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The Electronic Spectra of the Hexafluoronickelate(III), Hexafluorocuprate(III), and Hexafluoroargentate(III) Anions

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The electronic spectra of the hexafluoronickelate(III), hexafluorocuprate(III), and hexafluoroargentate(III) anions have been studied by diffuse reflectance between 4 and 45 kK for the compounds K_3NiF_6, Na_3NiF_6, Cs_2KCuF_6, and Cs_2KAgF_6. The CuF_6^{3-} ion shows prominent ligand field bands at 14.1 and 20.4 kK, assigned to $^3A_{2g} \rightarrow {}^3T_{2g}$ and $^3A_{2g} \rightarrow {}^3T_{1g}$ transitions, respectively, with a weaker peak at 9.6 kK and a faint shoulder at 16.4 kK. The latter are ascribed to spin-forbidden transitions to ^1E_g and $^1A_{1g}$ states and the intense bands found at 29.5 and 37.2 kK to $\pi \rightarrow e_g$ charge-transfer excitations. The AgF_6^{3-} ion similarly shows the $^3T_{2g}$ and $^3T_{1g}$ bands at 18.4 and 23.4 kK, but the well-marked shoulder at 12.9 kK is now assigned to the $^1A_{1g}$ excitation and the very weak peak at 6.3 kK to the ^1E_g transition, while the charge-transfer bands appear at 27.5 and 37.5 kK. In both compounds spin–orbit coupling is important in determining the relative intensities of the spin-forbidden transitions and the widths of the $^3T_{2g}$ bands. Fitting of the d–d bands using the Tanabe–Sugano strong-field matrices yields, for the copper complex, $Dq = 1410$ cm^{-1}, $B_{35} = 641$ cm^{-1}, $B_{33} = 536$ cm^{-1}, $\beta_{35} = 0.55$, and $\beta_{33} = 0.46$, and for the silver complex, $Dq = 1840$ cm^{-1}, $B_{35} = 472$ cm^{-1}, $B_{33} = 375$ cm^{-1}, $\beta_{35} = 0.61$, and $\beta_{33} = 0.48$. The spectrum of the NiF_6^{3-} anion is analyzed in terms of a ^2E_g $(t_{2g}{}^6e_g)$ low-spin ground state, in which appreciable tetragonal Jahn–Teller distortion occurs. The ligand field bands are found at 6.8, 12.3, 15.7, and 19.2 kK in K_3NiF_6 and the spectrum of Na_3NiF_6 is identical except for the shift of the first two bands to 6.1 and 12.8 kK. The lowest energy band is assigned to a $^1A_1 \rightarrow {}^1B_1$ transition arising from the tetragonal ground state splitting, and the three other bands are similarly interpreted in terms of the D_4 splitting of the O_h $^2T_{1g}$, $^2T_{2g}$, and $^2T_{1g}$ $(t_{2g}{}^5e_g{}^2)$ levels. The intense bands at 32.0 and 37.0 kK are again assigned to $\pi \rightarrow e_g$ charge-transfer transitions. The d–d bands were fitted using the d^7 strong-field matrices for D_4 symmetry, assuming $Ds/Dt = 3.0$. This gave $Dq = 1620$ cm^{-1}, $B = 703$ cm^{-1}, $\beta = 0.63$, and $Dq = 423$ cm^{-1} for K_3NiF_6 and $Dt = 388$ cm^{-1} for the sodium compound. In all cases the degree of covalency indicated is high for fluoride complexes, but for Ni^{3+} and Cu^{3+} β reflects closely the decreasing stability of the higher oxidation states toward the end of the first transition series.

Introduction

Although fluoride complexes of the transition metals usually show the smallest tendency toward covalent bonding, our recent studies of the hexafluoro anions of quadrivalent nickel[1] and cobalt[2] indicate that large values of Dq, accompanied by very low values of β, the nephelauxetic ratio, may be found when the metal concerned is in a high oxidation state. However, for the hexafluoro complexes of trivalent metals of the first transition series, Dq lies always within the range of 1300–1700 cm^{-1}, and the known values of β are all relatively high (see Table I). Furthermore, the few data available[3] for divalent ions in octahedral fluoride environments indicate Dq to be about 700–800 cm^{-1} and β to lie between 0.90 and 0.95. It thus appeared desirable to undertake a systematic study of hexafluoro complexes of other trivalent metals in order to determine whether, for a given ligand, the values of β depended solely or primarily on the formal charge on the cation, or whether the nephelauxetic ratio reflected also the inherent stability of the particular oxidation state. We therefore now report the electronic spectra of the cesium potassium salts of the hexafluorocuprate(III) and hexafluoroargentate(III) anions, Cs_2KCuF_6 and Cs_2KAgF_6, and of the potassium and sodium salts of the hexafluoronickelate(III) anion, K_3NiF_6 and Na_3NiF_6, since in all of these compounds the transition metal is in an unusually high and relatively unstable oxidation state.

TABLE I

CRYSTAL FIELD SPLITTING CONSTANTS AND NEPHELAUXETIC RATIOS FOR HEXAFLUORO COMPLEXES OF TRIVALENT TRANSITION METAL IONS

	V[a]	Cr[b]	Mn[c]	Fe[b]	Co[d]	Ni[e]	Cu[e]
Dq	1685	1520	(1740)[f]	1400	(1310)[f]	(1620)[f]	1410
β	0.792	0.893	...	0.833	...	(0.63)[f]	0.55

[a] C. J. Ballhausen and F. Winther, *Acta Chem. Scand.*, **13**, 1729 (1959). [b] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press Ltd., London, 1964, pp 110, 285, 290. [c] O. G. Holmes and D. S. McClure, *J. Chem. Phys.*, **26**, 1686 (1957). [d] D. A. Cotton and M. D. Meyers, *J. Am. Chem. Soc.*, **82**, 5023 (1960). [e] Present work. [f] Estimated after allowance for Jahn–Teller effects.

