tially identical with the diffuse reflectance spectra of the solid compounds, suggesting that similar species are present in the solid and in solution. A slight decrease in the intensity of the peaks occurred over a period of time which may have been due to dissociation of the complex ion in nitromethane. Addition of ligand to the solutions suppressed the change in spectra. No change was observed in the conductance of these solutions indicating that, if dissociation occurs, it probably involves the coordinated nitrogen ligand. One might consider assigning the first two bands to the $^2E_g \rightarrow {}^2A_{1g}$ and $^2E_g \rightarrow {}^2B_{1g}$ ligand field transitions expected for a tetragonal distortion. The extinction coefficients however are much higher than those expected for simple d–d transitions. This may be an indication that there is some degree of ligand–metal orbital overlap involved which obscures the distinction between d–d transitions and charge transfer. The remaining bands are undoubtedly charge transfer in nature and it is not possible at this time to make any detailed assignments. The high-energy bands at 35,800, 37,200, and 43,900 cm^{-1} in the benzonitrile complexes can be attributed to charge transfer within the ligand as can the band at 37,000 cm^{-1} in the 2,4,6-trimethylpyridine complexes.[22]

Acknowledgment.—We wish to thank the National Science Foundation for financial support of this research under Grant No. GP-3810.

[22] P. M. Boorman, N. N. Greenwood, M. A. Hildon, and R. V. Parish, *Inorg. Nucl. Chem. Letters*, **2**, 377 (1966), have recently reported the preparation of $[WCl_4(dipy)^+]Cl^-$, which supports our results on the formation of stable +5 compounds.

Contribution from the Department of Chemistry, Indiana University, Bloomington, Indiana, and the Mellon Institute, Pittsburgh, Pennsylvania

Interpretation of the Spectra of Cyanoaquo Complexes of Chromium(III) by the Theory of Noncubic Ligand Fields[1]

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The visible and ultraviolet absorption spectra of a series of mixed cyanoaquo complexes of chromium(III) are measured and resolved by Gaussian analysis. The complexes studied include $Cr(CN)_5(H_2O)^{2-}$, *cis*-$Cr(CN)_4(H_2O)_2^-$, *cis*-$Cr(CN)_3(H_2O)_3$, *cis*-$Cr(CN)_2(H_2O)_4^+$, and $Cr(CN)(H_2O)_5^{2+}$, all of which have been isolated and characterized in this laboratory. The parent complex ions of the series, $Cr(CN)_6^{3-}$ and $Cr(H_3O)_6^{3+}$, have also been included in this study for comparison. The ligand field theory of cubic and noncubic fields, in the strong-field formalism and in the limit of zero spin–orbit interaction, is applied to interpret and assign the observed absorption bands of the spectra of these systems. The bands in the absorption spectrum of the trisubstituted complex do not show splittings and hence can be interpreted on the basis of ligand fields of pseudo-cubic symmetry. The observed bands are nevertheless assigned the trigonal symmetry designations, and the energies of the absorption maxima are in agreement with those of the calculated trigonal levels using axial ligand field parameters of small magnitude. The spectra of the monosubstituted complexes, $Cr(CN)_5(H_2O)^{2-}$ and $Cr(CN)(H_2O)_5^{2+}$, are treated on the basis of axial perturbations applied to the cubic field potentials of their parent ions, $Cr(CN)_6^{3-}$ and $Cr(H_2O)_6^{3+}$, respectively. The *cis* complexes, $Cr(CN)_4(H_2O)_2^-$ and $Cr(CN)_2(H_2O)_4^+$, are similarly treated in relation to their parent molecule of pseudo-cubic symmetry, *cis*-$Cr(CN)_3(H_2O)_3$. The $^4T_{2g}$ cubic band splits into two well-defined components in the penta- and the dicyano complexes, while in the monocyano species the splitting of this band is manifested only by appreciable asymmetric broadening. These components are given tetragonal assignments, and the Dt value has been evaluated by fitting to be -300 cm^{-1} for the substitution of CN^- by H_2O, and $+300$ cm^{-1} for the reverse substitution. With a Dt value of appropriate sign and a consistent set of parametric values for B, C, Dq, and κ ($= Ds/Dt$), the remaining portions of these spectra and the spectrum of *cis*-$Cr(CN)_4(H_2O)_2^-$ are interpreted. Alternate assignments are found to be possible for the components of the second cubic band. Since *cis*-disubstituted complexes are monosubstituted derivatives of the pseudo-cubic, symmetrically trisubstituted *cis* complex, justification is provided for treating them under tetragonal fields on the basis of the crystal-field model. This treatment in turn leads to some interesting predictions of spectral relations for the *cis* and *trans* isomers of d^3 complexes which can serve as spectral criteria for distinguishing between such isomers. The spectra of the known *cis–trans* pairs of Cr(III) complexes conform to these predictions.

I. Introduction

The ligand field theory has been used successfully for the interpretation of the magnetic and spectral phenomena of transition metal complexes in cubic symmetry. The optical spectra may be favorably described in terms of a single ligand field parameter, Dq, in addition to the Racah electron correlation parameters, A, B, and C. These are generally viewed as empirical parameters to be determined from experimental spectra. In ligand fields of symmetries lower than cubic, such as tetragonal and trigonal, which can arise by the superposition of an axial perturbation along the 4-fold or the 3-fold axis of an octahedral potential, two additional parameters, $D\mu$ (μ = s, σ) and $D\nu$ (ν =

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[1] (a) This work was supported in part by the U. S. Atomic Energy Commission under Contract No. AT(11-1)-256 (Document No. COO-256-63). (b) Presented in part before the Division of Inorganic Chemistry at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, at the 9th International Conference on Coordination Chemistry, St. Moritz-Bad, Switzerland, Sept 1966, and at the 153rd National Meeting the American Chemical Society, Miami Beach, Fla., April 1967.

[2] (a) Taken in part from a thesis submitted by R. Krishnamurthy to the Graduate School of Indiana University in partial fulfillment of the requirements for the Ph.D. degree in Chemistry, 1966. (b) Indiana University. (c) Mellon Institute.

t, τ) arise, where s and t refer to tetragonal and σ and τ to trigonal fields. These parameters are associated with the second-order and the fourth-order spherical harmonics, Y_2^0 and Y_4^0, respectively, and lead to an additional splitting of the otherwise degenerate electronic levels of cubic symmetry. Consequently, in distorted octahedral systems or in mixed-ligand complexes, observation of the splittings of the cubic absorption bands can provide useful information on the asymmetry of the ligand fields.

Recently, a series of cyanoaquo complexes of Cr(III) with the formulas $Cr(CN)_n(H_2O)_{6-n}^{(3-n)+}$ (n = 1–5) has been isolated and characterized in this laboratory. The isolation of these complexes and the kinetics of their aquation reactions are being reported in separate communications. On the basis of the ion-exchange, spectral, and kinetic evidence, the complexes $Cr(CN)_4(H_2O)_2^-$, $Cr(CN)_3(H_2O)_3$, and $Cr(CN)_2(H_2O)_4^+$ have all been assigned the *cis* geometrical configurations. These complexes are of especial interest for several reasons. First, they are six-coordinate, monomeric systems in which the Cr^{3+} ion is situated in bonding environments formed by two different ligands, CN^- and H_2O, which are widely separated in the spectrochemical series. Second, they exemplify systems with symmetries lower than cubic. A study of this series of complexes provides an opportunity for gaining information on the relation of structure and symmetry to spectral and kinetic properties.[3]

In this communication we present a detailed discussion of the spectra of these complexes and report the first systematic attempt to interpret the absorption spectra of chromium(III) complexes in noncubic fields[4,5] on the basis of complete ligand field calculations in the limit of zero spin–orbit coupling. We also present some new guide lines which are useful for distinguishing between the spectra of the *cis* and *trans* isomers of chromium(III) complexes.

II. Experimental Section

The complexes $Cr(CN)_5(H_2O)^{2-}$, $Cr(CN)_4(H_2O)_2^-$, $Cr(CN)_3(H_2O)_3$, $Cr(CN)_2(H_2O)_4^+$, and $Cr(CN)(H_2O)_5^{2+}$ were isolated and characterized by ion-exchange techniques and chemical analyses. Only one of the possible geometrical isomers was isolated in the cases of the tetra-, tri-, and dicyano complexes, and, in each case, the spectral and kinetic evidence indicates that the isolated species is the *cis* isomer. No evidence for the existence of polymers or multiple isomers was obtained. The visible and the ultraviolet absorption spectra of the separated species were measured on a Cary Model 14 recording spectrophotometer in the wavelength range 200–750 mμ. Sets of matched quartz–silica cells of 1.00, 5.00, and 10.00 cm were used, with appropriate blank solutions placed in the reference cell. The absorption spectra were plotted on a frequency scale, ν (cm^{-1}), *vs.* extinction coefficient, ϵ, and resolved into Gaussian components on an analog computer at the Mellon Institute.[6] The oscillator strength, f, was calculated using the formula $f = 4.60 \times 10^{-9}(\epsilon_{max}\nu_{1/2})$, where $\nu_{1/2}$ is the half-band width in cm^{-1} and ϵ_{max} is the extinction coefficient at the frequency maximum. Absorption maxima and the extinction coefficients for all the cyano complexes are listed in Table I.

TABLE I

ABSORPTION SPECTRAL DATA OF CYANOAQUO COMPLEXES OF CHROMIUM(III)[a]

Complex	λ_{max}, mμ	ν_{max}, cm^{-1}	ϵ_{max}, cm^{-1} M^{-1}
$Cr(CN)_6^{3-}$	377	26,525	85.9
	307	32,573	59.5
$Cr(CN)_5(H_2O)^{2-}$	~420	~23,800	89
	382	26,178	106.0
	312	32,051	50.0
cis-$Cr(CN)_4(H_2O)_2^-$	427	23,420	110.0
	332	30,120	50.0
cis-$Cr(CN)_3(H_2O)_3$	467	21,433	115.0
	362	27,624	26.0
cis-$Cr(CN)_2(H_2O)_4^+$	~538	18,518	18.0
	467	21,433	45.0
	378	26,455	20.0
$Cr(CN)(H_2O)_5^{2+}$	~571.5	17,500	~12.5
	525	19,047	26.0
	393	25,445	20.5
$Cr(H_2O)_6^{3+}$	575	17,400	13.4
	406	24,630	15.4
	256	39,062	8.8

[a] Only the spin-allowed absorption maxima are included here.

III. Theory

1. Cubic Ligand Fields.—Many of the formal aspects of the theory of cubic ligand fields for the d^3 configuration have been described.[7-10] Calculations based on the weak-field scheme were first carried out by Finkelstein and Van Vleck[11] in order to explain the Zeeman effect in chrome alum and the origin of the ruby lines. Tanabe and Sugano,[12] on the basis of the strong-field coupling scheme, derived the complete electrostatic matrices of d^n (n = 2–8) configurations in cubic symmetry. Only those aspects of the theory which are pertinent to the present problem are considered here. The formalism employed is the strong-field case in the limit of zero spin–orbit interaction.

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(3) For an interpretation of the spectra of cyanide complexes and an explanation of their electronic structures, see (a) J. R. Perumareddi, A. D. Liehr, and A. W. Adamson, *J. Am. Chem. Soc.*, **85**, 249 (1963); (b) J. R. Perumareddi and A. D. Liehr, Abstracts, Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, June 1964 and June 1965; (c) J. R. Perumareddi and A. D. Liehr, Abstracts, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965.

(4) The initial attempt to explain the splittings of the spin-allowed cubic bands by W. Moffitt and C. J. Ballhausen, *Ann. Rev. Phys. Chem.*, **7**, 107 (1956), made use of diagonal elements only. See also C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., New York, N. Y., 1962, and Ph.D. Thesis, Copenhagen, 1958. Application of this approach to the explanation of the spectra of Co(III) and Cr(III) complexes has been made by R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709 (1965).

(5) Semiempirical molecular orbital approaches have been proposed by H. Yamatera, *Bull. Chem. Soc. Japan*, **31**, 95 (1958), by D. S. McClure, "Advances in the Chemistry of Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p 498, and by C. E. Schäffer and C. K. Jørgensen, *Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd.*, **34**, No. 13 (1965).

(6) We are indebted to Dr. E. W. Baker of the Mellon Institute for his assistance in obtaining Gaussian components on the computer. The analog computer on which the analyses were performed is on loan from the National Heart Institute. For design and operational details of the instrument, see F. W. Noblè and J. E. Hayes, *Ann. N. Y. Acad. Sci.*, **115**, 644 (1964).

