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The Electronic Spectra of the Hexafluorometalate(III) Complexes of the First Transition Series

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The electronic spectra of the hexafluorometalate(III) anions of the first transition series have been studied by diffuse reflectance between 4 and 50 kK for the compounds K_3TiF_6, K_3VF_6, K_3CrF_6, K_3MnF_6, K_3FeF_6, and K_3CoF_6. For the Mn(III) and Co(III) complexes the identification of a number of spin-forbidden d–d transitions made it possible to estimate values of the Racah electron repulsion parameter, B, and the nephelauxetic ratio, β, and for the full series the fitting parameters derived were as follows: Ti, $Dq = 1730$ cm^{-1}; V, $Dq = 1640$ cm^{-1}, $B = 670$ cm^{-1}, $\beta = 0.78$; Cr, $Dq = 1520$ cm^{-1}, $B = 740$ cm^{-1}, $\beta = 0.81$; Mn, $Dq = 1740$ cm^{-1}, $Ds = 1600$ cm^{-1}, $Dt = 520$ cm^{-1}, $B = 780$ cm^{-1}, $\beta = 0.80$; Fe, $Dq = 1300$ cm^{-1}, $B = 800$ cm^{-1}, $\beta = 0.77$; Co, $Dq = 1410$ cm^{-1}, $B = 765$ cm^{-1}, $\beta = 0.70$. The Laporte-allowed charge-transfer transitions are located, respectively, at 47.7, 43.3, >52, >50, 48.8, and 40.6 kK, and it is shown that these values, together with those previously found for the NiF_6^{3-} and CuF_6^{3-} complexes, can be successfully interpreted in terms of the spin-pairing energy concept of Jørgensen. Furthermore, the optical electronegativities, χ_{opt}, derived from the data show a good linear correlation with q, the orbital occupation number of the d shell, and increasing values of χ_{opt} are found as expected to be associated with decreasing values of β.

Introduction

Although a great number of spectroscopic investigations of the MF_6^{3-} ions of the first transition series have now been reported,[2a] adequate diagramatic presentation has often been lacking, and in many cases the results have covered only a rather limited spectroscopic range. Thus Bedon, *et al.*,[2b] studied a number of salts of the TiF_6^{3-} anion with particular reference to the single d–d band at about 16–19 kK but detected no charge-transfer transitions below 50 kK, while neither Clark[3] nor Machin and Murray[4] succeeded in finding any bands above 30 kK for K_3VF_6. Similarly, for the high-spin d^4 and d^6 systems, MnF_6^{3-} and CoF_6^{3-}, attention has largely been restricted to the bands arising from the $^5E_g \rightarrow {}^5T_{2g}$ and $^5T_{2g} \rightarrow {}^5E_g$ transitions, respectively. Thus Oelkrug's[5] spectrum of K_3MnF_6 does not extend beyond 26 kK, and for the CoF_6^{3-} ion the spectra of Cotton and Meyers[6] span only the region between 8 and 20 kK. For FeF_6^{3-} the spectrum given by Jørgensen[7] for the $(enH)_3$ salt adequately covers the d–d region, although the nature of the cation precludes its extension to the charge-transfer excitations, and only for NiF_6^{3-} and CuF_6^{3-}, in which the Laporte-allowed bands occur at relatively low energies, have these transitions been identified.[8]

On the other hand, for the M(IV), MF_6^{2-} series, the positions of the charge-transfer bands are well established[1] and it has been shown[9] that these values are readily amenable to interpretation in terms of the spin-pairing energy approach introduced by Jørgensen.[10] Consequently we felt it desirable to remedy this lack of information concerning the charge-transfer bands of the MF_6^{3-} series, and we have therefore studied the anions of Ti, V, Cr, Mn, Fe, and Co, over the range 4–50 kK, using the potassium salt throughout. Furthermore, since only the bands arising from quintet–quintet d–d transitions for the d^4 and d^6 anions had been properly studied, it was not possible to derive values of the Racah repulsion parameter, B, and of the nephelauxetic ratio, β, for the MnF_6^{3-} and CoF_6^{3-} ions. Accordingly it was hoped that this investigation might establish the positions of some of the spin-forbidden quintet–triplet transitions for these systems from which it should, in principle, be possible to estimate B and β.

Experimental Section

Hexafluorometalate Salts.—These were prepared according to literature procedures, and all gave satisfactory analytical figures for both fluorine and the transition metal. Potassium hexafluorotitanate(III) was obtained as a dark violet-blue solid by reduction of K_2TiF_6 in hydrogen and subsequent hydrolysis, following Ehrlich and Pietzka,[11] and potassium hexafluorovanadate(III), as a green solid by the reduction of V_2O_5 with KI according to Nyholm and Sharpe.[12] The potassium salts of the hexafluorochromate(III), hexafluoromanganate(III), and hexafluoroferrate(III) anions were all prepared by fusion of the corresponding pentafluoroaquo salts with KHF_2 according to Peacock,[13] and were, respectively, bright green, pink, and colorless. Potassium hexafluorocobaltate(III) was obtained as a bright blue solid by the direct fluorination of $K_3Co(CN)_6$ according to Klemm, Brandt, and Hoppe.[14]

Diffuse Reflectance Measurements.—These were carried out as before[8,15,16] between 4 and 50 kK, both at room and liquid nitrogen temperatures, using a Beckman DK 2A spectroreflectometer with a magnesium oxide reference. Intensities are expressed in terms of the Kubelka–Munk function, F_R, which may be related to the extinction coefficient by the expression $F_R = \epsilon c/0.434s$, where c is the density per molecular weight and s is the scattering coefficient.

Results and Discussion

In Figures 1–6 and in Table I are presented the diffuse reflectance spectra of the K_3 salts of the MF_6^{3-} anions

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(1) Ph.D. student supported by the Royal Saudi Arabian Government.

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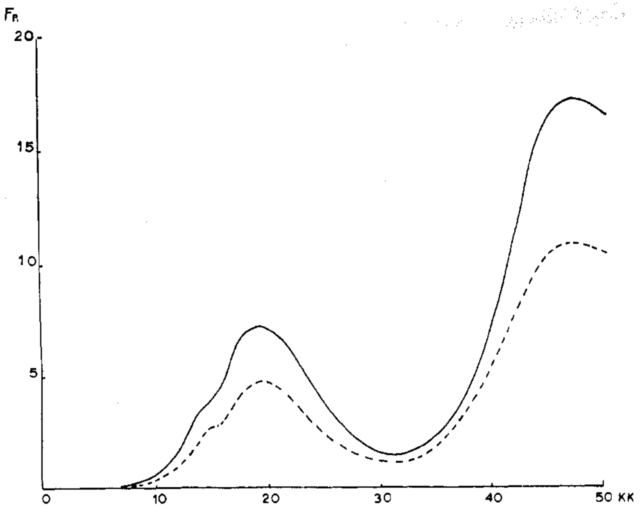

Figure 1.—The diffuse reflectance spectrum of potassium hexafluorotitanate(III): —, room temperature; - - -, liquid nitrogen temperature.