The hexafluorocuprate(III) ion was first obtained as the potassium salt K_3CuF_6 by Klemm and Huss,[4] by the action of fluorine at 250° on a 3:1 mixture of KCl and Cu_2Cl_2, and hexafluoroargentate(III) ion was obtained by Hoppe and Homann[5] as the cesium potassium salt Cs_2KAgF_6, by the fluorination of a 2:1:1 mixture of CsCl, KCl, and $AgNO_3$ at 300°. The CuF_6^{3-} ion was found[4] to have a magnetic moment of 2.8 BM, very close to the spin-only value, and the AgF_6^{3-} ion was found to have[5] a moment of 2.6 BM, the low value being ascribed to possible impurities in the sample. Both Cs_2KAgF_6 and Cs_2KCuF_6 have[5] cubic, K_2NaCrF_6-type lattices.

Potassium hexafluoronickelate(III) was first pre-

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(1) G. C. Allen and K. D. Warren, *Inorg. Chem.*, **8**, 753 (1969).

(2) G. C. Allen and K. D. Warren, *ibid.*, **8**, 1902 (1969).

(3) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press Ltd., London, 1964.

(4) W. Klemm and E. Huss, *Z. Anorg. Chem.*, **258**, 221 (1949).

(5) R. Hoppe and R. Homann, *Naturwissenschaften*, **53**, 501 (1966).

pared by Klemm, Brandt, and Hoppe[6] by the action of fluorine at 340° on a 3:1 mixture of KCl and Ni_2SO_4. A slightly impure sodium salt was also obtained and the potassium salt was shown to have a cubic, K_3FeF_6-type lattice and a magnetic moment rising from 2.12 BM at 90°K to 2.54 BM at 294°K, thus suggesting a low-spin ($t_{2g}^6e_g$) ground state. However the temperature dependence of the magnetic moment is unusually large for a low-spin d^7 complex: in $Co(NO_2)_6^{4-}$ for example it amounts[7] only to 0.1 BM.

Experimental Section

Hexafluorometalate Salts.—Cesium potassium hexafluorocuprate(III) and cesium potassium hexafluoroargentate(III) were prepared by Mr. R. Homann and potassium and sodium hexafluoronickelate(III) by Dr. H. Henkel, both of the University of Giessen, Giessen, West Germany. The samples were supplied to us sealed under vacuum in our silica cells by courtesy of Professor Hoppe. The Na_3NiF_6 sample contained some NaF as impurity.

Diffuse Reflectance Measurements.—These were carried out as before,[1] 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, and converted to extinction coefficients, ϵ, by the relationship $F_R = \epsilon c/0.434s$ where c = density/molecular weight and s is the scattering coefficient. Oscillator strengths were then derived using the half-height band widths obtained from Gaussian analysis of the curves. The value of s (1.73) obtained by Kortum[8] for $KMnO_4$ was taken as typical for transition metal complexes. Since the particle size of our samples (20 ± 5 μ) was sufficiently small effectively to eliminate any regular reflectance component below about 25 kK, s is essentially constant in that region.

Results

The diffuse reflectance spectra of the salts are recorded in Tables II and III, and typical plots are presented in Figures 1–3. For the copper compound two broad but well-defined ligand field bands are found at 14.1 and 20.4 kK, and a weak narrow band is found at 9.6 kK. A faint shoulder appears at 16.4 kK, and the intense allowed charge-transfer bands appear at 29.5 and 37.2 kK. The silver complex shows a broad ligand field band at 18.4 kK and another at 23.4 kK which is partially obscured by the charge-transfer transition at 27.5 kK, the higher energy charge-transfer band lying at 37.5 kK. In addition, a very weak peak is seen at 6.3 kK, and a definite shoulder is seen at 12.9 kK.

For K_3NiF_6 four ligand field bands, all of comparable intensity, are found at 6.8, 12.3, 15.7, and 19.2 kK, and the strong charge-transfer bands lie at 32.0 and 37.0 kK. For Na_3NiF_6 the first two bands appear at 6.1 and 12.8 kK.

Table II

The Diffuse Reflectance Spectra of Cs_2KCuF_6 and Cs_2KAgF_6

Band position, kK	Assignment	ϵ	f
	Cs_2KCuF_6		
9.6	${}^3A_{2g} \rightarrow {}^1E_g$	2.2	1.3×10^{-5}
14.1	${}^3A_{2g} \rightarrow {}^3T_{2g}$	204	1.9×10^{-3}
16.4	${}^3A_{2g} \rightarrow {}^1A_{1g}$	Weak	...
20.4	${}^3A_{2g} \rightarrow {}^3T_{1g}$	189	3.1×10^{-3}
29.5	$\pi \rightarrow e_g$	Strong	...
37.2	$\pi \rightarrow e_g$	Strong	...
	Cs_2KAgF_6		
6.3	${}^3A_{2g} \rightarrow {}^1E_g$	0.5	2.6×10^{-6}
12.9	${}^3A_{2g} \rightarrow {}^1A_{1g}$	6.4	4.1×10^{-5}
18.4	${}^3A_{2g} \rightarrow {}^3T_{2g}$	384	8.0×10^{-3}
23.4	${}^3A_{2g} \rightarrow {}^3T_{1g}$	377	6.9×10^{-3}
27.5	$\pi \rightarrow e_g$	Strong	...
37.5	$\pi \rightarrow e_g$	Strong	...

Table III

The Diffuse Reflectance Spectrum of K_3NiF_6[a]

Band position, kK				
Obsd	Calcd	Assignment[b]	ϵ	f
6.8[c]	6.7	${}^2A_1 \rightarrow {}^2B_1$	28	0.5×10^{-3}
12.3[c]	11.7	${}^2A_1 \rightarrow {}^2E$		
	14.0	${}^2A_1 \rightarrow {}^2A_2$	36	0.5×10^{-3}
15.7	16.1	${}^2A_1 \rightarrow {}^2E$		
	16.8	${}^2A_1 \rightarrow {}^2B_2$	79	1.1×10^{-3}
19.2	18.6	${}^2A_1 \rightarrow {}^2A_2$	118	2.1×10^{-3}
	19.4	${}^2A_1 \rightarrow {}^2E$		
	26.1	${}^2A_1 \rightarrow {}^2E$	?	...
	26.2	${}^2A_1 \rightarrow {}^2B_2$		
32.0	...	$\pi \rightarrow e_g$	Strong	...
37.0	...	$\pi \rightarrow e_g$	Strong	...