(7) J. S. Griffith, "The Theory of Transition-Metal Ions," Cambridge University Press, Cambridge, 1961.

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

(9) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press Ltd., London, 1962.

(10) T. M. Dunn, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, New York, N. Y., 1960.

(11) R. Finkelstein and J. H. Van Vleck, *J. Chem. Phys.*, **8**, 790 (1940).

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

In strong octahedral fields, the energies of the quartet states of the d^3 system are

$$^4A_{2g}\ (t_{2g}{}^3):\quad 3A - 15B - 12Dq \text{ (ground state)} \qquad (1)$$

$$^4T_{2g}\ (t_{2g}{}^2\, e_g):\quad 3A - 15B - 2Dq \qquad (2)$$

$$^4T_{1g}\ (t_{2g}{}^2\, e_g):\quad 3A - 3B - 2Dq \qquad (3)$$

$$^4T_{1g}\ (t_{2g}\, e_g{}^2):\quad 3A - 12B + 8Dq \qquad (4)$$

If configuration interaction between the two $^4T_{1g}$ states is taken into account, an off-diagonal matrix element, $6B$, arises because of electron correlation and the energies of the two interacting $^4T_{1g}$ states become

$$^4T_{1g\pm}:\quad -{}^1/_2(15B - 6Dq) \pm {}^1/_2(225B^2 - 180DqB + 100Dq^2)^{1/2} \qquad (5)$$

Thus, the exact energies of the spin-allowed quartet–quartet transitions calculated from eq 1, 2, and 5, in order of increasing energy, are

$$^4A_{2g} \longrightarrow {}^4T_{2g}\ (\nu_1):\quad 10Dq\ (=\Delta)$$

$$^4A_{2g} \longrightarrow {}^4T_{1g}\ (\nu_2):\quad {}^1/_2(15B + 3\Delta) - {}^1/_2(225B^2 - 18B\Delta + \Delta^2)^{1/2}$$

$$^4A_{2g} \longrightarrow {}^4T_{1g}\ (\nu_3):\quad {}^1/_2(15B + 3\Delta) + {}^1/_2(225B^2 - 18B\Delta + \Delta^2)^{1/2}$$

The $t_{2g}{}^3$ configuration also gives rise to the doublet states ^2E_g, $^2T_{1g}$, and $^2T_{2g}$. The spin-forbidden bands of very low intensities observed at the low-energy end of the visible region are due to the $^4A_{2g} \rightarrow (^2E_g, {}^2T_{1g}), {}^2T_{2g}$ transitions.

2. **Noncubic Ligand Fields.**—We shall treat the trigonal and tetragonal field complexes as slightly distorted cubic field complexes. Calculations based on this assumption can be carried out by incorporating the axial fields (V_∞) as perturbations over the strong-field coupling scheme of the cubic fields (V_C). In this representation, the strong-field octahedral functions are used as the basis set with proper orientation.[13] These functions decompose in trigonal and tetragonal symmetries as shown in Table II. Because of the use of octahedral functions as the first-order functions in noncubic fields, the latter are said to be octahedrally oriented. In this weak-axial strong-field treatment, the cubic ligand field parameter is diagonalized while the electron correlation and the axial parameters are contained in diagonal as well as off-diagonal elements. The resulting energy matrices are very similar to the cubic matrices with the exception that different cubic representations belonging to the same noncubic representation are connected by the axial field parameters (in addition to, of course, the presence of these parameters in the diagonal elements). If the axial parameters are set equal to zero, the matrices of the noncubic fields reduce to those of cubic field. A detailed discussion of this and other coupling schemes, their significance, and the unitary transformations connecting them will be published elsewhere.[14]

Table II

Decomposition of Cubic Representations in Trigonal and Tetragonal Fields[a]

Cubic	Trigonal	Tetragonal
$A^C{}_{1g}$	$A^T{}_1$	$A^Q{}_1$
$A^C{}_{2g}$	$A^T{}_2$	$B^Q{}_1$
$E^C{}_{ga}$	$E^T{}_a$	$A^Q{}_1$
$E^C{}_{gb}$	$E^T{}_b$	$B^Q{}_1$
$T^C{}_{1ga}$	$A^T{}_2$	$A^Q{}_2$
$T^C{}_{1g\binom{b}{c}}$	$E^T{}_{\binom{a}{b}}$	$E^Q{}_{\binom{a}{b}}$
$T^C{}_{2ga}$	$A^T{}_1$	$B^Q{}_2$
$T^C{}_{2g\binom{b}{c}}$	$E^T{}_{\binom{a}{b}}$	$E^Q{}_{\binom{a}{b}}$

[a] Superscript Q of the tetragonal levels refers to quadrate, meaning tetragonal.

All the parameters that arise from the various perturbations discussed above are the same as those of the cubic fields with the exception of the axial field parameters. Thus Dq and the A, B, and C parameters arise from the cubic ligand field potential and the electron correlation interactions, respectively. The axial field parameters result from the additional axial potential, V_∞, which in general is given by

$$V_\infty = eq\,[\sqrt{4\pi/5}R_2(r)\,Y_2{}^0(\bar\theta, \bar\phi) + \sqrt{4\pi/9}R_4(r)\,Y_4{}^0(\bar\theta, \bar\phi)]$$

where e and q are the electronic charge and the effective charge of the ligand, respectively, and $R_k(r) = r_<{}^k/r_>{}^{k+1}$, $r_<$ and $r_>$ being the lesser or greater of the electronic radius and metal–ligand bond distance. For tetragonal and trigonal potentials, $(\bar\theta, \bar\phi) \equiv (\theta, \phi)$ and (θ', ϕ') respectively.

We will use the definitions of Liehr[15] for the axial parameters to be consistent with the definition of Dq. These are

$$D\mu = \langle 2, \pm 1 | V_\infty{}^2 | \pm 1, 2\rangle = {}^1/_7 eq\langle R_2(r)\rangle$$

$$D\nu = \langle 2, \pm 2 | V_\infty{}^4 | \pm 2, 2\rangle = {}^1/_{21} eq\langle R_4(r)\rangle$$

where μ = s and ν = t in tetragonal fields, while in trigonal fields $\mu = \sigma$ and $\nu = \tau$. The integral $\langle R_n(r)\rangle$ equals $\int_0^\infty R(r)^2(r_<{}^n/r_>{}^{n+1})r^2\,dr$, where $R(r)$ is the radial part of the d-orbital wave function. Thus the ratio $\kappa\ (= D\mu/D\nu) = 3\langle R_2(r)\rangle/\langle R_4(r)\rangle$. Although this latter ratio of the radial parameters can be calculated[16] by using the radial functions, we prefer to treat them (in addition to Dq, B, and C) as fitting parameters, just as Dq, B, and C are treated in the cubic field situations.

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(13) The trigonally oriented orbitals have been given by A. D. Liehr, *J. Phys. Chem.*, **64**, 43 (1960) and are as follows

$$a_1(t_{2g}) = d_{\sigma'} = d_{3z'^2} - r^2$$

$$e_\pm(t_{2g}) = \sqrt{1/3}\,d_{\pi'\pm} - \sqrt{2/3}\,d_{\delta'\mp}$$

$$e_\pm(e_g) = \sqrt{2/3}\,d_{\pi'\pm} + \sqrt{1/3}\,d_{\delta'\mp}$$

where the primes refer to quantization of angular momenta along the threefold axis of symmetry, *i.e.*, along the (1,1,1) direction. Note that $d_{\pi'\pm} = \sqrt{1/2}(d_{x'z'} \pm i d_{y'z'})$ and $d_{\delta'\pm} = \sqrt{1/2}(d_{x'^2-y'^2} \pm i d_{x'y'})$.

(14) J. R. Perumareddi, *J. Phys. Chem.*, in press.

(15) See lecture notes by A. D. Liehr, "Geometry, Color, and Magnetism: The Ti(III) and Cu(II) Systems and their Relatives," available upon request from the Mellon Institute, Pittsburgh, Pa. 15213.

(16) Such calculations have been made by D. S. McClure, *J. Chem. Phys.*, **36**, 2757 (1962); H. A. Weakliem, *ibid.*, **36**, 2117 (1962); T. S. Piper and R. L. Carlin, *ibid.*, **33**, 1208 (1960); and J. R. Perumareddi, unpublished results, all of whom arrived at a value of 4 to 5 for the ratio $\langle R_2(r)\rangle/\langle R_4(r)\rangle$, whereas the experimental data on a limited number of Cu(II) complexes indicate a value near 1.0. See, for instance, W. E. Hatfield and T. S. Piper, *Inorg. Chem.*, **3**, 841 (1964); P. Day, *Proc. Chem. Soc.*, 18 (1964). Substituting this value of unity, $\kappa = D\mu/D\nu$ turns out to be 3.

TABLE III

THE TRIGONAL QUARTET ENERGY MATRICES OF d^3 ELECTRONIC CONFIGURATION[a]

${}^4A^{T}_{1}$	${}^4T^{C}_{2ga}$ $(t_{2g}{}^2e_g)$
${}^4T^{C}_{2ga}$ $(t_{2g}{}^2e_g)$	$-2Dq + D\sigma + 3D\tau + 3A - 15B - E$

${}^4A^{T}_{2}$	${}^4A^{C}_{2g}$ $(t_{2g}{}^3)$	${}^4T^{C}_{1ga}$ $(t_{2g}{}^2e_g)$	${}^4T^{C}_{1ga}$ $(t_{2g}e_g{}^2)$
${}^4A^{C}_{2ga}$ $(t_{2g}{}^3)$	${}^2/_3(-18Dq + 7D\tau) + 3A - 15B - E$	${}^2/_3(3D\sigma - 5D\tau)$	0
${}^4T^{C}_{1ga}$ $(t_{2g}{}^2e_g)$		$-2Dq + D\sigma + 3D\tau + 3A - 3B - E$	${}^2/_3(3D\sigma - 5D\tau) + 6B$
${}^4T^{C}_{1ga}$ $(t_{2g}e_g{}^2)$			${}^2/_3(12Dq + 3D\sigma + 2D\tau) + 3A - 12B - E$

${}^4E^{T}$	${}^4T^{C}_{2gb}$ $(t_{2g}{}^2e_g)$	${}^4T^{C}_{1gb}$ $(t_{2g}{}^2e_g)$	${}^4T^{C}_{1gb}$ $(t_{2g}e_g{}^2)$
${}^4T^{C}_{2gb}$ $(t_{2g}{}^2e_g)$	$-{}^1/_6(12Dq + 3D\sigma + 2D\tau) + 3A - 15B - E$	$-{}^1/_6(9D\sigma + 20D\tau)$	$-{}^1/_3(3D\sigma - 5D\tau)$
${}^4T^{C}_{1gb}$ $(t_{2g}{}^2e_g)$		$-{}^1/_6(12Dq + 3D\sigma + 2D\tau) + 3A - 3B - E$	$-{}^1/_3(3D\sigma - 5D\tau) + 6B$
${}^4T^{C}_{1gb}$ $(t_{2g}e_g{}^2)$			${}^1/_3(24Dq - 3D\sigma - 16D\tau) + 3A - 12B - E$

[a] Because these matrices are symmetrical, the elements below the diagonal are omitted.