TABLE I

THE DIFFUSE REFLECTANCE SPECTRA OF K_3TiF_6, K_3VF_6, K_3CrF_6, K_3MnF_6, K_3FeF_6, AND K_3CoF_6

Compd	Band position, kK	Intens, F_R	Assignment
K_3TiF_6			
	15.3 sh^a	...	$^2T_{2g} \rightarrow {}^2E_g$
	19.3^a	7.2	$^2T_{2g} \rightarrow {}^2E_g$(?)
	47.0	17.6	$\pi_u \rightarrow t_{2g}$
K_3VF_6			
	6.0	Weak	(?)
	10.3	0.36	$^3T_{1g} \rightarrow {}^1E_g, {}^1T_{2g}$
	15.1	1.12	$^3T_{1g} \rightarrow {}^3T_{2g}$
	23.6	3.06	$^3T_{1g} \rightarrow {}^3T_{1g}$
	42.2	8.4	$\pi_u \rightarrow t_{2g}$
K_3CrF_6			
	15.2	...	$^4A_{2g} \rightarrow {}^4T_{2g}$
	16.3	0.51	$^4A_{2g} \rightarrow {}^2E_g, {}^2T_{1g}$
	21.8 sh	...	$^4A_{2g} \rightarrow {}^4T_{1g}$
	23.0	0.99	$^4A_{2g} \rightarrow {}^2T_{2g}$
	35.0	0.50	$^4A_{2g} \rightarrow {}^4T_{1g}$
	>52	>2	$\pi_u \rightarrow t_{2g}$
K_3MnF_6^{a,b}			
	9.0	0.38	$^5B_{1g} \rightarrow {}^5A_{1g}$
	17.8	...	$^5B_{1g} \rightarrow {}^5B_{2g}$
	19.4	1.94	$^5B_{1g} \rightarrow {}^5E_g$
	23.3	Weak	$^5B_{1g} \rightarrow {}^3B_{1g}$
	26.2	Weak	$^5B_{1g} \rightarrow {}^3B_{2g}$
	43.5 sh	...	$\pi(t_{1g}) \rightarrow t_{2g}$(?)
	>50	>5	$\pi_u \rightarrow t_{2g}$
K_3FeF_6			
	16.6	0.12	$^6A_{1g} \rightarrow {}^4T_{1g}$
	21.7	0.09	$^6A_{1g} \rightarrow {}^4T_{2g}$
	27.0	0.19	$^6A_{1g} \rightarrow {}^4A_{1g}, {}^4E_g$
	29.8	0.18	$^6A_{1g} \rightarrow {}^4T_{2g}$
	31.9	0.25	$^6A_{1g} \rightarrow {}^4E_g$
	37.0	0.73	$^6A_{1g} \rightarrow {}^4T_{1g}$(?)
	42.6 sh	...	$\pi(t_{1g}) \rightarrow t_{2g}$(?)
	47.6	6.8	$\pi_u \rightarrow t_{2g}$
K_3CoF_6			
	5.5	Weak	$^5T_{2g} \rightarrow {}^3T_{1g}$(?)
	11.8^a	0.50	$^5T_{2g} \rightarrow {}^5E_g$
	16.4^a	1.29	
	19.6	Weak	$^5T_{2g} \rightarrow {}^3T_{1g}, {}^3T_{2g}$
	23.3	Weak	$^5T_{2g} \rightarrow {}^3E_g, {}^3T_{1g}$
	26.3	Weak	$^5T_{2g} \rightarrow {}^3T_{2g}$
	30.3 sh	...	$^5T_{2g} \rightarrow {}^3A_{2g}$(?)
	39.6	32	$\pi_u \rightarrow t_{2g}$

[a] Jahn–Teller split bands. [b] d–d bands assigned for D_{4h} symmetry; charge-transfer bands for O_h symmetry.

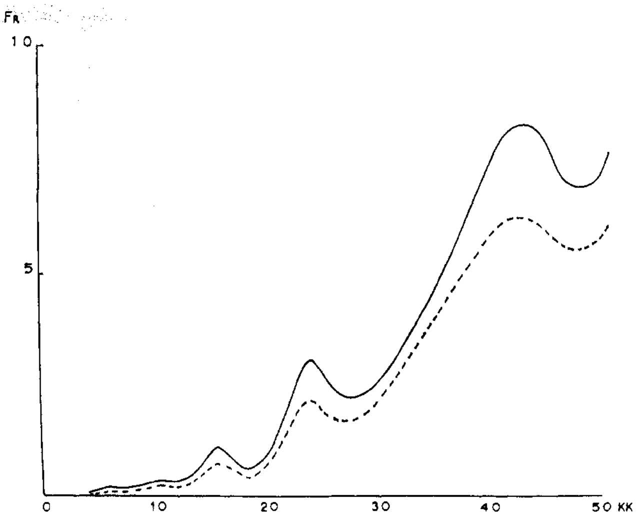

Figure 2.—The diffuse reflectance spectrum of potassium hexafluorovanadate(III): —, room temperature; - - -, liquid nitrogen temperature.

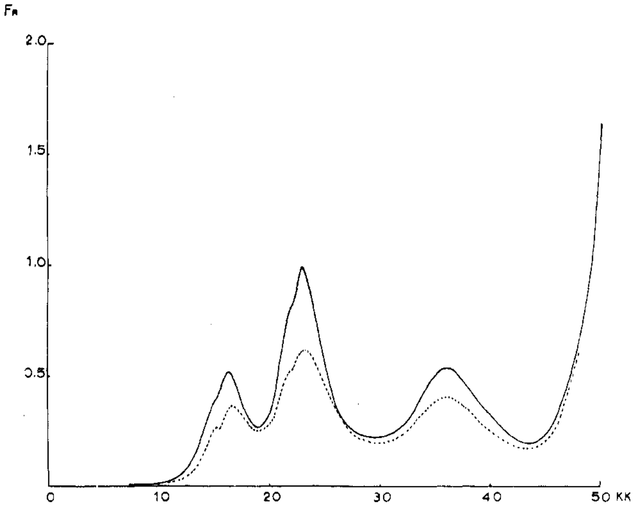

Figure 3.—The diffuse reflectance spectrum of potassium hexafluorochromate(III): —, room temperature; - - -, liquid nitrogen temperature.

of Ti, V, Cr, Mn, Fe, and Co, together with the corresponding band assignments. Since we are here concerned with a detailed interpretation of both the d–d and the charge-transfer regions of the spectra, we have not attempted, as we did previously,[8,15,16] to convert the measured band intensities to extinction coefficients and oscillator strengths, and a proper understanding of the actual F_R values consequently requires some degree of caution. This is because the scattering coefficient, s, is not independent of the wavelength over the whole spectral range and is also very sensitive to particle size. When the latter is small enough (*ca.* 20 μ) to eliminate any regular reflectance contributions, s is approximately constant up to about 25 kK and will probably lie quite close to the value of 2 deduced theoretically by Kortum.[17] At higher energies however the scattering coefficient increases sharply with frequency, often by as much as a factor of 20, and many charge-transfer transitions will thus appear to be greatly underestimated in intensity

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(17) G. Kortum, "Reflectance Spectroscopy," Springer-Verlag, Berlin, 1969.

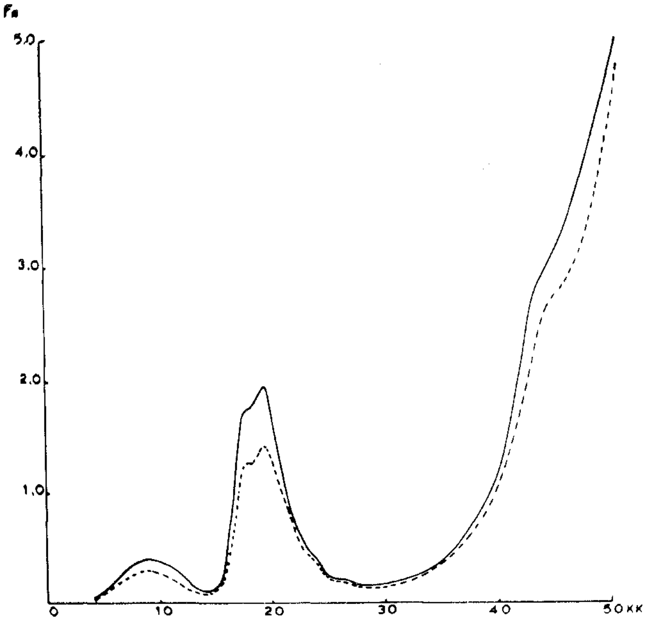

Figure 4.—The diffuse reflectance spectrum of potassium hexafluoromanganate(III): —, room temperature; - - -, liquid nitrogen temperature.