[a] Dq = 1620 cm^{-1}, B = 703 cm^{-1}, Ds/Dt = 3.0, and Dt = 423 cm^{-1}. [b] The symmetry labels for the ligand field bands relate to D_4 symmetry and for the charge-transfer bands to O_h symmetry. [c] Found at 6.1 and 12.8 kK, respectively, in Na_3NiF_6.

Discussion

The data for the copper and silver complexes are readily interpreted, using the standard Tanabe and Sugano[9] treatment, in terms of the crystal field splitting parameter, Dq, and the Racah interelectronic repulsion parameter, B. For d^8 systems in O_h symmetry, transitions from the ${}^3A_{2g}$ ground state to the ${}^3T_{2g}$ and the lower ${}^3T_{1g}$ levels involve, in the strong-field scheme, the excitation of one electron from the t_{2g} to the e_g level, whereas transitions to the lower ${}^1E_g$ and ${}^1A_{1g}$ levels take place within the same ($t_{2g}^6e_g^2$) configuration. It is found[10] that the energy gap between the ${}^3T_{2g}$ and ${}^3T_{1g}$ levels can be expressed in terms of repulsions between t_{2g} and e_g electrons alone, while the energies of the ${}^1E_g$ and ${}^1A_{1g}$ states, relative to the ground state, involve only e_g–e_g repulsions. Thus, from the value of B given by the ${}^3T_{2g}$ and ${}^3T_{1g}$ levels, the nephelauxetic ratio β_3. can be found, while ${}^1E_g$ and ${}^1A_{1g}$ give the value of β_{335}

In fitting the spectra we have set the ratio of the Racah interelectronic repulsion parameters, C/B, equal to 5.0 for Cu^{3+} on the basis of the values found by Tanabe and Sugano[9] for other trivalent ions of the first transition series—for example C/B = 4.73, 4.81, and 4.89 for Fe^{3+}, Co^{3+}, and Ni^{3+}. In fact for d^8 systems only the positions of the ${}^1E_g$ and ${}^1A_{1g}$ levels involve the parameter C and the transitions to ${}^3T_{2g}$ and ${}^3T_{1g}$ depend only upon B. By extrapolation from the data of Tanabe and Sugano[9] we find B = 1165 cm^{-1} for Cu^{3+} (g), but for Ag^{3+}, lacking the necessary spectroscopic

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(6) W. Klemm, W. Brandt, and R. Hoppe, *Z. Anorg. Allgem. Chem.*, **308**, 179 (1961).

(7) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 338 (1959).

(8) G. Kortum and H. Schöttler, *Z. Elektrochem.*, **57**, 353 (1953).

(9) Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **9**, 753, 766 (1954).

(10) C. K. Jørgensen, *Acta Chem. Scand.*, **12**, 903 (1958).

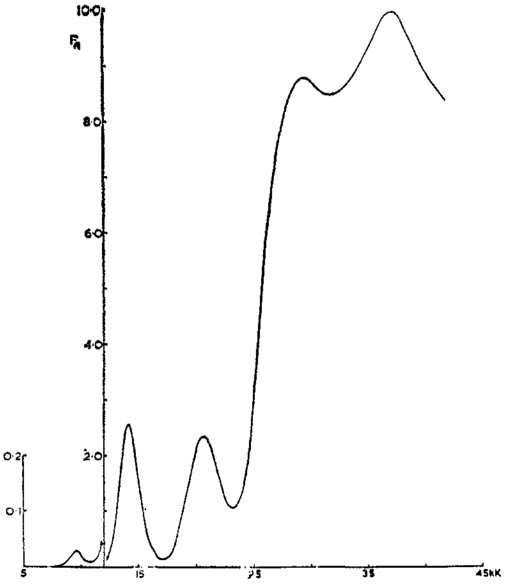

Figure 1.—The diffuse reflectance spectrum of cesium potassium hexafluorocuprate(III) at room temperature.

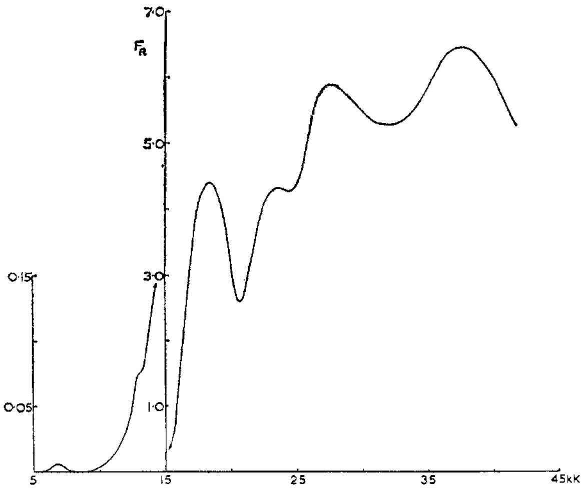

Figure 2.—The diffuse reflectance spectrum of cesium potassium hexafluoroargentate(III) at room temperature.