These definitions of $D\mu$ and $D\nu$ differ from those used by others[4,13,16,17] in that they are of opposite sign. The positive signs of the $D\mu$ and $D\nu$ parameters, as defined here, correspond to increased axial fields, and negative signs to decreased axial fields. This choice of signs has the advantage of representing changes in tetragonal field strength which parallel the convention accepted for Dq, the octahedral field strength parameter; *e.g.*, a positive value of Dt represents the application of an increased field, just as does a positive change in Dq. From these definitions, the nonvanishing matrix elements within the d manifold are

$$\langle 2,\pm 2|V_\infty|\pm 2,2\rangle = -2D\mu + D\nu$$
$$\langle 2,\pm 1|V_\infty|\pm 1,2\rangle = D\mu - 4D\nu$$
$$\langle 2,0|V_\infty|0,2\rangle = 2D\mu + 6D\nu$$

When these parameters are combined with the cubic Dq parameter, the requisite one-electron matrix elements for tetragonal fields turn out to be

$$\langle(x^2 - y^2)|V_Q|(x^2 - y^2)\rangle = 6Dq - 2Ds + Dt$$
$$\langle(z^2)|V_Q|(z^2)\rangle = 6Dq + 2Ds + 6Dt$$
$$\langle(xy)|V_Q|(xy)\rangle = -4Dq - 2Ds + Dt$$
$$\langle(zx)|V_Q|(zx)\rangle = -4Dq + Ds - 4Dt$$
$$\langle(yz)|V_Q|(yz)\rangle = -4Dq + Ds - 4Dt$$

and for trigonal fields they are[18]

$$\langle a_1(t_{2g})|V_T|a_1(t_{2g})\rangle = -4Dq + 2D\sigma + 6D\tau$$
$$\langle e_\pm(t_{2g})|V_T|e_\pm(t_{2g})\rangle = -4Dq - D\sigma - {}^2/_3D\tau$$
$$\langle e_\pm(e_g)|V_T|e_\pm(e_g)\rangle = 6Dq - {}^7/_3D\tau$$
$$\langle e_\pm(t_{2g})|V_T|e_\pm(e_g)\rangle = \sqrt{2}/3(3D\sigma - 5D\tau)$$

The energy matrices for both trigonal and tetragonal fields have been constructed for all the quartets and doublet levels of the d^3 configuration and will be published elsewhere by one of us.[14] As the quartet levels are important to the interpretation of the spectra being considered, we have reproduced in Tables III and IV the quartet matrices of both the trigonal and tetragonal fields. Notice that if the axial field parameters are set equal to zero, these matrices become identical with the Tanabe–Sugano cubic field matrices for the d^3 configuration, which is as expected.

As a starting point in the calculation of the trigonal-field energy levels, suitable values of B, (C/B), and Dq were determined from the spectrum of the C_{3v} complex, 1,2,3-$Cr(CN)_3(H_2O)_3$, on the assumption of pseudocubic symmetry. The trigonal energy matrices were then diagonalized for reasonable values selected for the axial field parameters $D\sigma$ and $\kappa = (D\sigma/D\tau)$. The resulting energy level diagram consistent with the trigonal symmetry is shown in Figure 1. Only the quartet and lower energy doublet levels are included. The splittings of the various cubic levels are shown as a function of the Dq parameter in the range 0–4000 cm^{-1}. In this figure, in the limit of $Dq = 0$, which is equivalent to a linear ligand field, are shown the appropriate representations of cylindrical symmetry ($D_{\infty h}$ or $C_{\infty v}$). At the right end of each level are shown the designations for trigonal symmetry along with their related cubic field designations. The quartet levels to which the transitions are most likely to occur are marked in heavy lines.

The trigonal splittings of the quartet cubic bands in Figure 1, ${}^4T_{2g} \rightarrow {}^4E + {}^4A_1$ and ${}^4T_{1g} \rightarrow {}^4E + {}^4A_2$, are of the order of 1000 cm^{-1}. Such a small splitting is consistent with the splittings observed in several trigonal Cr(III) systems.[16]

In the trigonal field, three low-energy doublet levels, (${}^2E$, ${}^2A_2$) and ${}^2E$, arise from the cubic ${}^2T_{1g}$ and ${}^2E_g$ states, respectively, of the $(t_{2g})^3$ configuration. These doublets are all degenerate in first order. Their transition energies, using only the diagonal elements, are

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(17) W. Moffitt and C. J. Ballhausen, *Ann. Rev. Phys. Chem.*, **7**, 107 (1956).

(18) The $D\sigma$ and $D\tau$ parameters are related to the trigonal splitting parameters v and v' of Pryce and Runciman [M. H. L. Pryce and W. A. Runciman, *Discussions Faraday Soc.*, **26**, 34 (1958)] and to K and K' of Sugano and Tanabe [S. Sugano and Y. Tanabe, *J. Phys. Soc. Japan*, **13**, 880 (1958)] by the following equations: $v' = K' = \sqrt{2}/3(3D\sigma - 5D\tau)$; $v = -3K = {}^1/_3(9D\sigma + 20D\tau)$.

Table IV

The Tetragonal Quartet Energy Matrices of d^3 Electronic Configuration[a]

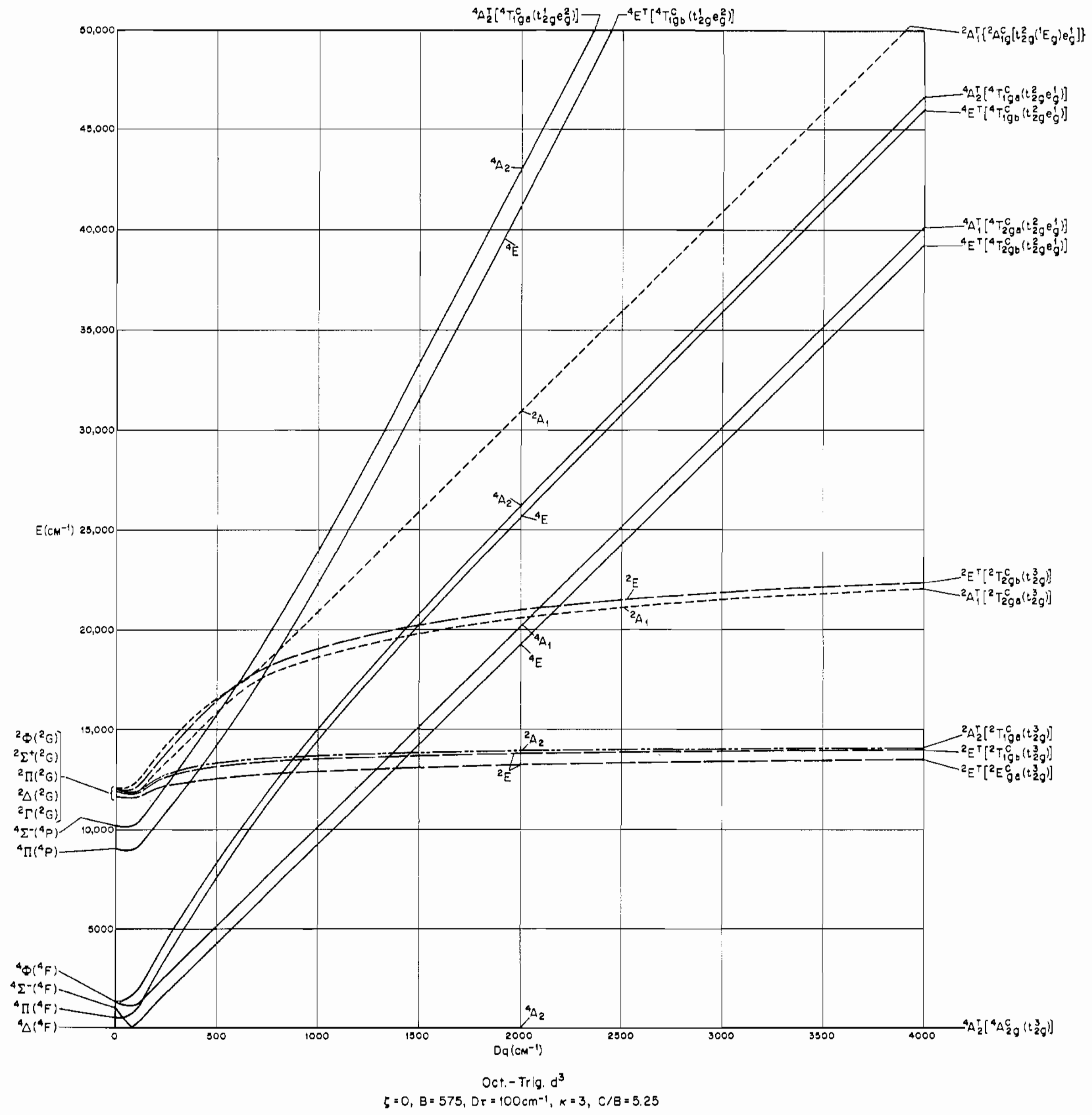
$^4B^{Q}_1$	$^4A^{C}_{2g}$ (t_{2g}^3)
$^4A^{C}_{2g}$ (t_{2g}^3)	$-12Dq - 7Dt + 3A - 15B - E$

$^4B^{Q}_2$	$^4T^{C}_{2g}$ $(t_{2g}^2e_g^1)$
$^4T^{C}_{2g}$ $(t_{2g}^2e_g^1)$	$-2Dq - 7Dt + 3A - 15B - E$

$^4A^{Q}_2$	$^4T^{C}_{1g}$ $(t_{2g}^2e_g^1)$	$^4T^{C}_{1g}$ $(t_{2g}^1e_g^2)$
$^4T^{C}_{1g}$ $(t_{2g}^2e_g^1)$	$-2Dq + 4Ds - 2Dt + 3A - 3B - E$	$+6B$
$^4T^{C}_{1g}$ $(t_{2g}^1e_g^2)$		$8Dq - 2Ds + 8Dt + 3A - 12B - E$

$^4E^{Q}$	$^4T^{C}_{2g}$ $(t_{2g}^2e_g^1)$	$^4T^{C}_{1g}$ $(t_{2g}^2e_g^1)$	$^4T^{C}_{1g}$ $(t_{2g}^1e_g^2)$
$^4T^{C}_{2g}$ $(t_{2g}^2e_g^1)$	$-2Dq + {}^7/_4Dt + 3A - 15B - E$	$-\sqrt{3}/4(4Ds + 5Dt)$	0
$^4T^{C}_{1g}$ $(t_{2g}^2e_g^1)$		$-2Dq - 2Ds - {}^3/_4Dt + 3A - 3B - E$	$+6B$
$^4T^{C}_{1g}$ $(t_{2g}^1e_g^2)$			$8Dq + Ds + 3Dt - 3A - 12B - E$

[a] Because these matrices are symmetrical, the elements below the diagonal are omitted.



Oct.-Trig. d^3

$\zeta = 0$, $B = 575$, $D\tau = 100\text{cm}^{-1}$, $\kappa = 3$, $C/B = 5.25$

Figure 1.—Simplified energy level diagram for d^3 configuration in trigonal fields: $\zeta = 0$, $B = 575\ \text{cm}^{-1}$, $C/B = 5.25$, $D\tau = 100\ \text{cm}^{-1}$, $\kappa = 3$.