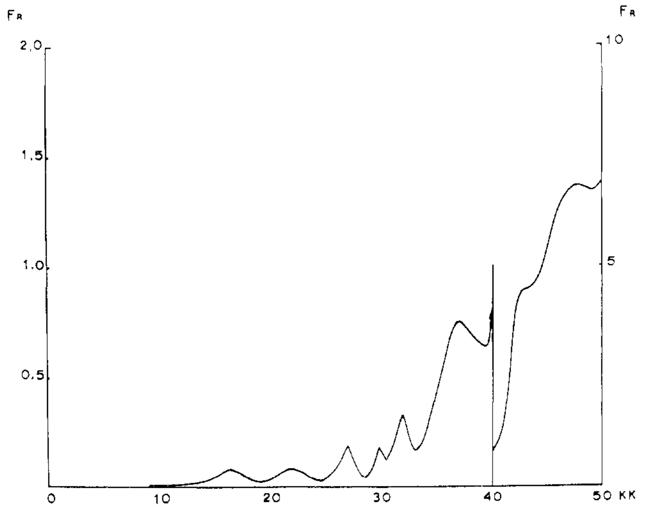

Figure 5.—The diffuse reflectance spectrum of potassium hexafluoroferrate(III): —, room temperature.

on the F_R scale. On the other hand though, the intensities of weak spin-forbidden d–d transitions sometimes appear to be exaggerated appreciably in reflectance, probably due to the difficulty in excluding all background absorption, so that it is usually best to assign bands as spin allowed, spin forbidden, or charge transfer, on the basis of their *relative* intensities, together with the rule of thumb observation that most spin-allowed d–d bands lying below about 25 kK have F_R values between about 0.5 and 3 for 3d octahedral complexes.

The spectra of the six K$_3$MF$_6$ salts have therefore been analyzed using the above considerations, and assignments have been made for both the d–d and charge-transfer transitions. We now deal first with the former region since the fitting parameters thus derived must be known before an adequate interpretation of the charge-transfer bands can be put forward.

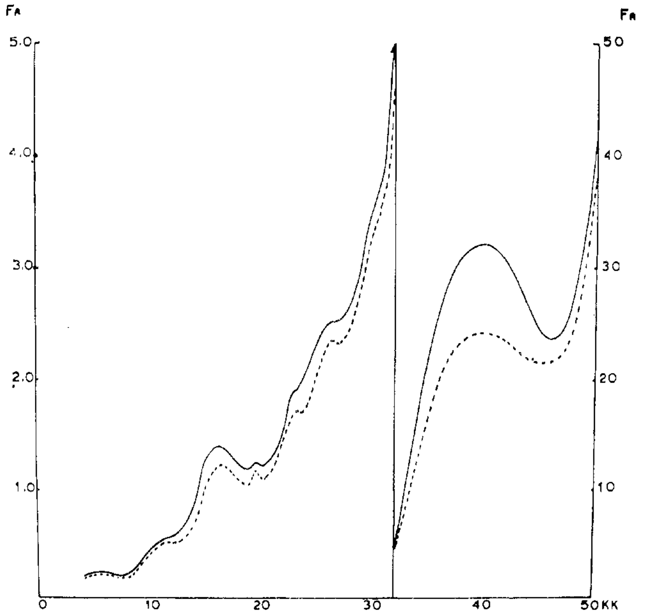

Figure 6.—The diffuse reflectance spectrum of potassium hexafluorocobaltate(III): —, room temperature; - - -, liquid nitrogen temperature.

Except for the Mn(III) complex, the K$_3$MF$_6$ compounds of the 3d series are known[18] to possess either cubic K$_3$FeF$_6$ or slightly distorted tetragonal (NH$_4$)$_3$ScF$_6$ lattices. We have therefore assumed strictly O_h symmetry about the metal in these cases, although it is possible that for Ti(III) the effective point symmetry may be lower. For K$_3$MnF$_6$ the anomalous cell dimensions reported by Peacock[13] support the postulation of an appreciable tetragonal Jahn–Teller distortion.

Assignment of d–d Transitions.—As indicated above the previous spectroscopic investigations of the MF$_6^{3-}$ anions of the 3d series have often failed to produce a full understanding of the corresponding d–d spectra. We therefore discuss in this section those aspects of our results which provide further insight into this problem.

(a) **K$_3$TiF$_6$.**—The Na$_2$K, K$_2$Na, and (NH$_4$)$_3$ salts of the TiF$_6^{3-}$ anion were previously studied by Bedon, Horner, and Tyree,[2b] using a KCl disk technique, and in each case a single band, split into two components, was observed and assigned as the d–d, $^2T_{2g} \rightarrow {}^2E_g$, transition. The respective peak positions for the three salts were 16.0 and 18.9, 16.1 and 18.9, and 15.1 and 19.0 kK, and our spectrum for the K$_3$ salt thus appears to resemble that for the ammonium compound, although Bedon, *et al.*,[2b] gave no indication of the relative intensities of the two components.

In the rigorously cubic K$_2$NaTiF$_6$ the TiF$_6^{3-}$ unit is strictly octahedral, and the splitting of the band was attributed to a tetragonal Jahn–Teller distortion for the upper ^2E_g state: The 3-kK splitting of the two components seems much too large to arise from a t$_{2g}$ orbital degeneracy and the still greater separation observed for the (NH$_4$)$_3$ salt was ascribed by Bedon, *et al.*,[2b] to deviations from O_h symmetry inherent in the crystal lattice. Moreover, the magnetic moment approaches much more closely to the spin-only value than does that of the K$_2$Na salt, this being the behavior predicted by

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[18] D. Babel, *Struct. Bonding (Berlin)*, **3**, 1 (1967).

Figgis[19] for ligand fields containing components of lower than octahedral symmetry.

It is therefore tempting to adopt a similar interpretation for the 15.3- and 19.3-kK bands of K_3TiF_6, but there are certain objections to this assignment. First of all, the 19.3-kK peak is unusually strong for a d–d transition and might therefore correspond to a Laporte-allowed excitation. Thus, semiempirical molecular orbital calculations by Boudreaux[20] give $10Dq$ as only 10 kK, with $\pi(t_{1u}) \rightarrow t_{2g}$ at 25 kK, although optical electronegativity considerations (*quod vide*) argue against the presence of a $\pi_u \rightarrow t_{2g}$ transition at such low energies. In this context it may be noted that the bands of comparable F_R values found at higher energies for the other $MF_6{}^{3-}$ anions, and assigned as $\pi_u \rightarrow t_{2g}$, almost certainly represent much more intense excitations because of the higher scattering coefficient in those regions.

Furthermore, very recent work by Nassiff, *et al.*,[21] has shown that for K_2NaTiF_6 the electronic spectrum shows the characteristically strong band at 19.3 kK, with the shoulder at 16.2 kK, but there is no observable splitting of the τ_{1u} vibrational mode. This result is not necessarily inconsistent with the operation of the Jahn–Teller effect for the ^2E_g excited state, very similar observations having been made by Cotton and Meyers[6,22] for the strictly cubic K_2NaCoF_6, in which such an effect appears well established. However, only small splittings of the τ_{1u} modes are found for K_3TiF_6 and for $(NH_4)_3TiF_6$, which both show magnetic moments very close to the spin-only value,[21] and it seems unlikely therefore that the intensity enhancement now found in the former compound can be attributed to any reduction in symmetry.

Nevertheless, for the corresponding hexachloro anion, in $(C_6H_5N)_3TiCl_6$, Fowles and Russ[23] observed a rather similar electronic spectrum with a well-marked peak at 12.8 kK and a weaker shoulder at 11.0 kK which were also assigned as components of the $^2T_{2g} \rightarrow {}^2E_g$ transition. Such a movement of both components to lower energies by about this amount would be expected for a d–d transition, but the juxtaposition of a d–d band and a charge-transfer transition for both $TiF_6{}^{3-}$ and $TiCl_6{}^{3-}$ is rather improbable.

However, the assignment of the 19.3-kK peak for K_3TiF_6 obviously remains in some doubt, and the Dq value of 1730 cm^{-1} obtained, following Bedon, *et al.*,[2b] from the mean of the 15.3- and 19.3-kK absorptions, must be regarded as tentative.