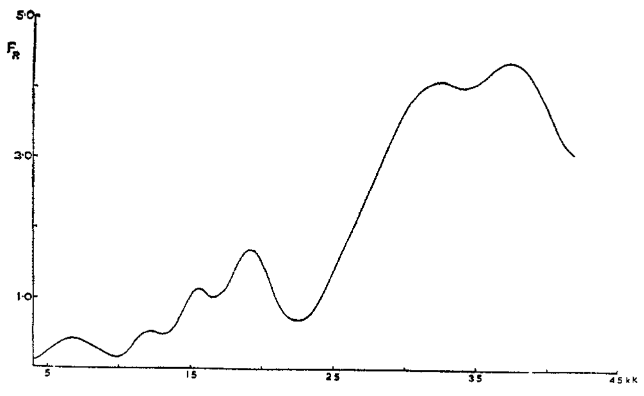

Figure 3.—The diffuse reflectance spectrum of potassium hexafluoronickelate(III) at room temperature.

data, we used the same value of C/B and determined B according to Jørgensen's[3] suggestion that $B[\mathrm{M}^{3+}(4\mathrm{d}^n)] = 0.666B[\mathrm{M}^{3+}(3\mathrm{d}^n)]$. This gave $B[\mathrm{Ag}^{3+}(\mathrm{g})] = 776\ \mathrm{cm}^{-1}$.

From the Tanabe–Sugano diagrams for d^8 systems, the two medium-intensity ligand field bands of $\mathrm{Cs_2KCuF_6}$ at 14.1 and 20.4 are readily assigned as ${}^3\mathrm{A}_{2g} \rightarrow {}^3\mathrm{T}_{2g}$ and ${}^3\mathrm{A}_{2g} \rightarrow {}^3\mathrm{T}_{1g}$ transitions, respectively, and the bands at 18.4 and 23.4 kK in $\mathrm{Cs_2KAgF_6}$ can be similarly ascribed. By use of the Tanabe–Sugano strong-field matrices we find, for $\mathrm{CuF_6}^{3-}$, $Dq = 1410\ \mathrm{cm}^{-1}$, $B_{35} = 641\ \mathrm{cm}^{-1}$, and $\beta_{35} = 0.55$, and for $\mathrm{AgF_6}^{3-}$, $Dq = 1840\ \mathrm{cm}^{-1}$, $B_{35} = 472\ \mathrm{cm}^{-1}$, and $\beta_{35} = 0.61$.

For the copper compound the ${}^1\mathrm{E}_g$ band requires $B_{33} = 536\ \mathrm{cm}^{-1}$ and $\beta_{33} = 0.46$. The ${}^1\mathrm{A}_{1g}$ band thus corresponds to the faint shoulder at 16.4 kK, which is therefore tentatively assigned as such. For the $\mathrm{AgF_6}^{3-}$ ion the 6.3- and 12.9-kK bands are readily assigned as ${}^1\mathrm{E}_g$ and ${}^1\mathrm{A}_{1g}$, respectively, thus yielding $B_{33} = 375\ \mathrm{cm}^{-1}$ and $\beta_{33} = 0.48$.

It thus follows that in both complexes the $\Gamma_5(\mathrm{t}_{2g})$ and $\Gamma_3(\mathrm{e}_g)$ subshells are expanded to different extents since in each case the nephelauxetic ratios β_{35} and β_{33} differ significantly. There is substantial evidence[11] that the σ-antibonding e_g orbital usually has a more expanded radial function than the t_{2g} level, which is only affected by π bonding, since in d^3 complexes such as those of Cr^{3+} β_{55} is always greater than β_{35} and in d^8 complexes of Ni^{2+} β_{33} is less than β_{35}. The present data follow this trend and the differences between the β values are comparable with those observed previously.[11]

For the isoelectronic d^8 complexes of Ni^{2+} there has often been considerable difficulty[12,13] in identifying the ${}^1\mathrm{E}_g$ transition when, as is often the case, it lies close to the lower ${}^3\mathrm{T}_{1g}$ level, with which it may interact *via* spin–orbit coupling. Here however the greater Dq values of the trivalent cations eliminate this problem. For $\mathrm{CuF_6}^{3-}$ Dq/B is 2.20 and the ${}^1\mathrm{E}_g$ level lies below both the ${}^3\mathrm{T}_{2g}$ and the ${}^3\mathrm{T}_{1g}$ states, while the ${}^1\mathrm{A}_{1g}$ level is above ${}^3\mathrm{T}_{2g}$. For the silver compound the higher value of Dq/B depresses both ${}^1\mathrm{E}_g$ and ${}^1\mathrm{A}_{1g}$ below ${}^3\mathrm{T}_{2g}$.

For $\mathrm{AgF_6}^{3-}$ both β_{35} and β_{33} are slightly greater than for the Cu^{3+} complex. These parameters are of course dependent on the assumption used in determining $B[\mathrm{Ag}^{3+}(\mathrm{g})]$ but are consistent with the general trend of increasing stability of the higher oxidation states on passing from the first to the second transition series. A large difference in β for the Cu^{3+} and Ag^{3+} complexes would not in any case be expected since neither of these ions represents a particularly stable valency.

By virtue of their intensities the strong bands at 29.5 and 37.2 kK in $\mathrm{CuF_6}^{3-}$ and at 27.5 and 37.5 kK in $\mathrm{AgF_6}^{3-}$ are assigned to allowed charge-transfer transitions, presumably $\pi \rightarrow \mathrm{e}_g$ excitations ($\mathrm{t}_{1u} \rightarrow \mathrm{e}_g$ and $\mathrm{t}_{2u} \rightarrow \mathrm{e}_g$ in a molecular orbital interpretation). The decrease in energy of the lower charge-transfer band on passing from copper to silver is consistent with the higher effective positive charge on the metal in the latter complex (see below), but it is not clear why the band at about 37 kK is relatively unaffected.

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(11) C. K. Jørgensen, *Progr. Inorg. Chem.*, **4**, 73 (1962).

(12) C. K. Jørgensen, "Orbitals in Atoms and Molecules," Academic Press, New York, N. Y., 1962.