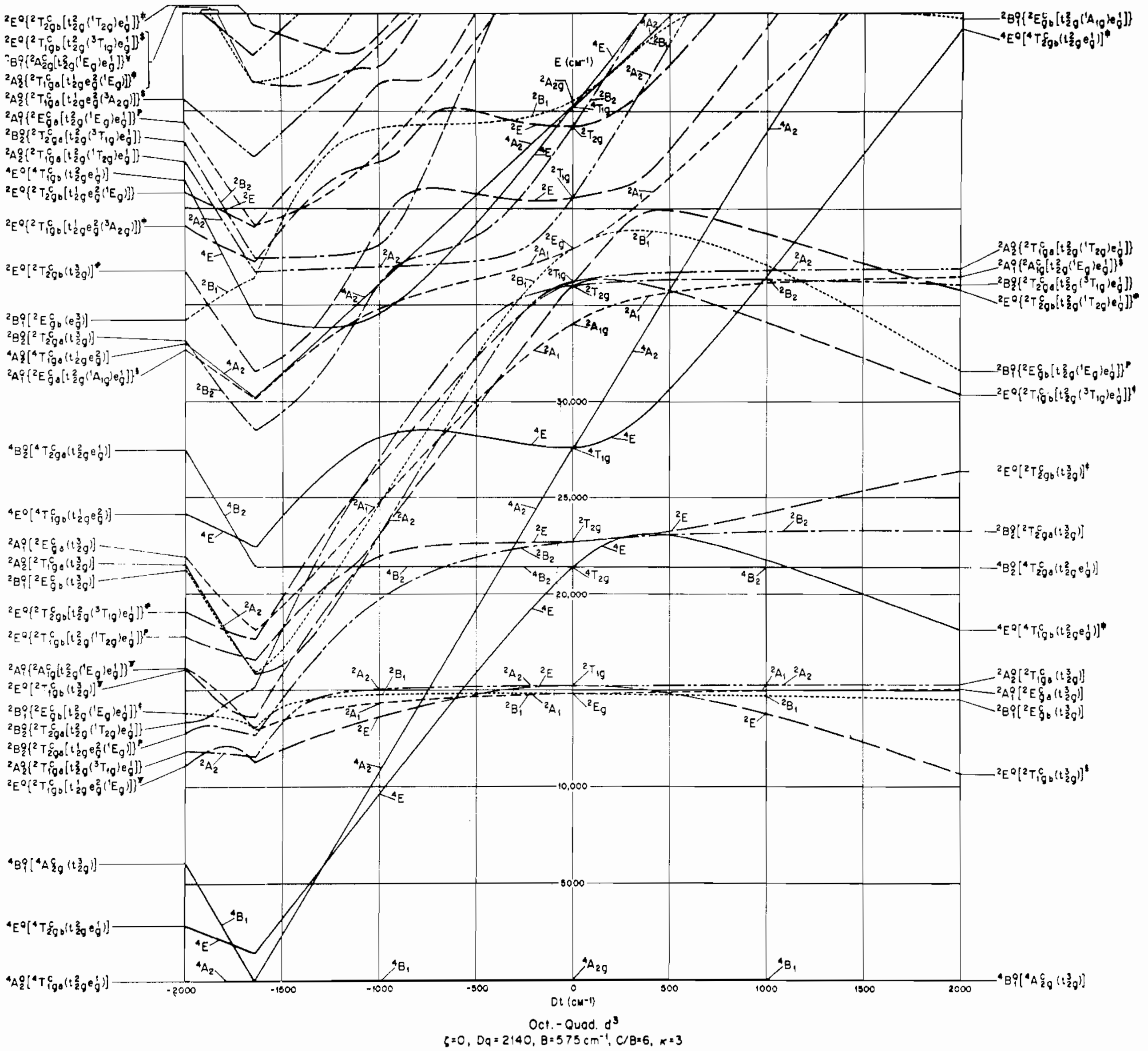


Figure 2.—Complete energy level diagram for d^3 configuration in tetragonal fields: $\zeta = 0$, $B = 575$ cm^{-1}, $C/B = 6$, $Dq = 2140$ cm^{-1}, and $\kappa = 3$. The various purity symbols have the following significance: §, 75 ± 2.5%; ≠, 70 ± 2.5%; ≢, 65 ± 2.5%; $, 60 ± 2.5%; ¢, 55 ± 2.5%; P, 50 ± 2.5%; ¥, 45 ± 2.5%; #, 40 ± 2.5%; ⌿, 35 ± 2.5%.

equal to $9B + 3C$ for the transitions $^4A_2 \rightarrow {}^2E$, (^2E, $^2A_2$). In an actual case, the degeneracy of the doublet levels is removed by configuration interaction.

In the case of the tetragonal matrices, it can be seen from Table IV that the $^4B_2$ component of $^4T_{2g}$ is placed at an energy $10Dq$ above the $^4B_1$ ground state. This result is exact and includes configuration interaction since these are 1×1 matrices. Because the $^4T_{2g}$ level is similarly $10Dq$ above the ground state in the cubic case, also including configuration interaction, the $^4B_2$ component of its tetragonal derivative should remain at the same frequency as the $^4T_{2g}$ transition of the parent cubic complex. The ^4E component of the $^4T_{2g}$ band should be placed approximately either + or − $^{35}/_4Dt$, relative to the position of the $^4B_2$ band. The ^4E component will be placed higher or lower in energy than $^4B_2$, depending upon whether the Dt value is positive or negative. The splitting of the second quartet band, $^4T_{1g}$, and the position of its components, ^4E and $^4A_2$, depend upon both the Racah parameter B and the axial field parameters Dt and Ds.

Since the splitting of the first quartet cubic band in tetragonal fields depends upon the Dt parameter, it is possible to fix Dq at a value appropriate to a particular parent octahedral complex and to construct an energy-level diagram as a function of the Dt parameter which can be used to interpret the spectra of its tetragonal derivatives. Figure 2 is a complete energy-level diagram obtained for the parameters $Dq = 2140$ cm^{-1}, κ ($=Ds/Dt$) = 3, $C/B = 5.75$, and Dt ranging from 0 to ±2000 cm^{-1}. In this diagram the quartet levels are shown as solid lines and the doublet levels as broken lines. At $Dt = 0$, the levels are those of octahedral symmetry and correspond to a one-dimensional cross section of a Tanabe–Sugano diagram. The value used for Dq (2140 cm^{-1}) is the average ligand field of the

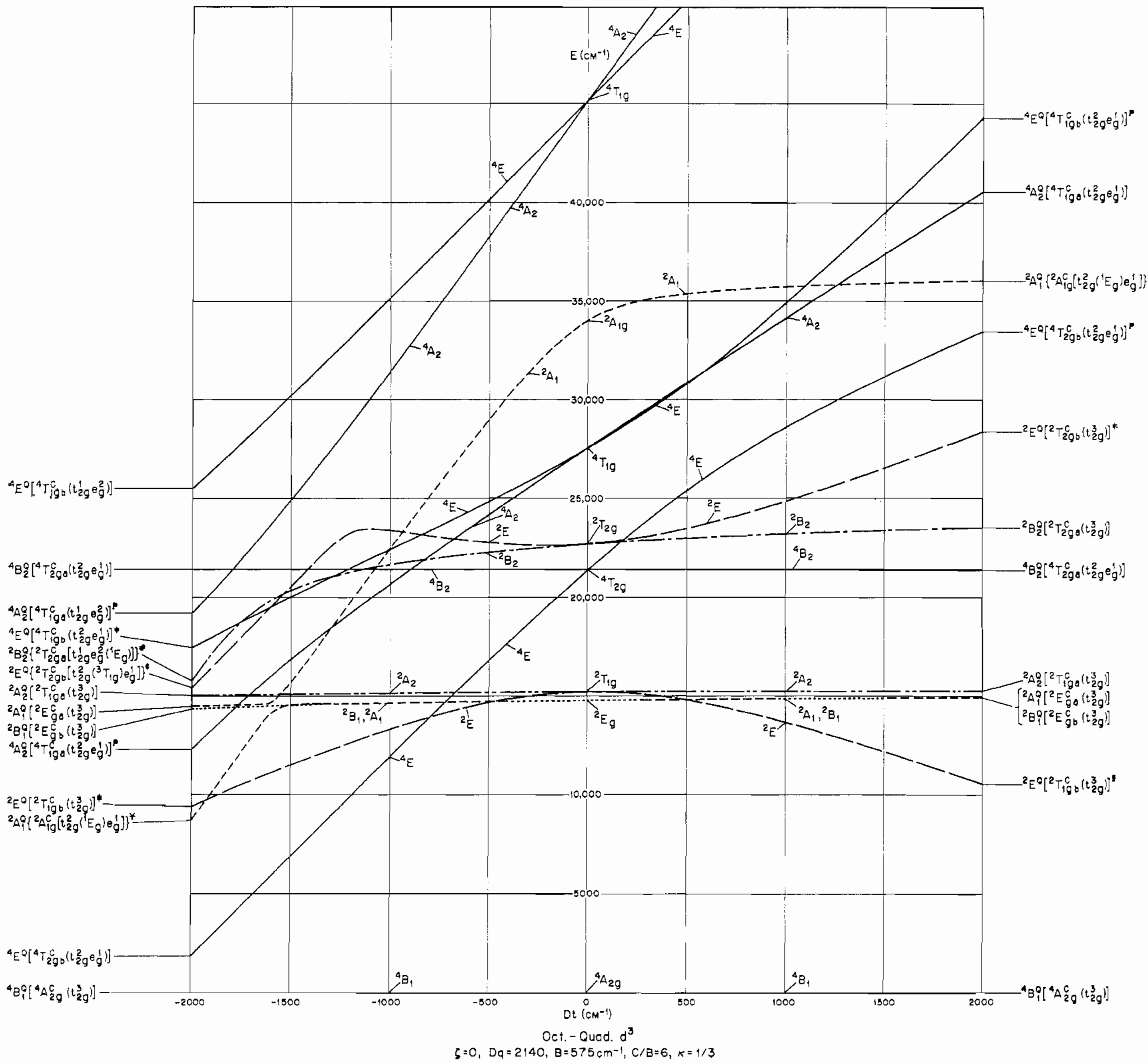


Figure 3.—Simplified energy level diagram for d^3 configuration in tetragonal fields; $\zeta = 0$, $B = 575$ cm^{-1}, $C/B = 6$, $Dq = 2140$ cm^{-1}, and $\kappa = {}^1/_3$ (see the caption of Figure 2 for the meaning of the per cent purity symbols).

pseudo-cubic complex, *cis*-$Cr(CN)_3(H_2O)_3$, and is also approximately equal to the fields of the hexaammine and tris-ethylenediamine complexes of chromium. At the extremes of both positive and negative *Dt* values are shown the strong-field designations for tetragonal symmetry. The corresponding cubic symmetry representations are shown in parentheses (see Table II). Notice the sharp, discontinuous change in ground state from $^4B_1$ to $^4A_2$ at $Dt = -1668$ cm^{-1}, which occurs when $(\Delta + 12B) \geq (4Ds + 5Dt)$, to a first approximation (see Table IV). At large negative (and positive) *Dt* values, therefore, the octahedral orientation is no longer significant. Figure 3 is a simplified diagram calculated for the same parametric values as Figure 2, except that $\kappa = {}^1/_3$ instead of 3. Only the quartet and low-energy doublet states are included. The reasons for the alternate choices of values for κ are given below.

In Figures 2 and 3, the $^4B_2$ level of the parent $^4T_{2g}$ cubic band is parallel to the $^4B_1$ ground state with an energy separation of $10Dq$ as expected. The positive *Dt* sides of the diagrams are applicable to a compressed octahedral complex or to the substitution of a ligand of the original cubic complex by a ligand of higher ligand field strength. The negative *Dt* portions of the figures correspond to axial elongation of the octahedron or to the substitution of an original cubic ligand by a ligand of lower ligand field strength.

The effects of configuration interaction between states of the same symmetry are not the same for positive and negative values of *Dt*. For example, for positive values of *Dt* the lower ^4E level is depressed and remains close to the $^4B_2$ level, while the upper ^4E state is raised (*cf.* Figure 2). The splittings of the first two cubic quartet bands are not given exactly by the energy differences of the components obtained using only the diagonal elements, *i.e.*, $^{35}/_4Dt$ for $^4T_{2g}$ components and

$(6Ds - {}^5/_4Dt)$ for ${}^4T_{1g}$ components. Since for negative Dt values the lowest ${}^4E$ component is placed below ${}^4B_2$, configuration interaction actually increases the splitting of the ${}^4T_{2g}$ band in this case. Larger splittings of the first cubic parentage band, ${}^4T_{2g}$, can be expected for negative values of Dt than for equal positive values.

An interesting situation arises when Dt and Ds are negative (see Figure 2). In this case, the level ordering of the four components will be ${}^4E < {}^4B_2 < {}^4A_2 < {}^4E$, in the order of increasing energy. For suitable values of B, Dt, and κ, it is possible to lower the energy of the ${}^4A_2$ level so close to ${}^4B_2$ as to cause near degeneracy, with the result that only a three-band spectrum may be observed instead of the expected four bands. Of course, a low value of κ may also give rise to no observable splitting of the second band (Figure 3), once again resulting in a three-band spectrum.

For positive values of Dt and Ds, the level ordering will be ${}^4B_2 < {}^4E < {}^4E < {}^4A_2$, in the order of increasing energy. The ${}^4E$ levels will interact configurationally and strongly repel each other, causing the splitting of the first cubic band to be decreased.

The conclusions regarding the quartet transitions of six-coordinate d^3 complexes in tetragonal fields are also quantitatively applicable to the spin-allowed transitions of six-coordinate complexes with a d^8 electronic configuration.[3c] In the latter case, however, the quartet states all become triplet states.

IV. Applications

1. Cubic Complexes: $Cr(CN)_6^{3-}$ and $Cr(H_2O)_6^{3+}$.—In fitting the energy levels observed in the cubic complexes $Cr(CN)_6^{3-}$ and $Cr(H_2O)_6^{3+}$ to the calculated values, it was convenient to fix the Dq value first, then the values of the Racah parameters, B and C. The value of Dq is given by the frequency of the first spin-allowed absorption band. The value of B was obtained by allowing for the configuration interaction between the two ${}^4T_{1g}$ states in octahedral fields.

Using the value of Δ and the frequency maximum of the second quartet absorption band, a trial value of B was obtained. The value of C was fixed by the observed spin-forbidden band, (${}^2E_g$, ${}^2T_{1g}$), located at approximately $9B + 3C$ above the ground level. Thus the Dq, B, and C values are chosen to fit the first two spin-allowed quartet transitions and the low-energy doublets. The calculated energy values[19] are obtained by solving the complete strong-field matrices which include full configuration interaction for all the levels. These calculated values are compared with the observed in Table V. Although the third spin-allowed band of weak intensity is observable in the spectrum of the hexaaquo complex (Figure 4), it is not seen in the case of the hexacyano complex (Figure 5) and is presumably buried under the charge-transfer band.