(b) **K_3VF_6.**—The $VF_6{}^{3-}$ anion has previously been investigated by Machin and Murray[4] and by Clark,[3] who studied the $(NH_4)_3$ and K_3 salts, respectively, both locating the $^3T_{1g} \rightarrow {}^3T_{2g}$ and $^3T_{1g} \rightarrow {}^3T_{1g}$ bands at 14.8 and 23.25 kK. Our results give slightly higher values for the two spin-allowed d–d transitions which may be fitted by the parameters $Dq = 1640\ cm^{-1}$, $B = 655\ cm^{-1}$, and $\beta = 0.76$ but agree exactly in placing the spin-forbidden $^3T_{1g} \rightarrow {}^1E_g, {}^1T_{2g}$ transition at 10.3 kK. Neither of the two earlier studies succeeded in finding the $^3T_{1g} \rightarrow {}^3A_{2g}$ transition, expected to lie at around 31 kK, but this band should in any case be rather weak since it corresponds formally to a two-electron excitation. Our spectrum does, however, show a pronounced flat on the low-energy side of the charge-transfer region between about 30 and 35 kK which would be consistent with the presence of this absorption.

In the past the reasons for the position of the spin-forbidden band have given rise to some controversy; thus, if the energies of the ^1E_g, $^1T_{2g}$ levels are calculated using the parameters derived from the spin-allowed bands, they are estimated to lie about 1 kK lower than the observed value. Ballhausen and Winther[24] explained this discrepancy by assuming that the $^3T_{1g}(t_{2g}{}^2)$ $VF_6{}^{3-}$ system was subjected to a trigonal Jahn–Teller distortion, lowering the effective symmetry to C_{3v} or D_3. In these symmetries the ^1E_g level is not split, remaining as ^1E, the $^1T_{2g}$ state yields a $^1A_1$ and a further ^1E level, and the resulting first-order interaction between the two ^1E states would ensure a substantial separation between them. Thus it was suggested that the two ^1E levels might be split by about 1.5 kK, thereby explaining the high position of the spin-forbidden band, although it did not prove possible to locate a band corresponding to the lower ^1E level.

In our spectrum a very weak band is observed at 6.0 kK, as well as the peak at 10.3 kK, but we feel the former to be spurious (probably due to traces of moisture which is known to absorb in this region), and therefore reject the assignment of this absorption as the lower of the two ^1E levels. Support for this view is provided by calculations using strong-field trigonal d^2 matrices[25] based on the $t^0{}_{2g}$, $t^{\pm}{}_{2g}$, $e^{\pm}{}_g$ basis set of Ballhausen,[26] which show that the $^3T_{1g}$ level should be split by a trigonal ligand field component by an amount comparable to the separation of the two ^1E states. Such a large splitting (4.3 kK) is inconsistent with the magnetic evidence: for $(NH_4)_3VF_6$ Machin and Murray[4] found that the magnetic moment (2.79 BM at room temperature) decreased quite sharply with temperature and showed, using the treatment given by Figgis,[27] that the splitting of the $^3T_{1g}$ ground state could not amount to more than about 150 cm^{-1}, with a $^3A_2$ component lying lowest. Since this appears[4] to be a general result for complexes with monodentate ligands, we therefore rejected the postulation of a significant ground-state splitting.

If however we assume with Tanabe and Sugano[28] a value of 4.43 for the C/B ratio for V(III), the assignment of the 10.3-kK peak as $^3T_{1g} \rightarrow {}^1E_g, {}^1T_{2g}$ yields a B parameter of 705 cm^{-1}; since this transition is an intrasubshell excitation, this value clearly corresponds to the B_{55} parameter (t_{2g}–t_{2g} repulsion), and leads to $\beta_{55} = 0.82$, whereas the nephelauxetic parameter derived from the spin-allowed bands (0.76) is β_{35} (e_g–t_{2g} repulsions). As pointed out by Jørgensen,[29] β_{55} will normally be at least slightly larger than β_{35} so that no further explanation of the apparently anomalous position of the $^3T_{1g} \rightarrow {}^1E_g, {}^1T_{2g}$ band need be sought. The difference between the two β values is relatively small and a

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[19] B. N. Figgis, *Trans. Faraday Soc.*, **57**, 198 (1961).

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[22] M. D. Meyers and F. A. Cotton, *J. Amer. Chem. Soc.*, **82**, 5027 (1960).

[23] G. W. A. Fowles and B. T. Russ, *J. Chem. Soc. A*, 517 (1967).

[24] C. J. Ballhausen and F. Winther, *Acta Chem. Scand.*, **13**, 1729 (1959).

[25] K. D. Warren, unpublished matrices.

[26] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962.

[27] B. N. Figgis, J. Lewis, J. Mabbs, and F. E. Webb, *J. Chem. Soc. A*, 1411 (1966).

[28] Y. Tanabe and S. Sugano, *J. Phys. Soc. Jap.*, **9**, 753, 766 (1954).

[29] C. K. Jørgensen, *Progr. Inorg. Chem.*, **4**, 73 (1962).

satisfactory overall fit of the bands is obtained with $Dq = 1640\ \text{cm}^{-1}$, $B = 670\ \text{cm}^{-1}$, and $\beta = 0.78$.

(c) **K_3CrF_6.**—Our spectrum for this compound closely resembles those earlier recorded for the CrF_6^{3-} ion by Ferguson, *et al.*,[30] by Jørgensen,[7] and by Schläffer, *et al.*[31] There are certain features concerning the analysis of the spectrum and the derivation of the fitting parameters which require attention. In the first place the Racah parameters deduced by Schläffer, *et al.*, are almost certainly too low since they were obtained by consideration only of the diagonal matrix elements for the O_h d^3 system and not by use of the complete Tanabe–Sugano matrices. Furthermore, the attempts[7,29] to derive both B_{35} and B_{55} seem to us, in this particular case, to be overoptimistic since the relatively small Dq value associated with the fluoride ligand results in the members of the ${}^4T_{2g}$, ${}^2E_g$, ${}^2T_{1g}$ and ${}^4T_{1g}(F)$, ${}^2T_{2g}$ groups of levels, respectively, being almost coincident. Thus the effects of spin–orbit coupling, which are usually small in the 3d series, will have important consequences, especially for transitions from the ${}^4A_{2g}$ ground state to the lower group of levels, and will render hazardous any attempt to derive different repulsion parameters for the spin-allowed and for the spin-forbidden bands, respectively.

We have therefore fitted our data using the complete d^3 spin–orbit matrices of Eisenstein,[32] assuming $C/B = 4.5$, following Tanabe and Sugano,[28] and using a single B and ξ parameter. A very satisfactory fit of the observed bands was obtained for $Dq = 1520\ \text{cm}^{-1}$, $B = 735\ \text{cm}^{-1}$, and $\xi = 275\ \text{cm}^{-1}$ (following Cole and Garrett[33]), giving $\beta = 0.80$, although one apparent anomaly arises. Thus the elegant luminescence studies of Schläffer, *et al.*,[31,34] have shown that for CrF_6^{3-} the lowest excited state is a quartet, while for ligands above F^- in the spectrochemical series a doublet lies lowest, but our fitting parameters lead to a state formally corresponding to the ${}^2E_g(t^3_{2g})$ level as the lowest excited state. However, inspection of the eigenvectors resulting from the diagonalization of the Γ_8 matrix shows that this level in fact contains more ${}^4T_{2g}(t^2_{2g}e_g)$ than ${}^2E_g(t_{2g}{}^3)$ character—50.5 and 47.5%, respectively. Similarly both Jørgensen[7] and Schläffer, *et al.*,[31] placed the ${}^2T_{2g}(t_{2g}{}^3)$ level below the ${}^4T_{1g}(F)(t_{2g}{}^2e_g)$ state, while our parameters lead to the opposite order. In this case though there is no unequivocal guide as to which multiplicity lies lowest, and, because of the appreciable spin–orbit mixing, intensity is not here a reliable criterion. However, our order is very sensitive to small changes in the fitting parameters and must accordingly be regarded as tentative.