(13) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

The values of the extinction coefficients and oscillator strengths derived from our F_R values for Cs_2KCuF_6 and Cs_2KAgF_6 are shown in Table II for the d–d bands. The intensities for the spin-forbidden transitions $^3A_{2g} \rightarrow {}^1E_g$ and $^3A_{2g} \rightarrow {}^1A_{1g}$ are naturally much smaller than for those to the $^3T_{2g}$ and $^3T_{1g}$ states. In both complexes the ^1E_g band appears as a narrow well-defined peak as expected for intrasubshell $(t_{2g}{}^6e_g{}^2)$ transitions. The $^1A_{1g}$ band is very faint in $CuF_6{}^{3-}$ but the shape of the shoulder representing this transition in $AgF_6{}^{3-}$ suggests that it too is a relatively narrow band.

The spin-allowed transitions $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3T_{1g}$ $(t_{2g}{}^5e_g{}^3)$ lead of course to much broader stronger bands but the shapes and relative intensities of all the d–d bands are best interpreted in terms of the complete spin–orbit strong-field matrices of Liehr and Ballhausen.[14] The values of ξ, the spin–orbit coupling constant, for Cu^{3+} and Ag^{3+} ions in the gas phase are not known but extrapolation from the data of Griffith[15] suggests the values 850 and 1900 cm^{-1}, respectively. Since ξ is reduced in most complexes to about 80–85% of the free ion value, we constructed Tanabe–Sugano type diagrams by diagonalization of the complete Liehr and Ballhausen matrices, using $\xi/B = 1.2$ for $CuF_6{}^{3-}$ and 3.6 for $AgF_6{}^{3-}$.

When spin–orbit coupling is admitted, the ground state for d^8 systems in O_h symmetry becomes Γ_5 in the double-group nomenclature and the ^1E_g and $^1A_{1g}$ states remain as single levels, Γ_3 and Γ_1, respectively, while the $^3T_{2g}$ and the lower $^3T_{1g}$ levels are each split into four components, the former giving Γ_2, Γ_3, Γ_4, and Γ_5, and the latter giving Γ_1, Γ_3, Γ_4, and Γ_5. The $\Gamma_3({}^1E_g)$ state can thus interact with the Γ_3 states of both $^3T_{2g}$ and $^3T_{1g}$, but the $\Gamma_1({}^1A_{1g})$ state can interact only with $^3T_{1g}$. Both spin-forbidden transitions can thus gain intensity by interaction with spin-allowed excitations.

From the eigenvectors resulting from the diagonalization of the spin–orbit matrices at the appropriate Dq/B values we may estimate the proportion of triplet character in the Γ_1 and Γ_3 states and also calculate the intensities of the transitions relative to the corresponding components of the spin-allowed excitations. For ^1E_g of $CuF_6{}^{3-}$ we find about 10% triplet character and predict an intensity $^1/_{15}$ that of Γ_3 of $^3T_{2g}$. Similarly $^1A_{1g}$ of $CuF_6{}^{3-}$ gives 25% triplet character with an intensity $^1/_4$ that of the Γ_1 component of $^3T_{1g}$. For $AgF_6{}^{3-}$ the results are: ^1E_g, 5%, $^1/_{64}$; $^1A_{1g}$, 7%, $^1/_{25}$.

These ratios cannot of course be obtained experimentally since they relate only to one component of the allowed transitions, but the $^1E_g{:}{}^3T_{2g}$ and $^1A_{1g}{:}{}^3T_{1g}$ intensity ratios are in qualitative agreement with the calculations. Thus for $AgF_6{}^{3-}$, we find $I({}^1E_g)/I({}^3T_{2g}) = {}^1/_{3000}$ and $I({}^1A_{1g})/I({}^3T_{1g}) = {}^1/_{170}$ while for $CuF_6{}^{3-}$, $I({}^1E_g)/I({}^3T_{2g}) = {}^1/_{140}$, the $^1A_{1g}$ band being too faint to permit estimation of its intensity. Thus the ^1E_g band is relatively weaker in $AgF_6{}^{3-}$ than in $CuF_6{}^{3-}$ as predicted, and the $^1A_{1g}$ band is stronger than the ^1E_g band in the silver compound, also as required. It must though be remembered that the calculated values are very sensitive to Dq/B for both spin-forbidden bands in the copper complex and for the $^1A_{1g}$ band in $AgF_6{}^{3-}$.

It is also of interest to compare the band widths of the $^3T_{2g}$ band in the two compounds. Our calculations show that the spin–orbit components Γ_2, Γ_3, Γ_4, and Γ_5 of this band should be substantially more widely separated for $AgF_6{}^{3-}$ than for $CuF_6{}^{3-}$. The calculated total splittings are about 600 and 1900 cm^{-1} and experimentally the half-height widths are 2.0 and 4.5 kK. At liquid nitrogen temperature we find evidence in Cs_2KAgF_6 for splitting of the $^3T_{2g}$ band into at least two and possibly three components. This we are more inclined to ascribe to spin–orbit splitting than to vibrational fine structure of which a careful search failed to reveal any indication in either Cs_2KAgF_6 or Cs_2KCuF_6.

The analysis of the spectrum of the hexafluoronickelate(III) ion, $NiF_6{}^{3-}$, is less straightforward. The ion has the d^7 configuration and the magnetic data[6] suggest a low-spin $(t_{2g}{}^6e_g)$ ground state, although the very large temperature dependence of the magnetic moment is surprising for an E_g level. However, our measurements show the presence of at least four ligand field transitions, of comparable intensities, and thus rule out the possibility of a high-spin ground state for which only two spin-allowed ligand field bands are permitted which correspond to one-electron excitations. Our results thus indicate a ^2E_g ground state, in agreement with observations[16,17] on the behavior of Ni^{3+} in Al_2O_3 hosts. For an E_g ground state though there is no orbital contribution to the magnetic moment and this quantity should therefore normally be essentially temperature independent, in contrast to the observed behavior. Even at 90°K the magnetic moment is significantly above the spin-only value and a thermal equilibrium between low- and high spin-configurations is therefore probable,[6] implying that the value of Dq/B lies only slightly beyond the $^4T_{1g}$–^2E_g crossover point. Following Tanabe and Sugano[9] we fixed the C/B ratio at 4.90 for Ni^{3+} which yields a value of 2.26 for Dq/B at the crossover point.