TABLE V

ABSORPTION SPECTRAL DATA OF $Cr(CN)_6^{3-}$ AND $Cr(H_2O)_6^{3+}$

Complex	Parameters	Obsd ν_{max}, cm^{-1} (10^3f)	Calcd ν_{max}, cm^{-1}	Assignment
$Cr(CN)_6^{3-}$	$Dq = 2650\ cm^{-1}$	12,800[a]	12,916	${}^2E_g$
	$B = 550\ cm^{-1}$	13,400[a]	13,295	${}^2T_{1g}$
	$C/B = 5.2$	19,000[b]	20,378	${}^2T_{2g}$
		26,500 (~1.70)	26,500	${}^4T_{2g}$
		32,573 (~1.48)	32,606	${}^4T_{1g}$
$Cr(H_2O)_6^{3+}$	$Dq = 1740\ cm^{-1}$	(~15000)	14,080	${}^2E_g$
	$B = 700\ cm^{-1}$		14,708	${}^2T_{1g}$
	$C/B = 4.25$	17,400 (0.20)	17,400	${}^4T_{2g}$
		. . .	21,275	${}^2T_{2g}$
		24,630 (0.31)	24,390	${}^4T_{1g}$
		39,062 (~0.21)	38,310	${}^4T_{1g}$

[a] Reference 3b. [b] R. Krishnamurthy and W. B. Schaap, *Inorg. Chem.*, **2,** 605 (1963).

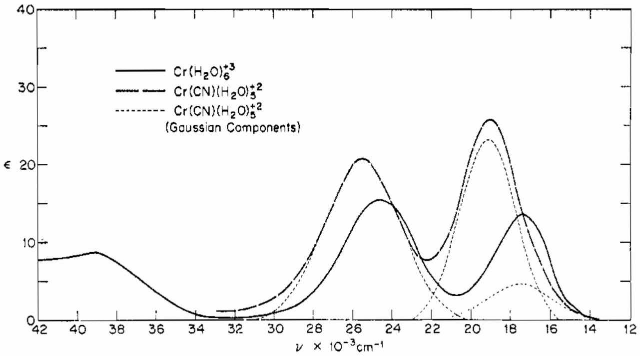


Figure 4.—Absorption spectra of $Cr(H_2O)_6^{3+}$ and $Cr(CN)(H_2O)_5^{2+}$ complex cations.

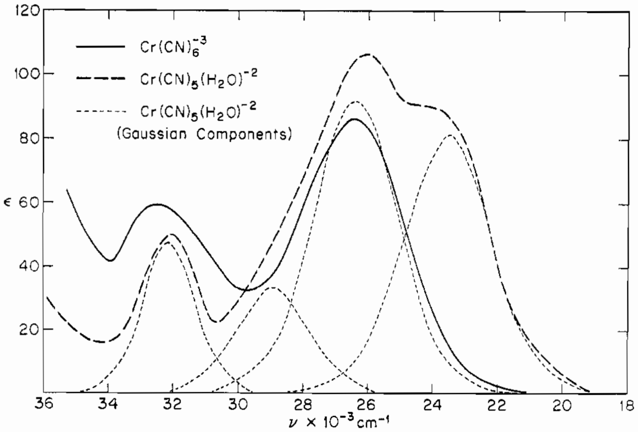


Figure 5.—Absorption spectra of $Cr(CN)_6^{3-}$ and $Cr(CN)_5(H_2O)^{2-}$.

2. Trigonal Complex: $Cr(CN)_3(H_2O)_3$.—This complex has been isolated in the course of these studies and has been assigned the 1,2,3 (*cis*) configuration (C_{3v}) on the basis of spectral and kinetic evidence. The absorption spectrum of this complex is found to consist of two spin-allowed bands, with maxima occurring at 21,433 and 27,624 cm^{-1}, and two weak spin-forbidden bands at 14,545 and 13,870 cm^{-1} (Figure 6). The spectrum of $Cr(CN)_3(H_2O)_3$ does not exhibit any observable splittings of the quartet bands, presumably due to the broadened band widths involved with solution spectra. (Polarized spectral studies on single crystals at low temperatures and possibly studies of magnetic circular dichroism are needed to provide further useful information on this complex.) The observed transition energy maxima are seen to be equal to the average of the energies calculated for the quartet components in the trigonal field. This observation, together with a con-

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(19) The matrices were solved on the IBM 7090 computer at the University of Pittsburgh.

sideration of the intensities of the bands, suggests that the closely spaced adjacent trigonal components overlap and are hidden under the observed bands.

Additional features of the spectrum of this complex are the transitions to the doublet levels at about 14,000 cm^{-1} (Figure 6). Only two weak bands of equal intensity are observed instead of the expected three because the ^2E and $^2A_2$ components of the $^2T_{1g}$ level have a calculated separation of only 125 cm^{-1}, which cannot be resolved in the solution spectrum. The lower energy band at 13,870 cm^{-1} is assigned to the transition to ^2E, and the 14,445 cm^{-1} band to $^2A_2$ and ^2E transitions. A comparison of the calculated energies of the doublet and the quartet levels with those observed for $Cr(CN)_3(H_2O)_3$ is shown in Table VI.

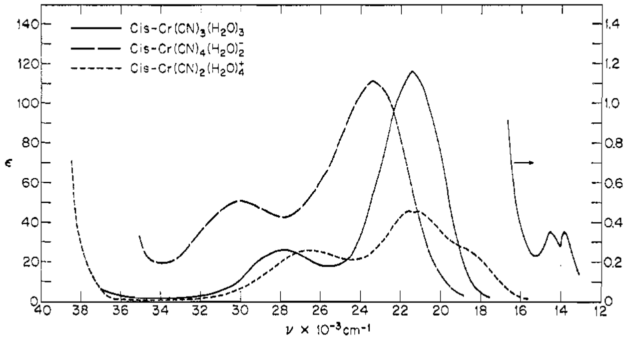

Figure 6.—Absorption spectra of *cis*-$Cr(CN)_4(H_2O)_2^-$, *cis*-$Cr(CN)_3(H_2O)_3$, and *cis*-$Cr(CN)_2(H_2O)_4^+$.

Table VI

Absorption Spectral Data of *cis*-$Cr(CN)_3(H_2O)_3$

Complex	Parameters	Obsd ν_{max}, cm^{-1} (10^3f)	Calcd ν_{max}, cm^{-1}	Assignment
cis-$Cr(CN)_3(H_2O)_3$	$Dq = 2140\ cm^{-1}$	13,870 (~0.0016)	13,250	$^2E\ (^2E_g)$
	$B = 575\ cm^{-1}$	14,545 (0.0016)	13,825	$^2E\ (^2T_{1g})$
	$D\tau = 100\ cm^{-1}$		13,950	$^2A_2\ (^2T_{1g})$
	$C/B = 5.25$	21,433 (1.9)	20,662	$^4E\ (^4T_{2g})$
	$\kappa = 3$		21,536	$^4A_1\ (^4T_{2g})$
		27,624 (0.53)	27,062	$^4E\ (^4T_{1g})$
			27,633	$^4A_2\ (^4T_{1g})$

3. Tetragonal (C_{4v}) Complexes: $Cr(CN)(H_2O)_5^{2+}$ and $Cr(CN)_5(H_2O)^{2-}$.—Since both these complexes belong to the C_{4v} point group, their spectra can be treated on the basis of tetragonal fields. The spectrum of the monocyano complex consists of two spin-allowed bands with maxima at 19,200 and 25,500 cm^{-1}, along with a very weak spin-forbidden doublet band at 14,700 cm^{-1}. The former spin-allowed band shows an appreciable asymmetric broadening on the lower energy side. Gaussian analysis shows components with frequency maxima at 17,500, 19,200, and 25,500 cm^{-1}. The spectra of the monocyano complex and its parent ion, $Cr(H_2O)_6^{3+}$, are shown together in Figure 4 to facilitate a comparison between the two.

The 17,500 cm^{-1} band of the monocyano complex is at essentially the same frequency as the $^4T_{2g}$ band (17,400 cm^{-1}) of the parent cubic ion, $Cr(H_2O)_6^{3+}$. Since the $^4B_2$ band of a tetragonal complex should be at the same frequency as the $^4T_{2g}$ band of its parent cubic complex, according to the predictions noted earlier, we assign the 17,500 cm^{-1} band to the $^4B_2$ component. The 19,200 cm^{-1} band is then assigned to the ^4E component of $^4T_{2g}$. This assignment is consistent with the fact that Dt is positive for the substitution of a water molecule by a cyanide ligand. The band observed at 25,500 cm^{-1} shows no observable splitting. Fixing the values of $Dq = 1740\ cm^{-1}$, $Dt = +300\ cm^{-1}$, $\kappa\ (= Ds/Dt) = 1$, $B = 650\ cm^{-1}$, and $C/B = 4.6$, all appropriate to this complex, the tetragonal energy matrices were solved to calculate the energy levels. The value of $+300\ cm^{-1}$ was used for Dt because this value was obtained by an exact fitting to the splitting of the $^4T_{2g}$ band observed in the spectra of the penta- and the dicyano complexes.[20] Table VII shows a comparison of the experimental and theoretical energy levels together with their assignments.

The $^4A_2$ and ^4E components of the cubic $^4T_{1g}$ level are calculated to be split to an extent of 1140 cm^{-1}. A splitting of this order probably would not be observed in a solution spectrum. The absence of observable splitting of the $^4T_{1g}$ level in tetragonal fields can also be explained by using a value of κ lower than unity.

The absorption band maxima of $Cr(CN)(H_2O)_5^{2+}$ (ν = 25,450, 19,050, and *ca.* 17,500 cm^{-1}) may be expected to be of nearly the same energies as those of *trans*-$Cr(NH_3)_2(H_2O)_4^{3+}$ (ν = 25,520, 19,100, and *ca.* 17,450 cm^{-1}), because the Dq separation between CN^- and H_2O ligands is about twice the separation between NH_3 and H_2O. Thus the Dt value for substitution of one cyanide on $Cr(H_2O)_6^{3+}$ has the same sign and very nearly the same magnitude as that for substitution of two NH_3 groups at *trans* positions.

The spectra of the pentacyano complex and its parent ion, $Cr(CN)_6^{3-}$, are shown in Figure 5. These spectra present a striking confirmation of the theory of tetragonal fields discussed above. As expected, the frequency of the more intense $^4B_2$ band (26,400 cm^{-1}) of the pentacyano complex is essentially the same as that of the $^4T_{2g}$ band (26,500 cm^{-1}) of the parent cubic ion, $Cr(CN)_6^{3-}$. The band located at 23,500 cm^{-1} is then assigned to the ^4E component. The pronounced splitting of the $^4T_{2g}$ band in $Cr(CN)_5(H_2O)^{2-}$ contrasts in direction and magnitude with the lesser splitting of

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[20] Since the splitting of the first quartet band is well resolved in the spectra of $Cr(CN)_5(H_2O)^{2-}$ and *cis*-$Cr(CN)_2(H_2O)_4^+$, the value of Dt for these systems was evaluated by exact fitting and found to be $-300\ cm^{-1}$, including configuration interaction. This value was used consistently with all the other cyanoaquo complexes (with appropriate sign) to interpret and assign the absorption bands.