If, following Jørgensen,[7,29] we were to assume $B_{55} > B_{35}$, it would be possible to bring the calculated ${}^2E_g$ level about the ${}^4T_{2g}$ state, but this would at the same time raise the calculated energy of the ${}^2T_{2g}(t_{2g}{}^3)$ level unless an appreciable reduction in the C/B ratio was adopted. For the reasons outlined above we did not feel such refinements to be justified, and it should in this context be pointed out that Jørgensen's procedure for obtaining β_{55}, *via* second-order perturbation theory from the position of the ${}^2E_g$ transition, certainly tends to overestimate this parameter. This is because the higher ${}^2E_g$ states which interact with the ${}^2E_g(t_{2g}{}^3)$ level are assumed to lie only $10Dq$ above it, whereas the actual separation is appreciably greater.

(d) **K_3MnF_6.**—The spectrum of this salt has previously been investigated up to about 25 kK both by Oelkrug[5] and by Davis, Fackler, and Weeks.[35] The $MnF_6{}^{3-}$ ion is known to be a high-spin system, with a ${}^5E_g(t_{2g}{}^3e_g)$ ground state, and should therefore by virtue of the e_g orbital degeneracy show a substantial tetragonal Jahn–Teller distortion. Davis, *et al.*,[35] have put forward convincing arguments for assigning the band at 9.0 kK as arising from a transition between the Jahn–Teller split components of the ${}^5E_g$ ground state, and since our spectrum closely resembles those of the earlier workers,[5,35] we agree with them in the assignment of the bands at 9.0, 17.8, and 19.4 kK. From these bands we obtain the parameters $Dq = 1740\ \text{cm}^{-1}$, $Ds = 1600\ \text{cm}^{-1}$, and $Dt = 520\ \text{cm}^{-1}$, the last two quantities being the tetragonal crystal field parameters as defined by Ballhausen.[26] Unfortunately, since the energy of the ${}^5E_g \rightarrow {}^5T_{2g}$ transition does not depend upon B, this parameter cannot be found from the positions of its tetragonally split components.

Nevertheless, although the three lowest energy bands constitute the components of the only quintet–quintet transition, it should be possible to make an estimate for B if any of the spin-forbidden, quintet–triplet excitations could be located. In our spectrum two weak and relatively narrow bands are observed at 23.3 and 26.2 kK, the former corresponding to a weak sharp inflection at *ca.* 24 kK in Oelkrug's[5] K_3MnF_6 spectrum, upon which the author did not comment. These we assign as spin-forbidden transitions, and we have analyzed our data on the assumption of a ligand field of tetragonal (D_4) symmetry, using the electrostatic repulsion matrices for d^4 systems derived by Otsuka.[36] In our calculations we took $C/B = 4.6$, after Tanabe and Sugano, assumed the Dq, Ds, and Dt parameters to have the values determined from the spin-allowed transitions, and evaluated the one-electron parts of the diagonal matrix elements according to Ballhausen[26] (*cf.* ref 8). With only two of the many possible spin-forbidden transitions located, it is clearly not possible to obtain a unique fit of the bands, but we proceeded on the assumption that it is usually only the rather sharp bands, with the same electronic configuration as the ground state which will be at all easily detected. In D_4 symmetry the ground state has the configuration $e^2b_2a_1$ ($t_{2g} \rightarrow e + b_2$, $e_g \rightarrow a_1 + b_1$) and there are five triplet excited states also formally possessing this composition, ${}^3A_1$, ${}^3A_2$, 2 ${}^3B_1$, and ${}^3B_2$; we therefore diagonalized the appropriate matrices for various values of B corresponding to β ranging between 0.70 and 0.90. For $B = 782\ \text{cm}^{-1}$ ($\beta = 0.80$), the predicted levels are as shown in Table II, and it is clear that the three lowest triplet levels would not be expected to be distinguishable from the spin-allowed band at 19.6 kK, while the highest triplet level would be obscured by the onset of the charge-transfer transitions. This leaves the ${}^3B_{1g}$

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[30] J. Ferguson, K. Knox, and D. L. Wood, *J. Chem. Phys.*, **35**, 2236 (1961).

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[36] J. Otsuka, *J. Phys. Soc. Jap.*, **21**, 596 (1966).

TABLE II
CALCULATED BAND POSITIONS FOR
CrF_6^{3-}, MnF_6^{3-}, FeF_6^{3-}, AND CoF_6^{3-} [a]

CrF_6^{3-}, Ground State $^4A_{2g}(t_{2g}^3)$		MnF_6^{3-}, Ground State $^5B_{1g}(e_g^2b_{2g}a_{1g})$	
$^2E_g(t_{2g}^3)$	14.91	$^5A_{1g}(e_g^2b_{2g}b_{1g})$	9.00
$^4T_{2g}(t_{2g}^2e_g)$	15.29	$^5B_{2g}(e_g^2b_{1g}a_{1g})$	17.40
$^2T_{1g}(t_{2g}^3)$	15.95	$^3B_{1g}(e_g^2b_{2g}a_{1g})$	18.91
$^4T_{1g}(t_{2g}^2e_g)$	22.12	$^5E_g(e_gb_{2g}b_{1g}a_{1g})$	19.60
$^2T_{2g}(t_{2g}^3)$	22.64	$^3A_{2g}(e_g^2b_{2g}a_{1g})$	20.43
$^4T_{1g}(t_{2g}e_g^2)$	34.47	$^3A_{1g}(e_g^2b_{2g}a_{1g})$	21.32
		$^3B_{1g}(e_g^2b_{2g}a_{1g})$	23.61
		$^3B_{2g}(e_g^2b_{2g}b_{1g})$	25.81
		$^3B_{2g}(e_g^2b_{2g}a_{1g})$	39.84

FeF_6^{3-}, Ground State $^6A_{1g}(t_{2g}^3e_g^2)$		CoF_6^{3-}, Ground State $^5T_{2g}(t_{2g}^4e_g^2)$	
$^4T_{1g}(t_{2g}^4e_g)$	16.65	$^3T_{1g}(t_{2g}^5e_g)$	7.01
$^4T_{2g}(t_{2g}^4e_g)$	21.53	$^3T_{2g}(t_{2g}^5e_g)$	10.97
$^4A_{1g}(t_{2g}^3e_g^2)$	26.73	$^5E_g(t_{2g}^3e_g^3)$	14.50
$^4E_g(t_{2g}^3e_g^2)$	26.80	$^3T_{1g}(t_{2g}^4e_g^2)$	19.12
$^4T_{2g}(t_{2g}^3e_g^2)$	29.89	$^3T_{2g}(t_{2g}^4e_g^2)$	20.30
$^4E_g(t_{2g}^3e_g^2)$	32.44	$^3E_g(t_{2g}^4e_g^2)$	22.00
$^4T_{1g}(t_{2g}^3e_g^2)$	39.04	$^3T_{1g}(t_{2g}^4e_g^2)$	22.55
$^4A_{2g}(t_{2g}^3e_g^2)$	44.07	$^3T_{2g}(t_{2g}^4e_g^2)$	25.76
		$^3A_{2g}(t_{2g}^3e_g^3)$	30.91

[a] For calculations in which spin–orbit coupling was included the values given are the weighted means of those for the appropriate double group representations.

level predicted at 23.6 kK in good agreement with the observed band position but no level apparently corresponding to the peak at 26.2 kK. However, examination of the eigenvectors resulting from the diagonalization of the $^3B_{2g}$ matrix shows that the $^3B_{2g}$ $(e^2b_2a_1)$ level predicted at 39.8 kK interacts to a remarkably large extent with the $^3B_{2g}(e^2b_2b_1)$ band predicted at 25.8 kK and that this latter level in fact contains just over 50% of $^3B_{2g}(e^2b_2a_1)$ character. This assignment for the 26.2-kK band is therefore acceptable, although all the other states arising from the $e^2b_2a_1$ configuration are essentially pure configurations.

When the value of B used is either increased or decreased, the resulting fit becomes much less satisfactory: apart from the deterioration in the numerical fitting, more triplet bands than observed would be expected for $\beta \approx 0.9$ and fewer than observed for $\beta \approx 0.7$. We have therefore adopted the value $B = 782$ cm^{-1}, with $\beta = 0.80$, the latter result being in remarkably good agreement with the value of 0.81 deduced[1,8] from Jørgensen's g and k parameters. Finally, although we agree with Hatfield, *et al.*,[37] in locating the beginning of the higher intensity region at just over 40 kK, we found no trace of the very weak band reported to lie at about 29 kK. If however this band is real, it would require rather higher values of B and β to accommodate it on the basis of our approach.

