THE DOUBLE COMPLEX SALTS AND OF $K_3[Cr(CN_6)]$

Compound	Wavelength,[a] mμ	Lifetime $\times$ 10^6, sec +24°	$-193°$
[Cr(ur)$_6$][Cr(CN)$_6$]$\cdot$3H$_2$O	827	67	430
[Cr(imid)$_6$][Cr(CN)$_6$]	802	19	130
[Cr(atp)$_6$][Cr(CN)$_6$]	804	152	2200
[Cr(NH$_3$)$_6$][Cr(CN)$_6$]	832	2.1	3.0
[Cr(en)$_3$][Cr(CN)$_6$]$\cdot$2H$_2$O	833	25	85
[Cr(pn)$_3$][Cr(CN)$_6$]$\cdot$4H$_2$O	832	29	327
[Cr(tn)$_3$][Cr(CN)$_6$]$\cdot$2H$_2$O	832	159	202
K$_3$[Cr(CN)$_6$]	826	32, 6[b]	58, 12[b]

[a] The wavelength where the decay of the phosphorescence was measured. [b] The decay curve is not a simple exponential one; analysis of the curve indicates two exponential processes, each of which yields a lifetime.

C. Conclusions

The aforementioned results give rise to the conclusion that the excitation energy transfer from the donor to the $Cr(CN)_6^{3-}$ acceptor found previously for $[Cr(ur)_6][Cr(CN)_6]\cdot3H_2O$ takes place in all of these double salts and most probably occurs *via* a doublet–doublet transfer $^2E_g(ct) \leadsto {}^2E_g(an)$. The question as to the type of mechanism governing the energy transfer cannot be answered unequivocally in the present stage of the investigations.
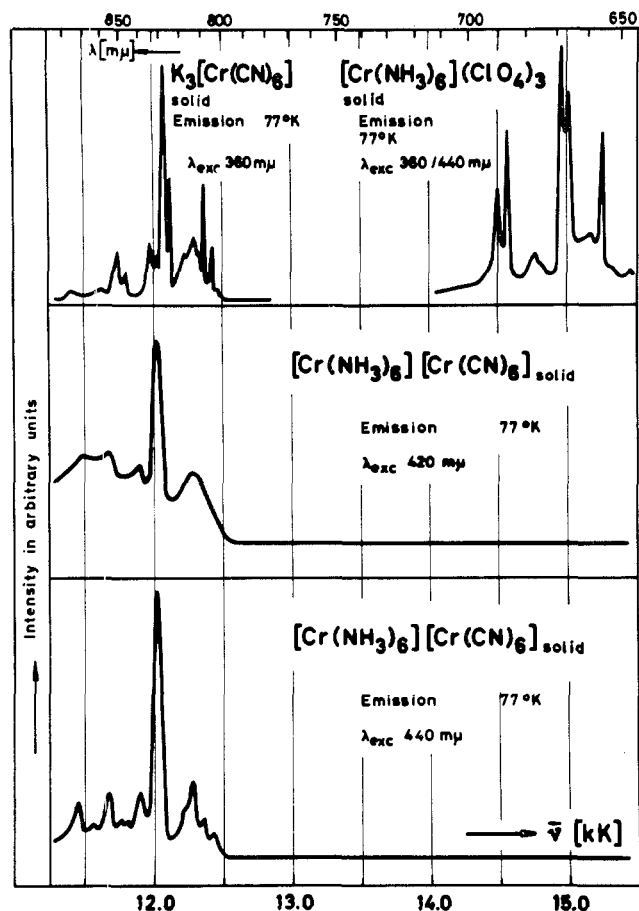
Figure 13.—Luminescence spectra of K₃[Cr(CN)₆] and [Cr(NH₃)₆](ClO₄)₃ and of [Cr(NH₃)₆][Cr(CN)₆].