It did not however prove possible to obtain a satisfactory fit of the ligand field bands using the Tanabe–Sugano matrices for d^7 O_h systems. The bands at 6.8, 12.2, 15.7, and 19.1 kK are all of moderate intensity, and it is not possible therefore to assign the 6.8-kK transition to a spin-forbidden $^2E_g \rightarrow {}^4T_{1g}$ excitation. This in any case gives a poor fit and would be contrary to the assumption of a thermal low-spin–high-spin equilibrium. If then we set Dq/B equal to 2.30 and fit the 6.8-kK band to the lowest $^2T_{1g}$ level, we predict, for the spin-allowed one-electron excitations, the values 7.2, 9.1, and 13.5 kK, and for higher values of Dq/B the correlation is even worse.

The inclusion of spin–orbit coupling also fails to improve the situation. The complete strong-field ma-

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trices for d^3 (and d^7) systems in O_h symmetry have been evaluated (see Liehr[18] and references cited therein) and for any reasonable values of the spin–orbit coupling constant the lower energy levels are not materially disturbed in the low-spin configuration. With this refinement the low-spin ground state becomes Γ_8 in the double-group nomenclature, indicating that the magnetic behavior will be complicated by the spin–orbit matrix elements which connect $\Gamma_8(^2E_g)$ with the two Γ_8 components of $^4T_{1g}$. However, the magnitude of the observed moment and its temperature dependence still appear[18a] to require Dq/B to lie at about 2.30–2.50 for $C/B = 4.90$.

Nevertheless for a ^2E_g (t_{2g}^6e) ground state we have a single electron in the doubly degenerate σ-antibonding level, a situation which would give rise to substantial Jahn–Teller configurational instability. (The inclusion of spin–orbit coupling does not affect this conclusion since the Γ_8 ground state is not a Kramer's doublet and can therefore be split by Jahn–Teller distortion.) It is known[19] that for ground states of E symmetry the octahedral arrangement undergoes tetragonal distortion by interaction with the ϵ_g vibrational mode leading to either elongation or compression along the fourfold axis and appreciable tetragonal ground-state splittings have been reported[19,20] for Cu^{2+} [d^9 ($t_{2g}^6e_g^3$), ^2E_g] and Mn^{3+} [d^4 ($t_{2g}^3e_g$), ^5E_g]. In the latter case tetragonal Jahn–Teller distortion affords quite a convincing explanation of the low-energy (8–12-kK) band found in many complexes.

We have therefore interpreted the spectrum of the hexafluoronickelate(III) anion by assuming tetragonal distortion of the NiF_6^{3-} octahedra and fitting the observed bands using the strong-field repulsion matrices (neglecting spin–orbit effects) for d^7 systems in D_{4h} symmetry. We set the ratio of the tetragonal splitting parameters Ds/Dt equal to 3.0, following the interpretation of Oelkrug's[21] MnF_6^{3-} spectrum given by Davis, Fackler, and Weeks[22] and took $Dq/B = 2.30$, just above the $^4T_{1g}$–^2E_g crossover. This latter value may be slightly too low but will not be seriously in error. The ratio Dt/B was then varied between -1.0 and $+1.0$ and the Tanabe–Sugano type of diagram shown in Figure 4 was constructed.

The matrices of electrostatic repulsion for d^3 (d^7) systems were obtained by evaluation of the matrix elements between the appropriate symmetry-adapted Slater determinental functions and were either identical with or related by a unitary transformation to those given by Otsuka.[23] It should be noted that the one-electron contributions to the diagonal matrix elements are incorrectly given in Otsuka's paper, owing to the erroneous assumption of the center of gravity rule for both the Ds and the Dt splittings. We have used Ds and Dt as defined by Ballhausen,[13] and thus positive values of Dt represent elongation along the fourfold axis, and negative values correspond to compression. Matrices for several d^n systems in D_4 symmetry have also been given by Brezuleanu and Ivanov,[24] but these contain numerous incorrect entries. A valid alternative approach has been given by Perumareddi[25,26] in which the tetragonal distortion in d^3 systems is treated as an axial perturbation to the strong-field cubic scheme.

Inspection of Figure 4 shows that a very reasonable fit of the observed ligand field bands for K_3NiF_6 can be obtained with $Dt/B = +0.60$, which yields $B = 703$ cm^{-1}, $\beta = 0.63$, $Dt = 423$ cm^{-1}, and $Dq = 1620$ cm^{-1}. For Na_3NiF_6 the displacement of the two lowest energy bands yields $Dt/B = 0.55$, $Dt = 388$ cm^{-1}, and the other parameters as before. This fitting thus corresponds to an elongation of the NiF_6^{3-} octahedra along the fourfold axis, although it is possible to obtain a fairly satisfactory correlation with $Dt/B = -0.75$, corresponding to a compressed octahedron. It will however be seen that for positive values of Dt/B the $^4A_2$ component of $^4T_{1g}$ lies only just above the ground state, as required by a low-spin–high-spin equilibrium, while for $Dt/B < 0$ the lowest lying quartet level (^4E of $^4T_{1g}$) rises rapidly above the ground state as Dt/B becomes more negative and at $Dt/B = -0.75$ is about 10 E/B units up. Furthermore, it has been pointed out by Liehr[27] that for E states ionic compounds would be expected to undergo compression by Jahn–Teller effects whereas more covalent complexes should show elongation. Since the value of β found for $Dt/B = +0.60$ is 0.63 and for $Dt/B = -0.75$ β is 0.50, it follows that only for a positive Dt/B (elongation) is the nephelauxetic ratio consistent with this criterion.