TABLE VII

ABSORPTION SPECTRAL DATA OF $Cr(CN)_5(H_2O)^{2-}$ AND $Cr(CN)(H_2O)_5^{2+}$

Complex	Parameters	Obsd ν_{max}, cm^{-1} (10^3f)	Calcd ν_{max}, cm^{-1} ($\kappa = 1$)	Assignment
$Cr(CN)_5(H_2O)^{2-}$ [a]	$Dq = 2650\ cm^{-1}$		12,881	$^2A_1$ (^2E_g)
	$B = 550\ cm^{-1}$		12,900	$^2B_1$ (^2E_g)
	$Dt = -300\ cm^{-1}$		13,226	^2E ($^2T_{1g}$)
	$C/B = 5.2$		13,283	$^2A_2$ ($^2T_{1g}$)
			20,227	$^2B_2$ ($^2T_{2g}$)
			20,299	^2E ($^2T_{2g}$)
		23,500 (1.17)	23,698	^4E ($^4T_{2g}$)
		26,400 (1.31)	26,500	$^4B_2$ ($^4T_{2g}$)
		29,000 (0.41)	29,878	$^4A_2$ ($^4T_{1g}$)
		32,100 (0.41)	31,458	^4E ($^4T_{1g}$)
$Cr(CN)(H_2O)_5^{2+}$	$Dq = 1740\ cm^{-1}$	(14,700)	13,837	$^2B_1$ (^2E_g)
	$B = 650\ cm^{-1}$		13,865	$^2A_1$ (^2E_g)
	$Dt = +300\ cm^{-1}$		14,339	^2E ($^2T_{1g}$)
	$C/B = 4.6$		14,390	$^2A_2$ ($^2T_{1g}$)
		~17,500 (0.082)	17,400	$^4B_2$ ($^4T_{2g}$)
		19,200 (0.35)	19,794	^4E ($^4T_{2g}$)
		...	21,174	$^2B_2$ ($^2T_{2g}$)
			21,203	^2E ($^2T_{2g}$)
		25,455 (0.44)	25,661	^4E ($^4T_{1g}$)
			26,802	$^4A_2$ ($^4T_{1g}$)

[a] Isolated by W. F. Coleman.

this band observed for $Cr(CN)(H_2O)_5^{2+}$, due to differences in the effects of configuration interaction predicted for negative and positive values of *Dt* (Figure 2). The separation between the $^4B_2$ and ^4E components in the case of the pentacyano complex is 2900 cm^{-1}, which is almost exactly equal to that observed for the *cis*-dicyano complex. This agreement supports the choice of the value $-300\ cm^{-1}$ for the *Dt* parameter.[20] The observed and theoretical energy levels of the spin-allowed transitions of the pentacyano complex and the assignments and the choice of the parametric values applicable to this complex are shown in Table VII. A ratio of $\kappa = 1.0$ has been chosen to fit the splitting of the second spin-allowed cubic band. The agreement with experimental frequencies is good.

The splitting of the first cubic band observed in $Cr(CN)_5(H_2O)^{2-}$ is also of very nearly the same magnitude as that observed in the spectra of $Cr(NH_3)_5I^{2+}$ and $Cr(NH_3)_5Br^{2+}$. All these complexes have negative *Dt* parameters of similar value because the difference in *Dq* values of the two types of ligands is very nearly the same.[14]

4. Tetragonal (C_{2v}) Complexes: $Cr(CN)_4(H_2O)_2^-$ and $Cr(CN)_2(H_2O)_4^+$.—These complexes can be considered to be the monosubstituted derivatives of the symmetrically trisubstituted, pseudo-cubic complex, $Cr(CN)_3(H_2O)_3$, and have been assigned the C_{2v}-*cis* configuration on the basis of kinetic as well as spectral evidence. The effective symmetry group of both these *cis* isomers can be treated as a tetragonal field for spectral purposes, and the spectra can be discussed in relation to that of their common parent complex, the tricyanotriaquo molecule. A justification of this treatment within the crystal field approximation and its extension to the spectral relations between the *cis* and *trans* isomers of chromium(III) complexes are presented in the Appendix.

The spectrum of the dicyano complex consists of two spin-allowed bands with maxima at 26,455 and 21,460 cm^{-1} and a well-defined shoulder at 18,518 cm^{-1}. A Gaussian analyzed spectrum of this complex can be seen in Figure 7. This spectrum is also displayed along with those of the tricyano and the tetracyano complexes in Figure 6, so that a comparison of these spectra can be made. The spectrum of the tetracyano complex exhibits two broad spin-allowed bands with maxima at 30,120 and 23,420 cm^{-1}.

These two spectra exhibit several significant differ-

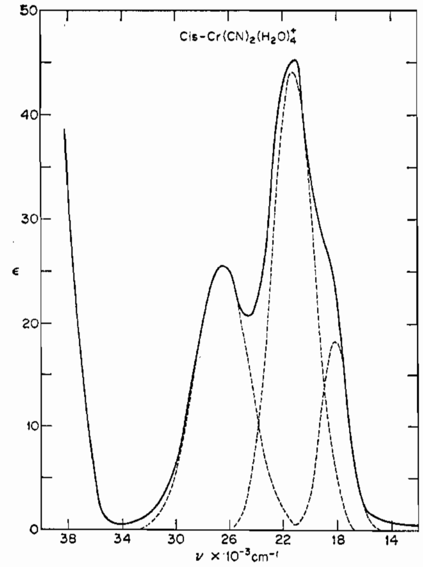

Figure 7.—Absorption spectrum of *cis*-$Cr(CN)_2(H_2O)_4^+$ and its Gaussian components.

Table VIII

Absorption Spectral Data of *cis*-$Cr(CN)_4(H_2O)_2^-$ and *cis*-$Cr(CN)_2(H_2O)_4^+$

Complex	*Dt*, cm^{-1}	Obsd ν_{max}, cm^{-1} (10^3f)	Calculated ν_{max} (cm^{-1}) and assignment (Dq = 2140, B = 575 cm^{-1})	
			$\kappa = 1/3$	$\kappa = 3$
cis-$Cr(CN)_4(H_2O)_2^-$	+300	23,420 (2.56)	21,400; $^4B_2$ ($^4T_{2g}$) 23,900 ^4E ($^4T_{2g}$)	21,400; $^4B_2$ ($^4T_{2g}$) 23,000; ^4E ($^4T_{2g}$)
		30,120 (1.39)	29,400; ^4E ($^4T_{1g}$) 29,500; $^4A_2$ ($^4T_{1g}$)	28,750; ^4E ($^4T_{1g}$) 32,400; $^4A_2$ ($^4T_{1g}$)
cis-$Cr(CN)_2(H_2O)_4^+$	−300	~18,518 (0.21)	18,600; ^4E ($^4T_{2g}$)	18,250; ^4E ($^4T_{2g}$)
		21,460 (0.73)	21,400; $^4B_2$ ($^4T_{2g}$)	21,400; $^4B_2$ ($^4T_{2g}$) 22,550; $^4A_2$ ($^4T_{1g}$)
		26,455 (0.57)	25,550; $^4A_2$ ($^4T_{1g}$) 25,900; ^4E ($^4T_{1g}$)	27,850; ^4E ($^4T_{1g}$)

ences. Upon replacement of one CN^- by H_2O in going from the tricyano to the dicyano complex, one of the bands in the dicyano spectrum remains at exactly the same frequency (21,460 cm^{-1}) as the first spin-allowed band of the tricyano complex, whereas the well-defined shoulder band appears on the lower energy side with a maximum at 18,518 cm^{-1}. The 21,460 cm^{-1} band is attributed to the $^4B_1 \rightarrow {}^4B_2$ transition and the 18,518 cm^{-1} band is then identified as the ^4E component. The assignment of these two components is in harmony with the predictions deduced for the tetragonal fields. The second spin-allowed band at 26,455 cm^{-1} does not show any observable splitting.

Upon replacement of one H_2O molecule by CN^- in the tricyano complex, the tetracyano species is formed. Both the spin-allowed bands observed in this complex are displaced toward higher energies, which is consistent with the spectrochemical series, and show larger band widths than the tricyano spectrum. About one-half the intensity of the unsplit spin-allowed band of lowest energy of the tetracyano complex is distributed directly under the first band of the tricyano complex. The expected splitting of the second band in the tetracyano system is also not seen, although the band width has noticeably increased.

The spectra of $Cr(CN)_2(H_2O)_4^+$ and $Cr(CN)_4(H_2O)_4^-$ can be interpreted with the aid of the energy level diagrams, Figures 2 and 3, noting that the *Dt* values are −300 and +300 cm^{-1}, respectively.[20] A comparison of the calculated and the observed transition energies, together with the oscillator strengths and the band assignments, is shown in Table VIII. In the case of the dicyano spectrum, for the ratio $\kappa = 1/3$ the splitting of the second spin-allowed band, $^4T_{1g}$, into ^4E and $^4A_2$ components is very small (Figure 3). For the ratio $\kappa = 3.0$, one of these components ($^4A_2$) would move closer to the $^4B_2$ component of the first band (Figure 2) at negative *Dt* values. This leads to near degeneracy of these two components which could overlap to give one broad, composite spin-allowed band. The greater oscillator strength of the middle band of the dicyano spectrum relative to the other two bands may be the result of the overlapping of the two bands, $^4A_2$ and $^4B_2$, of nearly the same intensities. In view of this, we prefer the assignments deduced with the ratio of $\kappa = 3.0$.

In the case of the tetracyano spectrum, the splitting of the first band $^4T_{2g}$ is not seen. The expected small splitting is implied in the appreciable band broadening and in the relatively high oscillator strength. Moreover, since this is a system with positive *Dt*, derived from the parent tricyano complex, the splitting of the first band is expected to be less than for the dicyano system (negative *Dt*) because of configuration interaction. The splitting of the second band, $^4T_{1g}$, is also not observed, although this band is very broad. This can in itself be explained by either the lower or the higher value of the ratio κ. For the ratio $1/3$, the splitting of this band is predicted to be small. A ratio of 3.0, however, should result in a splitting of an order of magnitude which is usually observable. Notice that the half-width of this band is larger than the splitting predicted for the ratio of 3 (*cf.* Figure 6), resulting in a relatively high oscillator strength.

The spectra of the di- and the tetracyano complexes may be compared with those of other chromium complexes which have very nearly the same values of the ligand field parameters. In the case[14] of $Cr(NH_3)_5I^{2+}$, *Dq* is 2155 cm^{-1} and *Dt* is −325 cm^{-1}, which are very close to the values of these parameters for *cis*-$Cr(CN)_2(H_2O)_4^+$. The spectra of these two complexes can therefore be expected to be very similar. The observed energy maxima for the iodopentaammine complex are at 18,315, 22,320, and 26,315 cm^{-1}, while the corresponding values for the dicyano complex are 18,518, 21,460, and 26,455 cm^{-1}. Similarly, *cis*-$Cr(CN)_4(H_2O)_2^-$ should be a very close spectral relative of *trans*-Cr-$(NH_3)_4(CN)_2^+$, which, unfortunately, is presently unknown. Spectral comparisons of the type noted here, their implications, and further predictions are discussed more fully in the Appendix.

5. Band Splitting in Mono- and Disubstituted Chromium Complexes.—As an addendum, we will consider the minimum values of the parameters, particularly, *Dt*, which will give rise to well-resolved splitting of the first cubic quartet band in substituted complexes of Cr(III). The discussion is based on the crystalline field model, which has been found in some cases to give approximately the same values of *Dt* as a more complete ligand-field treatment.[14] As noted previously, it is for negative values of *Dt* that the splitting of the first quartet is enlarged by virtue of configuration interaction. If the limit of observable splitting in solution spectra is taken to be about 2500 cm^{-1}, the value of *Dt* corresponding to this limit is 225 cm^{-1} (*cf.* $Cr(NH_3)_5$-

TABLE IX

EXAMPLES OF MONOSUBSTITUTED AND *cis*- AND *trans*-DISUBSTITUTED HEXACOORDINATE CHROMIUM(III) SYSTEMS EXPECTED TO SHOW SPLITTING OF THE $^4T_{2g}$ BAND

Complex	X	Y	Remarks
CrX_5Y	CN^-	H_2O, F^-, Cl^-, Br^-, I^-	The aquo complex is known and shows the expected splitting[a]
	NH_3	Cl^-, Br^-, I^-	Known and show the expected splitting[b]
trans-CrX_4Y_2	CN^-	NH_3, H_2O, F^-, Cl^-, Br^-, I^-	Unknown
	$^1/_2$ en, NH_3	H_2O, F^-, Cl^-, Br^-, I^-	The aquo, chloro, and bromo bisethylenediamine complexes are known and show the expected splitting[c]
	H_2O	Cl^-, Br^-, I^-	The chloro complex is known but the splitting is not observable in the published spectrum[d]
	F^-	Br^- (?), I^- (?)	Unknown
cis-CrX_2Y_4	CN^-, $^1/_2$ en, NH_3	Br^-, I^-	Unknown
	CN^-, $^1/_2$ en (?), NH_3 (?)	Cl^-	Unknown
	CN^-	H_2O, F^-	The aquo complex is known and shows the expected splitting[a]

[a] This work. [b] M. Linhard and M. Weigel, *Z. Anorg. Allgem. Chem.*, **266**, 49 (1951). [c] See ref 23. [d] E. L. King, Sr., M. J. M. Woods, O.P., and H. S. Gates, *J. Am. Chem. Soc.*, **80**, 5015 (1958).