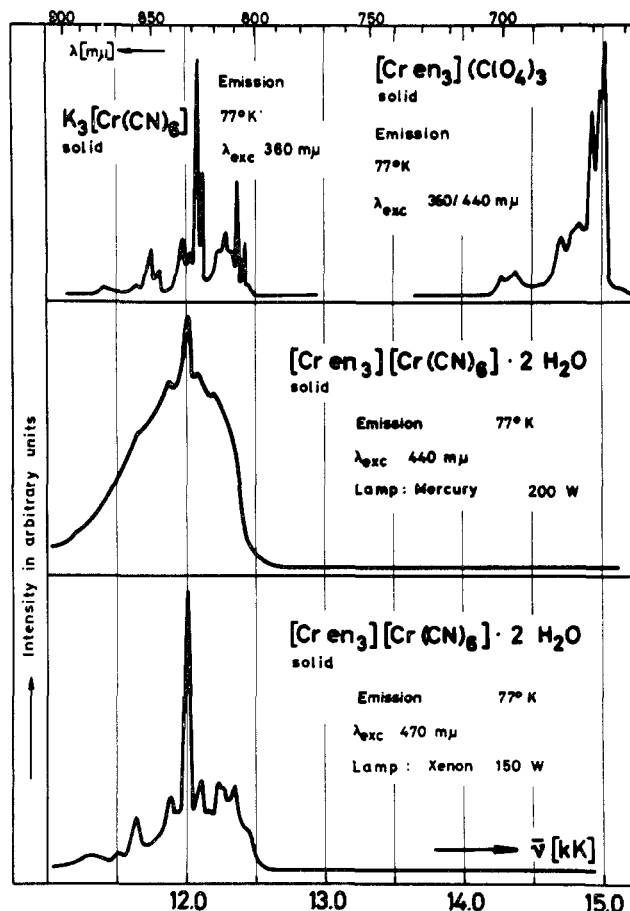Figure 14.—Luminescence spectra of K₃[Cr(CN)₆] and [Cr(en)₃](ClO₄)₃ and of [Cr(en)₃][Cr(CN)₆]·2H₂O.

According to Dexter,[2] in principle, one has to take into account either a resonance mechanism where multipole–multipole interactions (dipole–dipole, dipole–quadrupole, quadrupole–quadrupole) build the potential operator for an exchange mechanism. For both types of mechanism the transfer rate is proportional to the overlap of the emission spectrum of the donor with the absorption spectrum of the acceptor, that is, the integral

$$\int_0^\infty f_D(\bar{\nu})\,\epsilon_A(\bar{\nu})\,d\bar{\nu}$$

$\epsilon_A(\bar{\nu})$ is the molar decadic extinction coefficient of the acceptor, and $f_D(\bar{\nu})$ the spectral distribution of the luminescence of the donor measured in quanta and normalized to unity on a wave number scale.

However one has to consider also that in a crystal particular vibrations may be especially effective in allowing energy transfer. This can happen in a way not necessarily predictable by the above overlap principle. Orbach,[3] following a suggestion of Imbusch[4] developed a theory of phonon-assisted quadrupole–quadrupole transfer, where an effective Hamiltonian is constructed involving the orbit–lattice interaction and is supposed

to govern the energy transfer in ruby from single ions to singles and to pairs.

An exchange mechanism may be supposed to be the more probable, because the two Cr^{3+} ions in the double complex salts are in comparatively close contact. Thus an appreciable overlap between the electronic clouds of donor and acceptor is to be expected, which is a necessary condition for an exchange mechanism.

Another point which has to be considered is the amplification of the acceptor phosphorescence in the double salts compared to the phosphorescence in K₃[Cr(CN)₆]. This does not necessarily mean that the energy-transfer rate increases in these components. Another explanation is that the intersystem crossing yield in the donor changes with crystal structure and with the nature of the coordination atom. As a third possibility one has to consider that the quenching effects on the anion phosphorescence depend on the nature of the cation. It is not possible to decide which one of the three possibilities is responsible for the intensity effect. Probably they contribute simultaneously in influencing the emission intensity.

D. Experimental Section[5]

Preparation of the Double Salts.—The double complex salts [Cr(ur)₆][Cr(CN)₆]·3H₂O (light green) (Werner[6] gives 6H₂O for this salt), [Cr(imid)₆][Cr(CN)₆] (light green), [Cr(atp)₆]-

(2) D. L. Dexter, *J. Chem. Phys.*, **21**, 836 (1953).
(3) R. Orbach in "Optical Properties of Ions in Crystals," H. M. Crosswhite and H. W. Moos, Ed., Interscience Publishers, New York, N. Y., 1967, p 445.
(4) G. F. Imbusch, *Phys. Rev.*, **153**, 326 (1967).