(e) **K_3FeF_6.**—Although numerous magnetic investigations have shown the FeF_6^{3-} ion to possess a magnetic moment close to the spin-only value of 5.92 BM required by a high-spin $^6A_{1g}(t_{2g}^3e_g^2)$ ground state, only one spectroscopic study has been reported. This was carried out by Jørgensen[7] for $(enH)_3FeF_6$ (en = ethylenediamine), but the nature of the cation presumably precluded the extension of the spectral range above about 32 kK. Our spectrum of the potassium salt is similar in general form to Jørgensen's result, but all the d–d bands lie at rather higher energies, and it is possible that the transitions at 37.0 and 42.6 kK could also represent d–d excitations.

For a $^6A_{1g}$ ground state all the d–d transitions are necessarily spin forbidden and accordingly the intensities of the bands as indicated by the F_R values are all very small. As would be expected, the two lowest transitions, $^6A_{1g} \rightarrow {}^4T_{1g}(G)$ and $^6A_{1g} \rightarrow {}^4T_{2g}(G)$, are both fairly broad since they correspond to a change of configuration from $t_{2g}^3e_g^2$ to $t_{2g}^4e_g$. Conversely the next three transitions, $^6A_{1g} \rightarrow {}^4A_{1g}$, $^6E_g(G)$, $^4A_{1g} \rightarrow {}^4T_{2g}$, and $^6A_{1g} \rightarrow {}^4E_g(D)$, all represent transitions within the $t_{2g}^3e_g^2$ subshell and are, as would be predicted, quite sharp. An excellent fit of these first five bands is obtained with the matrices of Tanabe and Sugano[28] using $Dq = 1300$ cm^{-1}, $B = 800$ cm^{-1}, and $\beta = 0.77$, with $C/B = 4.7$, the fitting parameters all being slightly smaller than those obtained by Jørgensen.[7] The inclusion of spin–orbit coupling using the strong-field d^5 matrices of Schroeder,[38] with[32] $\xi = 460$ cm^{-1}, does not materially affect the fitting and also shows that spin–orbit splitting will not invalidate our conclusions concerning the band widths since the largest effect, for the higher $^4T_{2g}$ level, does not produce a spread of more than 1 kK.

The assignment of the rather stronger peak at 37.0 kK and the shoulder at 42.6 kK is somewhat more difficult. Our fitting parameters predict that two more d–d transitions within the $t_{2g}^3e_g^2$ manifold should lie in about this region, namely, $^6A_{1g} \rightarrow {}^4T_{1g}$ at 39.0 kK and $^6A_{1g} \rightarrow {}^4A_{2g}$ at 44.1 kK, and it is possible that the two observed absorptions correspond to these transitions which are gaining intensity by spin–orbit interaction with spin-allowed charge-transfer excitations. On the other hand either or both bands may represent parity-forbidden $\pi_g \rightarrow t_{2g}$ charge-transfer transitions, possibly $t_{1g} \rightarrow t_{2g}$. We incline to the former view for the lower band and to the latter for the 44.1-kK transition, but we did not feel justified in modifying our fit of the d–d transitions so as to accord more closely with the observed positions for these bands.

(f) **K_3CoF_6.**—The CoF_6^{3-} anion is unique among Co(III) complexes in possessing a high-spin $^5T_{2g}(t_{2g}^4e_g^2)$ ground state, as demonstrated by the magnetic moment determinations of Klemm, *et al.*,[14] and of Cotton and Meyers.[6] The only previous spectroscopic study of the CoF_6^{3-} system was carried out by the latter authors, but the range covered extended only from 8 to 20 kK.

For a high-spin d^6 system only a single spin-allowed d–d transition, $^5T_{2g} \rightarrow {}^5E_g$, would be expected, but Cotton and Meyers[6] found for several CoF_6^{3-} salts that the spectrum consisted of a broad band split into two peaks of approximately equal intensities. For K_3CoF_6 the observed peak positions were 11.4 and 14.5 kK, and the splitting was attributed, for all CoF_6^{3-} salts, to a tetragonal Jahn–Teller splitting of the excited ^5E_g level. However, since our spectrum, although broadly similar, differs in some important respects from that of Cotton and Meyers, it is necessary to consider it in some detail before their conclusion can be verified.

First of all we find a very weak broad absorption centered at about 6.0 kK, in the uninvestigated low-energy region, but the most significant difference is that the band attributed to the quintet–quintet transition

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(37) W. E. Hatfield and W. E. Parker, *Inorg. Nucl. Chem. Lett.*, **1**, 7 (1965).

(38) K. Schroeder, *J. Chem. Phys.*, **37**, 1587 (1962).

is now split to an appreciably greater extent (peaks at 11.8 and 16.4 kK), while the lower energy component is much the weaker in intensity. It is therefore necessary to consider whether it might be possible to assign the 16.4-kK peak as ${}^5T_{2g} \rightarrow {}^5E_g$ and the 11.8-kK band as a spin-forbidden transition. Since CoF_6^{3-} is the only high-spin Co(III) complex, Dq/B would be expected to lie close to the spin crossover point, and under these circumstances the triplet state lying just below the ${}^5E_g$ level would be the ${}^3T_{2g}(t_{2g}{}^5e_g)$ state.

There are however a number of arguments against such an assignment. First of all it would lead to Dq = 1640 cm^{-1}, which would require B to be greater than 820 cm^{-1} for CoF_6^{3-} to be high-spin, assuming[28] C/B = 4.8. This corresponds to $\beta \approx 0.75$, which is a little higher than would be expected on the basis of the nephelauxetic behavior of other Co(III) complexes. Furthermore, a more cogent argument against the assignment of the 11.8-kK peak as ${}^5T_{2g} \rightarrow {}^3T_{2g}$ lies in the fact that there are no nonvanishing spin–orbit matrix elements connecting ${}^3T_{2g}$ with the nearby ${}^5E_g$ level. First-order perturbation calculations indicate that this band could not possibly acquire its observed intensity, relative to the 16.4-kK band, by spin–orbit interaction with the ${}^5T_{2g}$ ground state or by secondary effects, and examination of the eigenvectors resulting from the diagonalization of the complete strong-field spin–orbit matrices (see below) confirms this opinion. The assignment of the 11.8-kK band as ${}^5T_{2g} \rightarrow {}^3T_{1g}(t_{2g}{}^5e_g)$ is similarly not feasible since this would require a still larger value of B, and the spin–orbit matrix elements connecting ${}^3T_{1g}(t_{2g}{}^5e_g)$ with ${}^5E_g$ are also all zero. Thus, since there are no other triplet levels to which the 11.8-kK band could reasonably be assigned, we agree with Cotton and Meyers in postulating an excited-state Jahn–Teller distortion for the ${}^5E_g$ level, and, taking the average of the two peak positions, we obtain Dq = 1410 cm^{-1}.

The weak broad band at 6.0 kK is probably somewhat exaggerated in intensity due to the difficulty of eliminating background absorption, but its position is consistent with an assignment as ${}^5T_{2g} \rightarrow {}^3T_{1g}(t_{2g}{}^5e_g)$. Although there are no nonzero spin–orbit matrix elements connecting the ${}^3T_{1g}$ and ${}^5E_g$ levels, the former can interact with the ${}^5T_{2g}$ ground state and the energy separation is now sufficiently small for it to gain an observable intensity. This assignment is also consistent with the broadness of the band since the transition would represent a $t_{2g}{}^4e_g{}^2 \rightarrow t_{2g}{}^5e_g$ excitation.