Cl^{2+}).[14] A *Dt* value of -225 cm^{-1} would require a *Dq* separation of about 800 cm^{-1} between the two types of ligands in a monosubstituted complex and a *Dq* separation of about 400 cm^{-1} between the ligands of a *trans*-disubstituted complex. This means that the systems represented by the formulas CrX_5Y and *trans*-CrX_4Y_2 listed in Table IX should all show good resolution of the components of the first cubic band. Complexes included in Table IX which have been characterized do show such resolution in their spectra.

In order to observe a well-defined splitting in the *cis* complexes, we have to turn to the *cis* counterparts of *trans* systems of positive *Dt*, which at the same time have a *Dq* separation of ≥ 800 cm^{-1} between the two types of ligands. Examples of such *cis* complexes are included in Table IX under the formula *cis*-CrX_2Y_4. Among all the *cis* systems mentioned in the table, *only cis*-$Cr(CN)_2(H_2O)_4^+$ has been discovered and, interestingly enough, shows the predicted splitting. On the other hand, such a splitting is not usually seen in the spectra of the inverted *cis* systems, *cis*-CrX_4Y_2, because these would have positive values of *Dt* and be subject to the militating effects of configuration interaction. Because of the close spacing of the two components of the $^4T_{2g}$ band, they may add up and appear as a single, more intense asymmetric band in these systems. (Of course, it should be noted that bands of higher intensity are expected in *cis* systems anyway due to the lower symmetry.) Because most of the *cis*-disubstituted complexes of Cr(III) which have been characterized until now belong to the category *cis*-CrX_4Y_2, where $Dq_X > Dq_Y$, this may be the explanation for the previously puzzling phenomenon mentioned in the literature[21] that *cis*-disubstituted chromium complexes do not show splitting of the first cubic band, whereas the corresponding *trans* complexes do. It would be worthwhile to isolate, characterize, and study the spectra of the *cis* complexes of the type listed in Table IX to verify the predictions presented here.

V. Summary

Ligand field theory, which has been successfully applied to the interpretation of the spectra of pure cyanide complexes of transition metals,[3a,b] has been extended to the interpretation of the visible absorption spectra of mixed cyanide complexes of lower symmetry as exemplified by the cyanoaquo complexes of chromium(III). The complex ions $Cr(CN)(H_2O)_5^{2+}$ and $Cr(CN)_5(H_2O)^{2-}$ have been treated by the theory of tetragonal fields. Further assumptions based on the crystal field model have been made to include the two *cis*-disubstituted complex ions under tetragonal fields. The molecule *cis*-$Cr(CN)_3(H_2O)_3$ has been treated by trigonal field theory. Although its spectrum does not show any splitting of the cubic spin-allowed quartet bands, it agrees well in regard to band positions with the average energies of the trigonal components calculated with an appropriate set of parameters.

The spectra of all the tetragonal systems have been consistently explained with a *Dt* value of -300 cm^{-1} for substitution of a cyanide ion by a water molecule or $+300$ cm^{-1} for the reverse substitution. The convention used in assigning signs to *Dt* values is qualitatively consistent with that generally accepted for comparing changes in *Dq* values, *i.e.*, a *positive Dt* value corresponds to an increased axial field in comparison to the parent, etc. Because of our assumption that the *cis*-disubstituted complexes can be considered to be monosubstituted derivatives of *cis*- or 1,2,3-$Cr(CN)_3(H_2O)_3$, it follows that *Dt* is positive for the tetracyano complex and negative for the dicyano species. These signs are in agreement with the conclusion arrived at from crystal-field theory that the signs of *Dt* for *cis* systems should be opposite to those of the corresponding *trans* systems.

The conclusion that the splitting of the lowest energy, spin-allowed quartet band in tetragonal complexes will be large only for negative values of *Dt*, because of configuration interaction, is borne out by the fact that well-resolved splitting of the first quartet band has been observed only for the pentacyano and the *cis*-dicyano complexes, which are the only mixed cyanoaquo

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(21) See, for instance, W. A. Baker, Jr., and M. G. Phillips, *Inorg. Chem.*, **5**, 1042 (1966).

complexes isolated which have negative values of *Dt*. The other two tetragonal complexes, the tetracyano and the monocyano complex species, show only band broadening, although in the latter system there is a positive indication of a two-component band structure from the large asymmetry. The assignments of the two components of the first quartet band have been made on the basis that the energy of the $^4B_2$ band should be the same as that of the $^4T_{2g}$ cubic band of the parent complex.

The remaining spectral features of the *cis*-dicyano complex have been explained on the basis of two ratios of κ, the smaller of which gives rise to no observable splitting of the second quartet band, and the larger of which lowers the energy of the $^4A_2$ component of the second quartet, bringing it so close to that of the $^4B_2$ band of the first quartet that a three-band spectrum is observed instead of the expected four-component structure.

Acknowledgments.—We wish to thank Mr. R. L. Anderson and his associate, Mr. J. Beasley of the Mellon Institute, for computer programming, and Mr. J. F. Benes and E. L. Helgerman, of the Mellon Institute Research Drafting Department, for expert tracings of the complicated energy level diagrams obtained from the computer. We also wish to thank Miss Diane K. Wakefield and Mr. W. F. Coleman, both of Indiana University, for providing some of the spectral data.

VI. Appendix

Spectral Predictions of the Crystal Field Model for *cis* and *trans* Isomers of d^3 Complexes.—We will now justify the treatment of the spectra of *cis*-disubstituted complexes under tetragonal field theory and, subsequently, discuss spectral criteria for distinguishing between *cis* and *trans* isomers of chromium(III) complexes. The discussion here is based on the simple crystal-field model.

In a symmetrically trisubstituted six-coordinate complex, such as MX_3Y_3, ligands X and Y are located opposite each other along each of the three axes $\pm x$, $\pm y$, $\pm z$ in the Cartesian coordinate system. The sums of the charges or of the effective dipole moments, which represent the perturbations from the three pairs of ligands (X and Y) in *trans* positions, are identical along each of the axes. If Z is a ligand such that its ligand field strength is one-half of the sum of the *Dq* values of X and Y, the pseudo-cubic complex MX_3Y_3 (C_{3v}) may be treated as MZ_6 (O_h). For example, since $Dq_{NH_3} = {}^1/_2(Dq_{CN^-} + Dq_{H_2O})$, the *cis*-$Cr(CN)_3(H_2O)_3$ isomer can be regarded as equivalent to $Cr(NH_3)_6{}^{3+}$ in a spectral sense. On this basis, the general shapes of their spectra, as well as the corresponding frequency maxima of the spin-allowed bands, may be expected to be similar, though the band intensities may differ. Experimentally, in the case of the tricyano complex $\nu_1 = 21{,}433$ cm^{-1} and $\nu_2 = 27{,}624$ cm^{-1}; for the hexaammine these bands are observed at 21,500 and 28,500 cm^{-1}, respectively. Similarly, the spectrum of *cis*-$[Cr(en)(enH)Cl_3]^+$ can be compared with the spectrum of $Cr(H_2O)_6{}^{3+}$. In this case, $Dq_{H_2O} \cong {}^1/_2(Dq_{en} + Dq_{Cl^-})$. Experimentally, the band maxima are found to be 17,700 and 23,900 cm^{-1} for this complex, whereas for the hexaaquo ion they occur at 17,400 and 24,400 cm^{-1}.

A *trans*-disubstituted derivative of MZ_6, such as MZ_4X_2, is equivalent to the *cis*-MX_4Y_2. The latter system can be formed from MX_3Y_3 by replacing one Y group by an X group. Figure 8 shows the various geometrical relationships among MX_3Y_3, MZ_6, *trans*-MZ_4X_2, and *cis*-MX_4Y_2, in addition to those among MX_6, MX_5Y, and *trans*-MX_4Y_2. The tetragonal *Dt* parameters for these systems can be related to the differences in the *Dq* parameters of the ligands X, Y, and Z. These relations are[22]

$$\text{for } MX_5Y\text{:}\quad Dt = -{}^2/_7(Dq_X - Dq_Y) \qquad \text{(A-1)}$$

$$\text{for } trans\text{-}MX_4Y_2\text{:}\quad Dt = -{}^4/_7(Dq_X - Dq_Y) \qquad \text{(A-2)}$$

$$\text{for } cis\text{-}MX_4Y_2\text{:}\quad Dt = +{}^2/_7(Dq_X - Dq_Y) \qquad \text{(A-3)}$$

These relations can be easily derived. For example, in the case of MX_5Y, if we write the effective potential as the sum of cubic (V_{O_h}) and the axial (V_∞) field potentials, *i.e.*

$$V_{eff} = V_{O_h}(6X) + V_\infty(-X + Y)$$

then from the definition of *Dt*, we have

$$Dt = {}^1/_{21}e(-q_X + q_Y)\langle R_4(r)\rangle$$

By substituting the definition $Dq_X = {}^1/_6eq_X\langle R_4(r)\rangle$ and $Dq_Y = {}^1/_6eq_Y\langle R_4(r)\rangle$, we get $Dt = -{}^2/_7(Dq_X - Dq_Y)$. Since for *trans*-$MX_4Y_2$ the axial potential is twice that of MX_5Y, it follows that $Dt = -{}^4/_7(Dq_X - Dq_Y)$. *cis*-$MX_4Y_2$ is assumed to be equivalent to the *trans*-disubstituted derivative of MZ_6 (*i.e.*, MZ_4X_2), if $Dq_Z = {}^1/_2(Dq_X + Dq_Y)$. Thus for the *cis* complex

$$Dt = -{}^4/_7[{}^1/_2(Dq_X + Dq_Y) - Dq_X] = +{}^2/_7(Dq_X - Dq_Y)$$

The above relationships are consistent with the well-known rule that the splitting for a *cis* isomer is the same as that for the monosubstituted complex, but

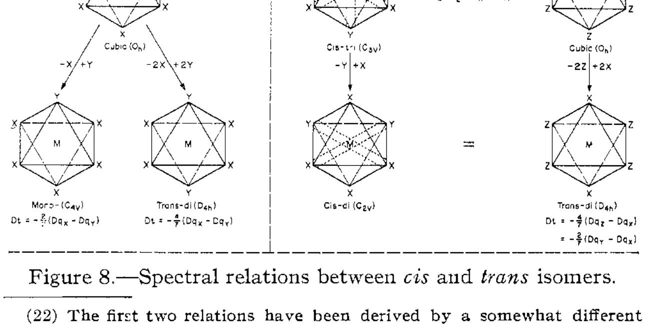

Figure 8.—Spectral relations between *cis* and *trans* isomers.

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[22] The first two relations have been derived by a somewhat different approach by Wentworth and Piper.[4] C. J. Ballhausen and C. K. Jørgensen, *Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd.*, **29**, 14 (1955), and Ballhausen[8] have given the relative band splittings for the three cases, though not in terms of *Dq*.

one-half of that for the corresponding *trans* isomer. In addition, because of the positive sign of Dt for the *cis* isomer, its energy levels are inverted with respect to those of the *trans* isomer and the monosubstituted complex.

The above relationships are of a general nature and can now be combined with the conclusions drawn for the d^3 configuration in tetragonal fields, leading to further relationships that serve as useful guide lines for distinguishing between *cis* and *trans* isomers of Cr(III) complexes. We consider only the splitting of the first quartet cubic band, ${}^4T_{2g}$, of the parent complex, CrX_6. For *trans*-MX_4Y_2

$$\Delta E({}^4B_{1g} \longrightarrow {}^4B_{2g}) = 10Dq_X \qquad \text{(A-4)}$$

$$\Delta E({}^4B_{1g} \longrightarrow {}^4E_g) \simeq 10Dq_X + {}^{35}/_4Dt \qquad \text{(A-5a)}$$

Substituting for Dt from (A-2)

$$\Delta E({}^4B_{1g} \longrightarrow {}^4E_g) \simeq 5Dq_X + 5Dq_Y \qquad \text{(A-5b)}$$

For *cis*-MX_4Y_2

$$\Delta E({}^4B_1 \longrightarrow {}^4B_2) \simeq 5Dq_X + 5Dq_Y \qquad \text{(A-6)}$$

$$\Delta E({}^4B_1 \longrightarrow {}^4E) \simeq 5Dq_X + 5Dq_Y + {}^{35}/_4Dt \qquad \text{(A-7a)}$$

Substituting for Dt from (A-3)

$$\Delta E({}^4B_1 \longrightarrow {}^4E) \simeq {}^{15}/_2Dq_X + {}^5/_2Dq_Y \qquad \text{(A-7b)}$$

Notice that ΔE of (A-7b) is the average of ΔE of (A-4) and (A-5b).