(5) C. H. Möbius, Diplomarbeit, Frankfurt am Main, 1968.
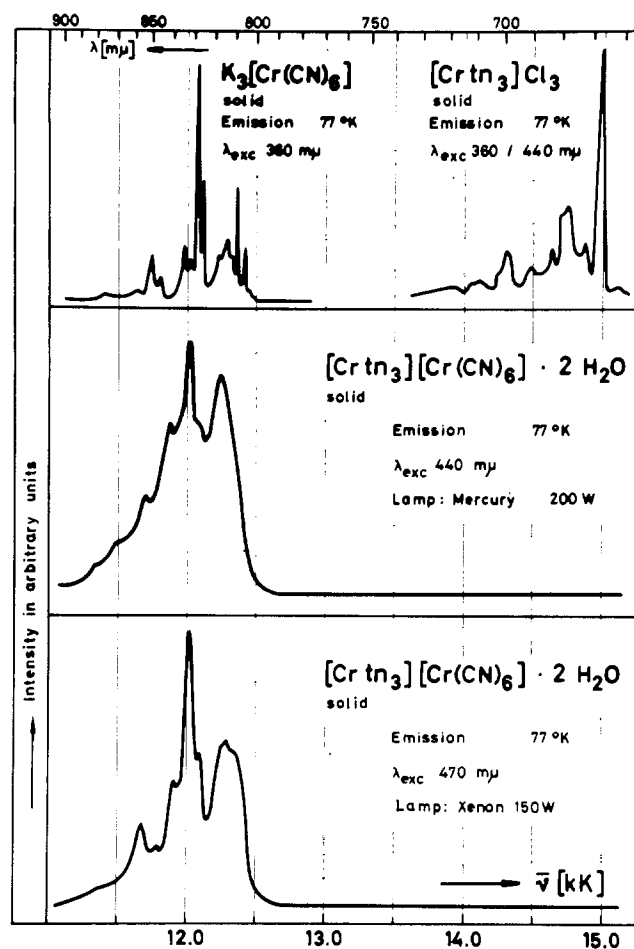(6) A. Werner, *Ann. Chem.*, **322**, 296 (1902).

Figure 15.—Luminescence spectra of K₃[Cr(CN)₆] and [Cr(tn)₃]Cl₃ and of [Cr(tn)₃][Cr(CN)₆]·2H₂O.

Figure 16.—Luminescence spectra of K₃[Cr(CN)₆] and [Cr(pn)₃](ClO₄)₃ and of [Cr(pn)₃][Cr(CN)₆]·4H₂O.

[Cr(CN)₆] (light green), [Cr(NH₃)₆][Cr(CN)₆] (yellow),[7] [Cr-(en)₃][Cr(CN)₆]·2H₂O (yellow),[8] [Cr(tn)₃][Cr(CN)₆]·2H₂O (yellow), and [Cr(pn)₃][Cr(CN)₆]·4H₂O (yellow)[9] have been prepared by mixing aqueous solutions of appropriate concentrations of K₃[Cr(CN)₆] with the respective cationic components [Cr-(ur)₆]Cl₃·H₂O, [Cr(imid)₆]Cl₃, [Cr(atp)₆]Cl₃, [Cr(NH₃)₆](NO₃)₃, [Cr(en)₃]I₃·H₂O, [Cr(tn)₃]Cl₃, and [Cr(pn)₃]I₃·H₂O. The double salts precipitate immediately. They were separated by filtration, washed, and dried in a vacuum desiccator filled with silica gel.

The above formulas were checked by analysis for Cr, C, H, and N. Details of preparation and analysis are given elsewhere.[5]

Absorption and Reflectance Spectra.—Reflectance spectra of the double salts were measured with a Cary 14 with reflectance attachment; absorption spectra were obtained with the same instrument using aqueous solutions of the compounds in 1–10-cm cells. The results are seen in Figures 1–7. The molar decadic extinction coefficient ϵ is plotted *vs.* wave numbers. Each figure shows the solution spectra of the Cr(CN)₆³⁻ and the CrA₆³⁺ or Cr(A-A)₃³⁺ components (solid curves) together with a dashed curve, which is obtained by a superposition of the curves of the two components. Besides the spin-allowed d → d bands, the intercombination bands are shown. Because of their small intensity they are plotted in some of the drawings on another scale.