At 19.6, 23.3, and 26.3 kK, respectively, are found a small narrow peak and two well-defined shoulders, all of which are considerably sharper at liquid nitrogen temperature. When resolved from the background due to the beginnings of the charge-transfer region, all these absorptions correspond to very weak sharp bands which we therefore assign as spin-forbidden transitions to states with the same configuration as the ${}^5T_{2g}(t_{2g}{}^4e_g{}^2)$ ground level. From the diagrams and matrices of Tanabe and Sugano[28] the 19.6-kK band can clearly be assigned to transitions to the lowest lying, almost coincident, ${}^3T_{1g}$, ${}^3T_{2g}(t_{2g}{}^4e_g{}^2)$ levels, while the 23.3- and 26.3-kK shoulders are consistent with transitions to the higher lying ${}^3T_{1g}$ and ${}^3T_{2g}(t_{2g}{}^4e_g{}^2)$ states, respectively, and a good fit of all the bands up to 27 kK is obtained using the parameters Dq = 1410 cm^{-1}, B = 765 cm^{-1}, and β = 0.70. It may be noted in passing that the 19.6-kK peak is clearly discernible in the spectrum of Cotton and Meyers,[6] although they do not remark upon it, and we have already suggested the above assignment for it.[1]

The inclusion of spin–orbit coupling in our calculations generally supports these assignments. Using the strong-field d^4,d^6 matrices of Schroeder,[39] with[33] ξ = 580 cm^{-1}, we find that the four triplet levels in question should contain between about 0.5 and 2.0% quintet character, derived by interaction with the ${}^5E_g$ level, and this should be an appreciable underestimate since the Jahn–Teller splitting of the ${}^5E_g$ state causes the upper component to lie closer to these triplet levels than is assumed in diagonalizing the appropriate matrices. Moreover, it is also possible that the higher levels are beginning to gain some intensity by interaction with spin-allowed charge-transfer excitations.

The assignment of the broad inflection at 30.3 kK must necessarily be speculative: the band corresponds quite closely with the predicted position of the ${}^5T_{2g} \rightarrow {}^3A_{2g}(t_{2g}{}^3e_g{}^3)$ transition, but it could equally well represent a parity-forbidden charge-transfer band of the $t_{1g} \rightarrow t_{2g}$ type.

Assignment of Charge-Transfer Transitions.—The assignment of the Laporte-allowed charge-transfer transitions is, for the Ti, V, Fe, and Co complexes, a fairly straightforward matter, these broad, intense bands being designated as shown in Table I. For CrF_6^{3-} and MnF_6^{3-} the maxima of the $\pi_u \rightarrow t_{2g}$ transitions lie beyond the range of the instrument, although in each case the beginning of the allowed charge-transfer region is apparent, and it is clear that for the Mn compound the peak should lie at rather lower energies than for CrF_6^{3-}, since the band is better developed at 50 kK for the former. For the purpose of interpreting the positions of the charge-transfer bands we have therefore made the tentative assumptions that the peaks will lie between 50 and 55 and between 55 and 60 kK, respectively, for the Mn(III) and Cr(III) compounds, this being based upon the shapes of the Laporte-allowed bands in the other four complexes.

Until recently very little progress has been made in rationalizing the positions of the charge-transfer bands in the hexahalo complexes of the 3d series, although the behavior of such compounds in the 4d and 5d groups was well understood.[40] For the MF_6^{3-} complexes of the first transition series the allowed charge-transfer bands tend to lie at fairly high energies, beyond the range of many spectrometers, but it has recently been shown[9] that the corresponding bands for the MF_6^{2-} series, which lie at much lower energies, can easily be interpreted in terms of the spin-pairing energy treatment of Jørgensen.[10,40] Accordingly it is of interest to determine whether the positions of the charge-transfer bands in the MF_6^{3-} series are susceptible to similar treatment.

Jørgensen[7,40] showed that the positions of the $\pi \rightarrow \gamma_5(t_{2g})$ and $\pi \rightarrow \gamma_3(e_g)$ transitions could be adequately accommodated by expressions of the forms

$$(\pi \rightarrow \gamma_5) = V + kD + q(A - E)$$

and

$$(\pi \rightarrow \gamma_3) = V + k'D + q(A - E) + \Delta$$

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[39] K. Schroeder, *J. Chem. Phys.*, **37**, 2553 (1962).

[40] C. K. Jørgensen, *Mol. Phys.*, **2**, 309 (1959).

TABLE III

VALUES OF THE PARAMETERS k AND k'

		d^0	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9
k	l[a]	$-{}^3/_4$	$-{}^5/_4$	$-{}^7/_4$	$+{}^7/_4$	$+{}^5/_4$	$+{}^3/_4$	...	...	...	...
	h[b]					$+{}^9/_4$	$+{}^{11}/_4$	$+{}^9/_4$	$+{}^7/_4$	...	...
k'	l[a]	$-{}^3/_4$	$-{}^5/_4$	$-{}^7/_4$	$-{}^9/_4$	$-{}^7/_4$	$-{}^5/_4$	$-{}^3/_4$	$-{}^5/_4$	$+{}^5/_4$	$+{}^3/_4$
	h[b]					$-{}^{11}/_4$	$+{}^{11}/_4$	$+{}^9/_4$	$+{}^7/_4$		

[a] Low spin. [b] High spin.

for complexes of cations formally possessing a d^q configuration. Here V is a parameter depending on the nature of the ligand, the oxidation state of the metal, and the particular transition series, and D is the spin-pairing energy. E contains the variation of the orbital energy of the t_{2g} electrons with the occupation number q, and A is approximately equal to the corresponding Racah parameter. For a metal ion configuration with total spin S the spin-pairing energy contribution is $-S(S + 1)D$ whence the values of k and k' for the various d^q systems are easily obtained. Some of these have been given by Jørgensen,[7,40] but a full list is given in Table III.

For the MF_6^{3-} anions of Ti, V, Cr, Mn, Fe, and Co the positions of the charge-transfer bands are in fact well reproduced by the parameters $V = 60.0$ kK, $E - A = +5.5$ kK, and $D = 6.0$ kK (*cf.*[9] 48.5, 4.5, and 5.5 kK, respectively for the M(IV) series), assuming a constant value of D throughout. Actually the average value of D for a given d^q configuration can be shown[41] to be equal to ${}^7/_6\ ({}^5/_2B + C)$, so that D ranges from 5.4 to 6.7 kK, but this does not materially affect the quality of the fitting. It should of course also be possible to fit the charge-transfer bands for the NiF_6^{3-} and CuF_6^{3-} anions[8] using the same set of parameters, and the calculated values for all the MF_6^{3-} ions are shown in Table IV. For the low-spin d^7 NiF_6^{3-} ion and for CuF_6^{3-} the charge-transfer bands represent $\pi \rightarrow \gamma_3$ excitations, and the calculated results therefore include the value of Δ.

TABLE IV

CALCULATED POSITIONS OF CHARGE-TRANSFER BANDS IN MF_6^{3-} COMPLEXES

M(III)	B, cm^{-1}	C/B	D, kK	ΔE, kK Calcd	ΔE, kK Obsd
Ti	...	...	(5.0)[a]	48.25	47.7
V	670	4.4	5.40	39.55	43.3
Cr	740	4.5	6.04	54.1	55–60
Mn	780	4.6	6.46	52.5	50–55
Fe	800	4.7	6.72	51.0	48.8
Co	765	4.8	6.51	41.6	40.6
Ni	703	4.9	5.82	30.6[c]	32.0
Cu	536[b]	5.0	4.69	36.0[c]	37.0

[a] Extrapolated value. [b] B_{33} value. [c] $\pi \rightarrow \gamma_3$ transitions.

For the Ni(III) complex the agreement between the calculated and observed values is very satisfactory, but for CuF_6^{3-} the value derived is some 7.7 kK higher than the lowest band assigned[8] to a $\pi \rightarrow e_g$ transition. In view of the very good agreement obtained for all the other members of the series it seems likely therefore that it is the 37.2-kK band in CuF_6^{3-} which corresponds to the Laporte-allowed $\pi_u \rightarrow e_g$ transition, while the 29.5-kK peak represents a parity-forbidden $\pi_g \rightarrow e_g$ excitation. This explanation would also resolve the difficulty of the extraordinarily high optical electronegativity derived[1] for Cu(III), and a similar interpretation appears probable for the $4d^8$ AgF_6^{3-} system.