The above equations permit one to deduce the following new predictions for the *cis* and *trans* isomers, CrX_4Y_2.

(i) From eq A-4, A-5b, and A-7b, it follows that the energy of the ${}^4E$ component of the *cis* isomer is the average of the energies of the ${}^4B_{2g}$ and ${}^4E_g$ components of the corresponding *trans* isomer. As a result of this, the ${}^4E$ band of the *cis* complex should be positioned midway between the energy maxima of the two *trans* components. Furthermore, the location of this band should be on the higher or lower energy side of the *cis*-${}^4B_2$ band according as $Dq_X > Dq_Y$ or $Dq_X < Dq_Y$, respectively.

(ii) From eq A-5b and A-6, it is seen that the energy of the ${}^4E_g$ component of the *trans* complex is the same as that of the *cis*-${}^4B_2$ component. Consequently, the band maxima of these two components should be located at about the same frequency, which is also the frequency of the first spin-allowed band in a *cis*- or 1,2,3-trisubstituted MX_3Y_3 complex and is the mean of the frequencies of the first quartet bands for CrX_6 and CrY_6.

These relationships have been summarized schematically in Figure 9, in which are shown the splitting of the ${}^4T_{2g}$ cubic band and the relative ordering and positions of the ${}^4E$ and ${}^4B_2$ components of the *cis* and *trans* isomers. The predictions noted here are best illustrated with examples of Cr(III) complexes known to exist in both isomeric forms. Figures 10–12 show the spectra of *cis* and *trans* isomers of $[Cr(en)_2Y_2]$, where Y = H_2O, Cl^-, or Br^-, respectively.[23] Figure 13 shows the spectra of *cis* and *trans* isomers[23c] of $[Cr(en)_2(H_2O)Br]^{2+}$. In all these cases, it can be seen that there is a band in the *trans* species placed at almost the same position as the ${}^4T_{2g}$ cubic band of $Cr(en)_3{}^{3+}$ and which can be assigned to the ${}^4B_2$ component. The ${}^4E$ component is then identified as the low-energy band, since in these examples $Dq_{en} > Dq_Y$. In all the *cis* series, as expected, there is a band almost at the center of the two *trans* components which can be assigned to the ${}^4E$ transition. The ${}^4B_2$ component of the *cis* series, which should roughly coincide with the ${}^4E$ level of the *trans* complex for these systems, appears as an asymmetric bulge in that region.

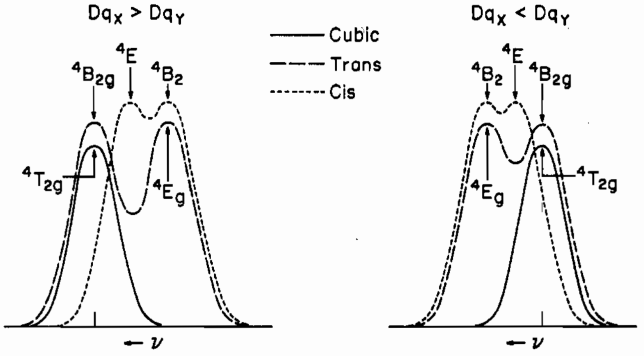

Figure 9.—Schematic representation of the splitting of the ${}^4T_{2g}$ band of a cubic complex, MX_6, and the relative positions of the ${}^4B_2$ and ${}^4E$ tetragonal components of its *cis* and *trans* derivatives, MX_4Y_2.

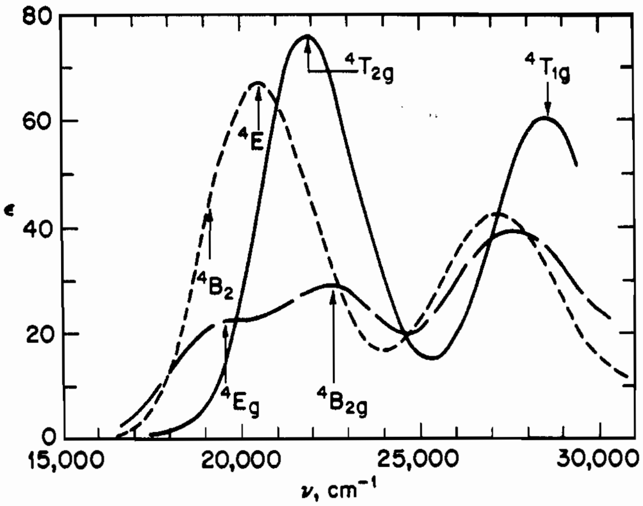

Figure 10.—Absorption spectra of $Cr(en)_3{}^{3+}$ (———) and of the *cis* (- - - -) and *trans* (— — —) isomers of $Cr(en)_2(H_2O)_2{}^{3+}$ (ref 23a).

A further criterion by which the ${}^4E$ component of a *cis* complex, CrX_4Y_2, can be identified is that this band should have nearly the same frequency maximum as that of the ${}^4E$ band of the monosubstituted complex, CrX_5Y. Comparison of the spectrum of *cis*-$Cr(CN)_4(H_2O)_2{}^-$ with that of $Cr(CN)_5(H_2O)^{2-}$, that of *cis*-$Cr(CN)_2(H_2O)_4{}^+$ with that of $Cr(CN)(H_2O)_5{}^{2+}$, and also those of

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[23] The spectra of the diaquo, dichloro, and dibromo systems, respectively, are taken from (a) F. Woldbye, *Acta Chem. Scand.*, **12**, 1079 (1958); (b) M. Linhard and M. Weigel, *Z. Physik. Chem.* (Frankfurt), **5**, 20 (1955); and (c) L. P. Quinn and C. S. Garner, *Inorg. Chem.*, **3**, 1348 (1964).

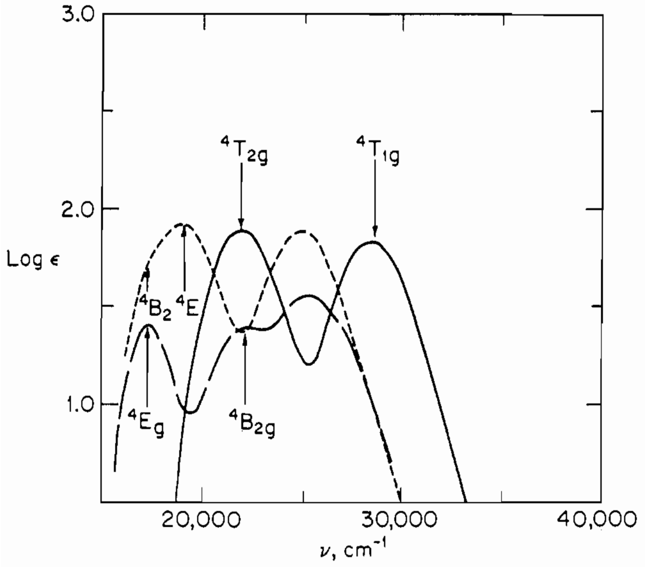

Figure 11.—Absorption spectra of $Cr(en)_3^{3+}$ (———) and of the *cis* (– – – –) and *trans* (— — —) isomers of $Cr(en)_2Cl_2^+$ (ref 23b).

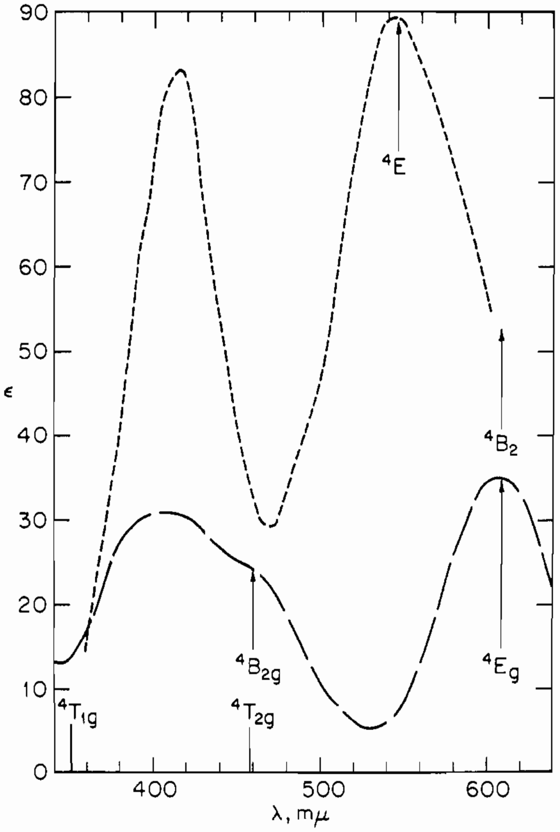

Figure 12.—Absorption spectra of the *cis* (– – – –) and *trans* (— — —) isomers of $Cr(en)_2Br_2^+$ (ref 23c). The absorption maxima of $Cr(en)_3^{3+}$ are shown in heavy vertical lines at the bottom.

cis-$Cr(en)_2X_2$ with those of appropriate acidopentaammines confirms this.

Comparison of the spectra of the *trans*-diacido(bisethylenediamine) complexes shows that the spectrum of *trans*-$[Cr(en)_2(H_2O)(Br)]^{2+}$ is almost identical with that of *trans*-$[Cr(en)_2Cl_2]^+$. This similarity implies that these complexes have very nearly the same values of ligand field parameters, particularly *Dq* and *Dt*. It is interesting to note that the average of the *Dq* values of H_2O and Br^- ligands is fairly close to the *Dq* value of Cl^- ion.[24] Because of the similarity of the harmonic terms appearing in the definitions of *Dq* and *Dt* (in contrast to *Dq* and *Ds*), a similar relationship may be expected between the values of the axial field parameter, *Dt*, for these complexes. Furthermore, the *average* of the values of *Dt* for the *trans*-diaquo- and *trans*-dibromobis(ethylenediamine) complexes is approximately equal to the *Dt* parameter for the *trans*-dichloro complex. In general, it appears that the extent of splitting and the position of the absorption maxima of *hetero-trans* complexes of the type CrA_4XY can be predicted from the spectra of the *homo-trans* complexes, CrA_4X_2 and CrA_4Y_2, and that the spectrum of *trans*-CrA_4XY will be closely similar to that of *trans*-CrA_4Z_2 if X, Y, and Z are ligands such that $Dq_Z \simeq {}^1/_2(Dq_X + Dq_Y)$.

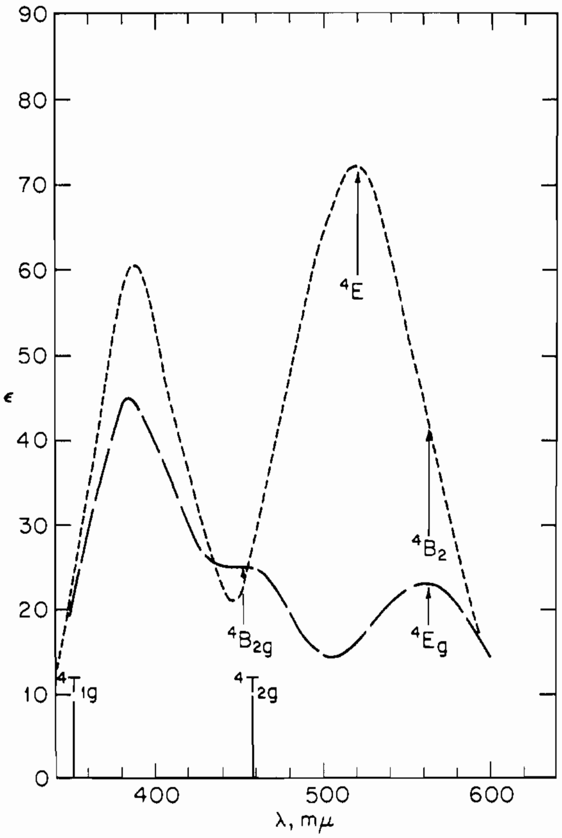

Figure 13.—Absorption spectra of the *cis* (– – – –) and *trans* (— — —) isomers of $Cr(en)_2(H_2O)Br^{2+}$ (ref 23c). The absorption maxima of $Cr(en)_3^{3+}$ are shown in heavy vertical lines at the bottom.

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[24] The *Dq* values of H_2O, Cl^-, and Br^- are 1740, 1320, and 1190 cm^{-1}, respectively. Because $Cr(Br)_6^{3-}$ is unknown, a direct evaluation of 10*Dq* for bromide ion coordinated to Cr(III) is not possible. However, by fitting *Dt* values to observed spectra, 10*Dq* for bromide ligands is estimated to be 11,925 cm^{-1}.