Below, the reflectance spectra of the double salts are given. The logarithm of the Kubelka Munk function[10] log f(R) is plotted *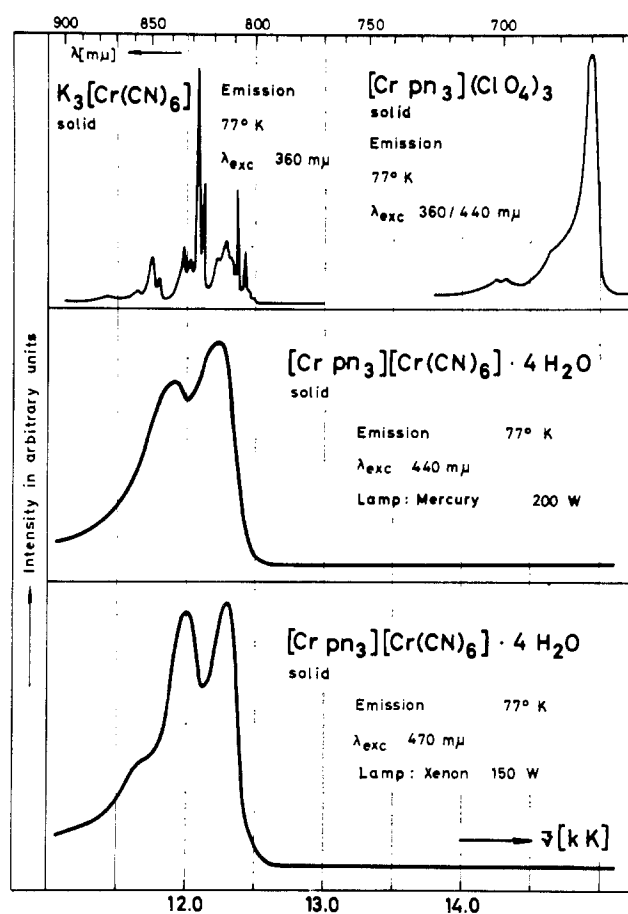vs.* wave numbers. We preferred to give for the separate components the solution spectra, because one gets in this way a clear impression of the absorption intensity, which is not possible in case of reflectance spectra. It should be mentioned that the reflectance spectra of the components are within experimental error identical with the solution spectra. The reflectance spectra of the double salts show only the intercombination band of the cation part, because the intercombination band of the anion part Cr-(CN)₆³⁻ is too weak to be observed in the double salt. This is due to the dilution (1:2) in the double salt compared to that in pure K₃[Cr(CN)₆].

Luminescence Spectra.—Luminescence measurements have been done using an apparatus previously described,[11] which has been modified in some parts. Samples of small crystals of the compounds housed in quartz cuvettes, which were fixed on a copper holder, were located inside a transparent quartz dewar[12] filled with liquid nitrogen. The temperature of the sample was measured by means of a thermocouple. Excitation was done with a mercury high-pressure lamp (200-W Osram HBO 200), an iodine–tungsten lamp (24 V, 150 W, Osram), and a xenon high-pressure lamp (150-W Osram XBO 150). The radiation from the light source passed a Bausch & Lomb high-intensity grating monochromator. Entrance and exit slit widths were for all the experiments 6 mm. Having passed a 2-mm BG 38 filter (Schott), the exciting light was focused onto the sample. The luminescence light was filtered using a 3-mm RG 665 filter (Schott) and then focused onto the slit of a Spex Czerny–Turner grating monochromator, Type 1700-II, whose slit widths were 1 mm (entrance and exit slits). As detectors for the resolved luminescence radiation, a 10-stage head-on photomultiplier with S1 characteristics (Valvo 150 CVP) or a 14-stage head-on one with

(7) S. M. Jørgensen, *J. Prakt. Chem.*, **30**, 1 (1884).

(8) P. Pfeiffer, *Z. Anorg. Allgem. Chem.*, **24**, 279 (1900); L. A. Welo, *Phil. Mag.* **6**, 481 (1928).

(9) P. Pfeiffer and M. Heimann, *Ber.*, **36**, 1063 (1903).

(10) P. Kubelka and F. Munk, *Z. Techn. Physik*, **12**, 593 (1931).

(11) H. Gausmann and H. L. Schläfer, *J. Chem. Phys.*, **48**, 4056 (1968).

(12) H. L. Schläfer, H. Gausmann, and H. Witzke, *Z. Physik. Chem.* (Frankfurt), **56**, 55 (1967).

S20 characteristics (RCA 7265) was used. The Valvo photomultiplier tube was cooled with the vapor boiled off from a container with liquid nitrogen. The photocurrent was fed to the input of a galvanometer amplifier with dark-current compensation. The output of the amplifier was connected to an electronic paper chart potentiometer which allowed the spectra to be recorded automatically.