The determination of D and the assignment of the Laporte-allowed charge-transfer bands also allows the evaluation of Jørgensen's[10] optical electronegativity parameters for the MF_6^{3-} complexes. These are derived using the relationship

$$\sigma_{\text{cor}} = (\chi_{\text{opt}}(X) - \chi_{\text{opt}}(M^{n+})) \times 30\ \text{kK}$$

where $\chi_{\text{opt}}(X)$ is the optical electronegativity of the ligand and $\chi_{\text{opt}}(M^{n+})$ that of the metal cation corresponding to the oxidation state of the complex. For F^- $\chi_{\text{opt}}(X)$ is 3.9, using the Pauling scale. The value of σ_{cor} is obtained from the position of the lowest Laporte-allowed band, applying two corrections. First of all, if the band corresponds to a $\pi \rightarrow \gamma_3$ transition, we subtract Δ so as to make a direct comparison with $\pi \rightarrow \gamma_5$ excitation. Second, allowance is made for the change in the spin-pairing energy which accompanies the $d^q \rightarrow d^{q+1}$ transition. These corrections are readily deduced on the assumption[10,41] that the average contribution to the energy for terms with a given S value is $D(\langle S(S + 1)\rangle - S(S + 1))$, where $\langle S(S + 1)\rangle = 3q/4 - 3q(q - 1)/(16l + 4)$; these quantities have been given by Jørgensen[42] and the corrections listed explicitly elsewhere,[1] for both high- and low-spin situations.

For the first six members of the series the χ_{opt} values

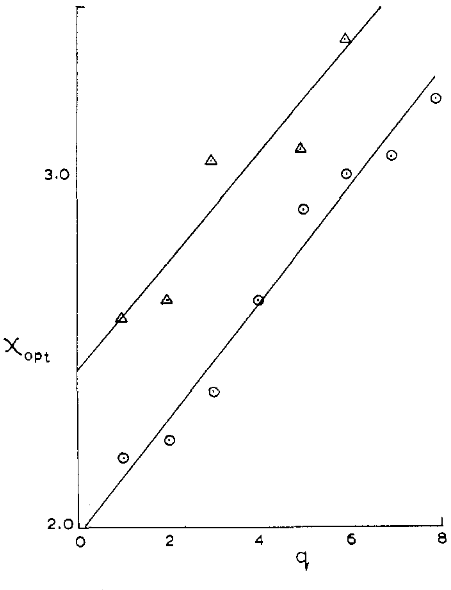

Figure 7.—Correlation between χ_{opt} and q for MF_6^{3-} and MF_6^{2-} anions: ○, M(III); △, M(IV).

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(41) C. K. Jørgensen, *Struct. Bonding (Berlin)*, **1**, 3 (1966).

(42) C. K. Jørgensen, *Solid State Phys.*, **13**, 375 (1962).

TABLE V

OPTICAL ELECTRONEGATIVITIES FOR MF_6^{3-} COMPLEXES

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
χ_{opt}	2.22	2.25	2.39	2.65	2.91	3.01	3.06	3.23

shown in Table V are all appreciably larger than those deduced previously for these oxidation states. Thus, although in principal χ_{opt} should be independent of the nature of the ligand and of the coordination scheme, this bears out Jørgensen's[43] view that values obtained from tetrahalo and other species might be somewhat too low. The revised values incidentally greatly improve the correlation between χ_{opt} and the occupation number q, which previously[9] showed a considerable scatter. The plot of χ_{opt} *vs.* q gives now a slope of 0.165 unit (*ca.* 5 kK), which is consistent with its interpretation[43] as $E - A$, and compares with 0.15 unit (*ca.* 4.5 kK) for the M(IV) series (see Figure 7).

We have elsewhere[9] noted the existence of a strong connection between the optical electronegativity and the nephelauxetic ratio and have put forward a theoretical justification for this relationship. From a conceptual standpoint this connection is readily understood since both parameters essentially assess the same characteristic, namely, the ease of electron accession toward the central metal cation, and it is seen from Figure 8 that the plots of χ_{opt} *vs.* β for both the M(III) and M(IV) series for the fluoride ligand provide further evidence for this connection. Two points not previously noted[9] are worth attention. First of all, the value of χ_{opt} is extremely sensitive to small changes in β. This is not surprising since the essential proportionality is between χ_{opt} and a repulsion integral of the J(3d,3d) type, containing F_0, F_2, and F_4 Slater–Condon integrals. Thus, a small change in β, which reflects the F_2 and F_4 values, will have a substantial effect on F_0 and hence on χ_{opt}.

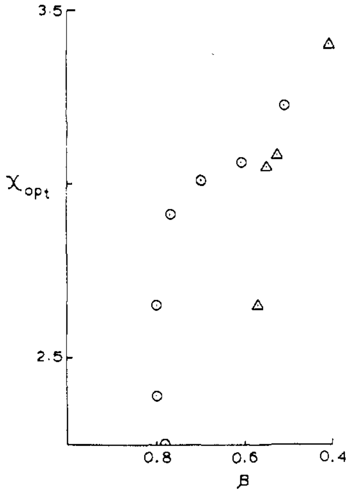

Figure 8.—Relationship between χ_{opt} and β for MF_6^{3-} and MF_6^{2-} anions: ○, M(III); △, M(IV).

Second, the fact that the relationship between β and χ_{opt} only becomes really apparent toward the end of the 3d series is also consistent: not only does the extent of covalency become much more marked near the end of the series, but the values of the B and the J(3d,3d) integrals also are known to increase in this sense.

Thus the investigation of the electronic spectra of the MF_6^{3-} species of the 3d series, completed in the present work, has confirmed the tendency for the nephelauxetic ratio to decrease toward the end of the series[8] and has provided further evidence for the dependence of χ_{opt} on the occupation number, q, of the 3d level and for the connection between χ_{opt} and β previously suggested.[9]

Acknowledgment.—We are much indebted to a referee for his helpful comments concerning the interpretation of the spectrum of K_3TiF_6.

(43) C. K. Jørgensen, *Mol. Phys.*, **6**, 43 (1963).

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The Polarized Crystal Spectra of Tris(octamethylpyrophosphoramide)cobalt(II), -nickel(II), and -copper(II) Perchlorates[1]

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Polarized single-crystal electronic spectra of the tris-octamethylpyrophosphoramide complexes of cobalt(II), nickel(II), and copper(II) in the isomorphous crystals $M(OMPA)_3(ClO_4)_2$ have been measured at temperatures down to 5°K. The high energy of charge transfer and the low value of Dq combine to permit observation of all predicted spin-allowed and most spin-forbidden transitions. Trigonal electric dipole selection rules are clearly obeyed in the spin-allowed bands with only slight vibronic breakdown. The $Co(OMPA)_3^{2+}$ and $Ni(OMPA)_3^{2+}$ spectra at 5°K have been fitted to electrostatic ligand field calculations with the following results: for $Ni(OMPA)_3^{2+}$, Dq = 0.731 kK, B = 0.950 kK, C = 3.74 kK; for $Co(OMPA)_3^{2+}$, Dq = 0.765 kK, B = 0.855 kK, C = 3.68 kK; for $Cu(OMPA)_3^{2+}$, Dq = 1.0 kK. Trigonal splittings are apparently insignificant in the $Co(OMPA)_3^{2+}$ and $Ni(OMPA)_3^{2+}$ spectra. The spectrum of $Cu(OMPA)_3^{2+}$ yields an apparent v of 1.0 kK, although analysis in terms of lower symmetry is suggested.

Introduction

The study of intrinsically trigonal complexes and of metal ions in trigonal sites in single crystals using polarized crystal spectroscopy has been extensive during the last 10 years.[2] Included are the studies of trivalent

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(1) Abstracted in part from the Ph.D. thesis of C. R. Taylor, Duke University, 1971. Presented in part at the Southeast Regional Meeting of the American Chemical Society, Richmond, Va., Nov 1969.

(2) N. S. Hush and R. J. M. Hobbs, *Progr. Inorg. Chem.*, **10**, 259 (1968).