It cannot of course be maintained that our set of fitting parameters is in any way unique, but they do provide an account of the electronic spectrum of the NiF_6^{3-} anion which is both self-consistent and also not at variance with the magnetic data. It is clear that the spectrum requires both the assumption of a low-spin ground state, with Dq/B slightly above the ^2E_g–$^4T_{1g}$ crossover, and also some measure of tetragonal distortion to account for the well-marked low-energy band at 6.8 kK. In this latter connection the shift of the 6.8- and 12.3-kK bands to 6.1 and 12.8-kK in the sodium salt may well be significant, since the only impurity present in our Na_3NiF_6 was sodium fluoride which would not be expected significantly to affect the spectrum. Our splitting diagram (Figure 4) shows that the tetragonal distortion, as represented by Dt/B, has by far the greatest influence on the ground state ($^2E_g \rightarrow {^2A_1} + {^2B_1}$) and on the lowest $^2T_{1g}$ state ($^2T_{1g} \rightarrow {^2A_2} + {^2E}$) and that for the latter the $^2A_2$ component scarcely varies at

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[18a] NOTE ADDED IN PROOF.—The results of C. G. Barraclough, *Trans. Faraday Soc.*, **62**, 1033 (1966), show that while the assumption of a thermal high-spin–low-spin equilibrium is not strictly necessary, the observed[6] temperature dependence of the magnetic moment should only occur when Dq/B lies very close to the crossover point, on the low-spin side.

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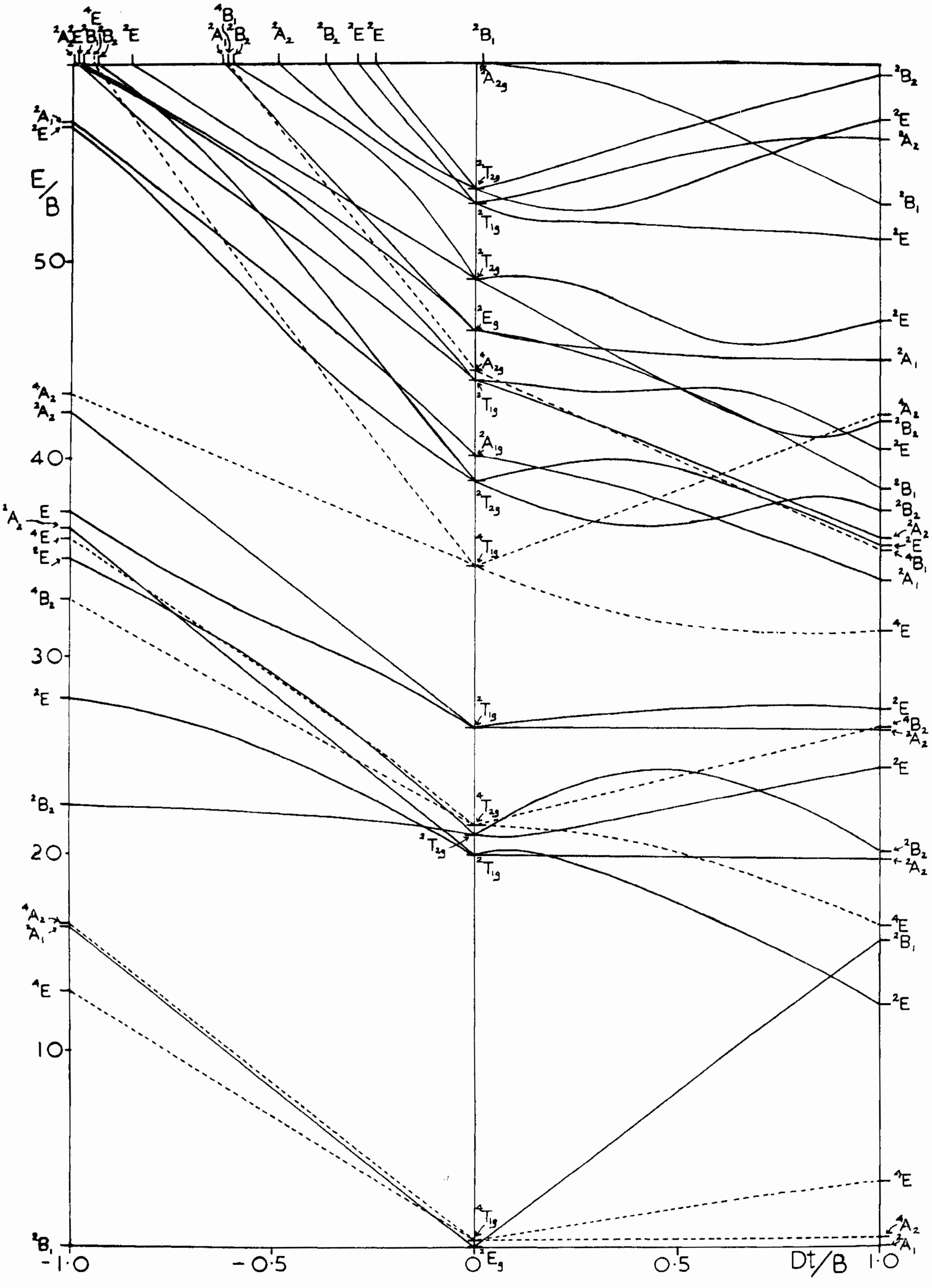

Figure 4.—Energy level diagram for d^7 configuration in tetragonal (D_4) field. $\xi = 0$, $Dq/B = 2.30$, $C/B = 4.90$, and $Ds/Dt = 3.0$.

all with Dt/B, although ^2E is strongly depressed as Dt/B increases. The observed spectra and their assignments and intensities are shown in Table III, and it is seen that the two lowest energy transitions should in fact correspond to $^2A_1 \rightarrow {}^2B_1$ and $^2A_1 \rightarrow {}^2E$ and that therefore the two bands noticeably shifted by the substitution of Na^+ for K^+ are assigned as those predicted to be most susceptible to tetragonal distortion. It would be expected that the Jahn–Teller distortion of the NiF_6^{3-} anion should be sensitive to some extent to the nature of the cation but in the absence of structural data for the sodium salt it is not possible to rationalize the effect further. It has though been pointed out[22] that Dt values of comparable magnitude, similarly derived, need not necessarily correspond to appreciable static distortions. If the potential barrier to pseudorotation about the threefold axis between the three degenerate potential minima is sufficiently small, then the observed splittings can relate to a dynamic Jahn–Teller effect in which O_h symmetry is preserved.