The results of the luminescence measurements are seen in Figures 10–16. Above, the luminescence spectra of the two components are given; below, the spectra of the respective double complex salts are shown. The luminescence intensity is given in arbitrary units and plotted *vs.* wave numbers. Comparing the emission of the double salts with that of pure $K_3[Cr(CN)_6]$ the observed differences in luminescence intensity are not seen from the figures. The relation of the phosphorescence intensity of the double salts to the intensity of $K_3[Cr(CN)_6]$ is given in Table I, column 4. This relation was obtained from the current of the photomultiplier taken for the band in the phosphorescence spectra, which has the greatest intensity. The values in column 4 are related to the emission of solid $K_3[Cr(CN)_6]$, whose intensity is set at unity. The first value for a given compound was obtained taking into account only the intensity of the lamp (the intensity distribution of the lamp has been measured using a bolometer which was calibrated by means of a standard light source) and the transmission of the BG 38 filter at the wavelength of the exciting light. The second value in addition includes corrections for the absorption coefficients of $K_3[Cr(CN)_6]$ and of the double complex salts taken from the absorption spectra of $K_3[Cr(CN)_6]$ and from the respective superposition curves. The oxygen-coordinated compounds $[Cr(ur)_6]Cl_3 \cdot H_2O$, $[Cr(atp)_6]$-$(ClO_4)_3$, and $[Cr(imid)_6](ClO_4)_3 \cdot 2H_2O$ exhibit both types of emission phosphorescence and fluorescence (dotted curves in Figures 11 and 12). The first compound at 77°K yields only phosphorescence; on raising the temperature, the broad-band fluorescence is seen; the more intense it is, the higher the temperature.

Lifetimes.[18]—Reported lifetimes (Table II) were measured by the following single-pulse method. The sample located in a cuvette within a transparent quartz dewar was excited by means of a giant-pulse ruby laser equipped with a second harmonic generator (347 mμ). The luminescence was detected by a Valvo 56 CVP photomultiplier (S1) after passing filters to eliminate laser radiation and a 0.25-m Jarrell–Ash Ebert monochromator. The photomultiplier and the voltage divider were cooled with the vapor boiled off from a liquid nitrogen reservoir. The resulting signal of the anode current was displayed on a Siemens oscilloscope, Oscillar M 214. Decay curves where photographed using a Polaroid camera equipped with high-speed film of Type 410. In Q-switch operation the excitation pulse had a half-width of ~20 nsec and about 2-MW average power. To prove simple exponential decays, the results were plotted on linear logarithmic paper. Lifetimes have been evaluated from these plots using the usual procedure.

(13) H. U. Zander, Thesis, Frankfurt am Main, 1969.

Circular Dichroism of Some Less Strained Model Compounds for the Ethylenediaminetetraacetatocobaltate(III) Ion[1]

By CAROLYN W. VAN SAUN and BODIE E. DOUGLAS

A series of model compounds for Co(EDTA)⁻ have been prepared and resolved. This series includes the following complex ions: 1,3-propanediaminetetraacetatocobaltate(III), Co(1,3-PDTA)⁻, *cis*-bis(iminodiacetato)cobaltate(III), *cis*-Co(IDA)₂⁻, and ethylenediaminetetrapropionatocobaltate(III), Co(EDTP)⁻. All of these complex ions have the same effective crystal field and general arrangement of chelate rings as Co(EDTA)⁻, but they have less strained chelate ring systems. The intensities of the visible absorption bands for these compounds are lower than those for Co(EDTA)⁻, but the net intensities of their CD bands are greater. The observed increase in rotational strength when the strain of the chelate ring system was decreased contradicts predictions of theoretical studies of optical activity of coordination complexes.

Introduction

Theoretical treatments of the optical activity of coordination compounds have thus far proved inadequate for explaining the circular dichroism (CD) spectra of these systems. The use of CD for obtaining structural information is based on empirical correlations, the theoretical bases for which are generally not understood. The present work was undertaken to determine the influence of various structural changes in the ligand on the rotational strengths of the d–d transitions of cobalt(III) in a series of complexes. Such information is vitally needed to guide future theoretical studies of the optical activity of coordination complexes.

The complexes prepared in this work are all related to the ethylenediaminetetraacetatocobaltate(III) ion, Co(EDTA)⁻. An X-ray structure determination has been done for this complex ion.[2] The complex contains five chelate rings with the cobalt(III) bonded to the two nitrogen atoms of the ethylenediamine and to one oxygen atom from each of the four carboxylate groups. Structural parameters such as bond lengths and angles show notable departures from regular octahedral

(2) H. A. Weakliem and J. L. Hoard, *J. Am. Chem. Soc.*, **81**, 549 (1959).