The spectrum of potassium hexafluoronickelate(III) was also determined at liquid nitrogen temperature: the spectrum was essentially the same as that recorded at room temperature, indicating that the latter does indeed represent dominantly the low-spin configuration, but a faint suggestion of fine structure on the 19.2-kK band, just visible at room temperature, becomes five small, but definite, maxima at 77°K. These peaks were too weak for accurate measurement of their positions, but spanned about 2.0 kK, giving an average spacing of 500 cm^{-1}, which would be of the right order of magnitude for an α_{1g} progression such as those found[1,2] in NiF_6^{2-} and CoF_6^{2-}. Even at liquid nitrogen temperature it was not possible to resolve the shoulder of the 32-kK band, which begins around 25 kK, and no confirmation of the presence of the d–d bands predicted at 26.1 and 26.2 kK could therefore be obtained.

It is seen from Table I that the values of β for the CuF_6^{3-} and NiF_6^{3-} ions are substantially less than those recorded for the fluoride complexes of trivalent vanadium, chromium, and iron. Since both CoF_6^{3-} and MnF_6^{3-} are high-spin complexes whose spectra consist essentially of a single transition ($^5T_{2g} \rightarrow {}^5E_g$ and $^5E_g \rightarrow {}^5T_{2g}$, respectively), it is not possible to obtain experimentally the corresponding values of β, but for Co^{3+} a reasonable estimate can be made using Jørgensen's h and k parameters.[3] We have $k = 0.35$ for Co^{3+} and $h = 0.8$ for F^-, whence $\beta(CoF_6^{3-}) = 0.72$. For Mn^{3+} the value of k is not known with certainty since a fully satisfactory analysis of the spectrum of the only well-established low-spin complex $Mn(CN)_6^{3-}$ has not yet been given, but Ballhausen's[13] tentative assignments with $Dq = 3000$ cm^{-1} and $B = 500$ cm^{-1} yields $k = 0.24$ and $\beta(MnF_6^{3-}) = 0.81$. The calculated β values, especially that for MnF_6^{3-}, are naturally subject to some uncertainty, but it is clear that the fluoride complexes of the trivalent ions of V, Cr, Mn, Fe, and Co all show fairly high nephelauxetic ratios and correspondingly small tendencies toward covalency.

On the other hand, the complexes of Ni^{3+} and Cu^{3+} show values of β which indicate substantial expansion of the radial function of the metal and an appreciable measure of covalent bonding. The values of β for the given ligand (fluoride ion) thus reflect quite closely the chemical stability of the particular hexafluoro complexes. For example, the compounds K_3MF_6, where M = V, Cr, Mn, Fe, and Co, can all be prepared with KHF_2 melts without recourse to elementary fluorine, are stable in air, and, with the exception of the Mn compound, are only slowly attacked by water. In contrast, the corresponding Ni and Cu compounds have been obtained only by the action of fluorine on mixtures of KCl and the appropriate metal salts and are rapidly hydrolyzed by water with the evolution of oxygen.

On the whole though, the parallel between the β values and the general chemical behavior of the trivalent cations of the first transition series is the more striking. If we examine the properties of the trivalent state for the ions V(III) to Cu(III), we find[28] initially that V(III), although not as stable as V(IV), is still an important oxidation state for this element and numerous hexacoordinated species are known. For chromium the trivalent state is easily the most stable, but Mn(III) and Fe(III) are slightly less stable with respect to their divalent states, while for cobalt the trivalent state is only more stable than the divalent when complexed. Finally Ni(III) and Cu(III) are very unstable valencies and their best characterized compounds are the hexafluoro anions in which lattice energy stabilization is probably all important. Thus the β values, obtained for a constant ligand (F^-) and a constant oxidation state (3+), indicate quite clearly the decreasing stability of the higher oxidation states toward the end of the first transition series.

The nephelauxetic ratio, β, is a measure of the extent of the expansion of the radial function of the metal cation on complex formation and thus reflects the tendency toward covalent bonding. It has been shown by Jørgensen[11] that decreasing values of β are associated with a reduction in the effective positive charge on the cation and on this basis the parallel between β and oxidation state stability is readily understood. Thus the smaller the value of β for M^{3+}, the greater the tendency to covalency, the smaller the effective positive charge on the metal, and the greater is the tendency to go down to M^{2+}.

Using the values of β_{35} found for Cu^{3+} and Ag^{3+} and that of β for Ni^{3+}, in the fluoride complexes, a rough quantitative estimate of the nephelauxetic effect may be made by Jørgensen's[11] method, assuming equal contributions from central field and symmetry-restricted covalency. For CuF_6^{3-} a ligand contribution of about 14% is indicated with an effective charge on the metal of only +1.45, while for AgF_6^{3-} the values are 12% and +1.65. For NiF_6^{3-} we find 11% and +1.80, but VF_6^{3-}, CrF_6^{3-}, and FeF_6^{3-} show ligand contributions of between 3 and 6% only and effective charges of +2.3 to +2.7, thus emphasizing the preference of Cu and Ni for the divalent state. From our Dq and β values Jørgensen's g and k parameters may be found: the figures are 15.7 and 0.56, respectively, for CuF_6^{3-}, 20.4 and 0.49 for AgF_6^{3-}, and 18.0 and 0.46 for NiF_6^{3-}. The data also confirm Jørgensen's general predictions[29] of the positions of the ^1E_g, $^3T_{2g}$, and $^3T_{1g}$ bands in CuF_6^{3-}, although both Dq and the B quantities are somewhat overestimated.

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