

# Ligand Field Theory of $d^3$ and $d^7$ Electronic Configurations in Noncubic Fields.

## II. Applications to Quadrate Chromium(III) Complexes<sup>1,2</sup>

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The quadrate energy matrices of  $d^3$  configuration derived by us earlier have been solved for suitable sets of parametric values and appropriate energy diagrams constructed to interpret the spectra of various monosubstituted and *trans*-disubstituted complexes of chromium(III). It has been concluded that at the present time there is no unique way of assigning all the observed bands in the systems considered. In all the complexes discussed, the first spin-allowed cubic band splits into two components which are given the definitive quadrate assignments, and the corresponding  $Dt$  values are evaluated. As the second spin-allowed cubic band does not split in most of these systems, alternative quadrate assignments have been found possible for different choices of values of  $B$  and  $\kappa$  parameters. It is suggested that further measurements of spectra of these and similar systems be made particularly on single crystals by means of polarized light and at low temperatures to verify our choices of assignments. Use of our calculations and energy diagrams for the study of the quadrate complexes of the  $d^3$  configuration, other than Cr(III), and also of the  $d^7$  configuration has been pointed out. It is emphasized however, that it is necessary to take into account full configuration interaction even at the initial stages of applications of theory without resorting to any approximations.

### I. Introduction

In the previous paper,<sup>2</sup> we have presented a detailed account of the theory of  $d^3$  and  $d^7$  electronic configurations in quadrate, trigonal, and cylindrical fields, where the symmetry adapted strong-field wave functions were derived and the energy matrices constructed as functions of  $Dq$ , and  $D\mu$ ,  $D\nu$ , the cubic and axial ligand field parameters, and  $A$ ,  $B$ ,  $C$ , the Racah electron correlation parameters. Spin-orbit interaction has not been included.<sup>3</sup>

It is the purpose of this paper to apply our quadrate calculations for the interpretation of the optical studies of  $d^3$  systems as exemplified by the substituted chromium(III) complexes belonging to quadrate symmetry. As has been pointed out in part I, these systems will be treated as deviations from cubic symmetry.

### II. Theoretical Digression

**Parameters.** It has been shown that in the quadrate fields all the parameters with the exception of  $Ds$  and  $Dt$  are the same as those that occur in cubic fields. Although the axial parameters  $Ds$  and  $Dt$  are used in our

present work as empirical parameters just as are the other cubic parameters in ligand field theory, it is instructive to examine these parameters in the limit of crystalline field theory. In quadrate fields, we will be concerned with either a monosubstituted octahedral or a pentacoordinate square pyramidal system both belonging to  $C_{4v}$  symmetry, or a *trans*-disubstituted octahedral or a tetracoordinate square planar system both belonging to  $D_{4h}$  symmetry. If the quadrate potential  $V_Q$  is expressed as a sum of cubic,  $V_C$ , and the axial,  $V_\infty$ , fields, then

$$V_Q = V_C + V_\infty \quad (1)$$

For a six-coordinate octahedral system

(1) Presented at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

(2) See preceding paper for part I: J. R. Perumareddi, *J. Phys. Chem.*, **71**, 3144 (1967).

(3) The available data on the spectra of substituted octahedral chromium(III) complexes have been obtained from a study of absorption spectra in solution giving rise to broad bands with low resolution. Hence, inclusion of spin-orbit interaction in our calculations at this stage is not warranted.

$$V_C = V_{Oh} = eqR_4(r) \sqrt{\frac{4\pi}{9}} \left[ \frac{7}{2} Y_4^0 + \frac{\sqrt{35}}{2} Y_4^{4c} \right] \quad (2)$$

where the  $e$  and  $q$  are the electronic charge and the effective charge of the ligand, respectively,  $R_4(r) = r_{<}^4/r_{>}^5$ ,  $r_{<}$  and  $r_{>}$  being the lesser and greater of the electronic radius and bond distance, and  $Y_4^{4c}$  is the cosine combination of  $Y_4^4$  and  $Y_4^{-4}$ , i.e.,  $Y_4^{4c} = 1/\sqrt{2} (Y_4^4 + Y_4^{-4})$ .

The generalized axial potential is given by

$$V_{\infty} = eq' \left[ R_2(r) \sqrt{\frac{4\pi}{5}} Y_2^0 + R_4(r) \sqrt{\frac{4\pi}{9}} Y_4^0 \right] \quad (3)$$

where  $R_2(r) = r_{<}^2/r_{>}^3$  and all others are the same as above.

From the definitions<sup>4</sup>

$$Dq = \langle 2, \pm 2 | V_{Oh} | \pm 2, 2 \rangle = \frac{1}{6} eq \langle R_4(r) \rangle$$

$$Dt = \langle 2, \pm 2 | V_{\infty}(Y_4^0) | \pm 2, 2 \rangle = \frac{1}{21} eq' \langle R_4(r) \rangle$$

$$Ds = \langle 2, \pm 1 | V_{\infty}(Y_2^0) | \pm 1, 2 \rangle = \frac{1}{7} eq' \langle R_2(r) \rangle \quad (4)$$

it follows that

$$\kappa \equiv Ds/Dt = 3 \langle R_2(r) \rangle / \langle R_4(r) \rangle$$

where

$$\langle R_l(r) \rangle = \int_0^{\infty} R_{kd}(r)^2 (r_{<}^l/r_{>}^{l+1}) r^2 dr$$

The radial integrals  $\langle R_2(r) \rangle$  and  $\langle R_4(r) \rangle$  can be evaluated if the radial wave functions,  $R_{kd}(r)$ , and the bond distances are known. In a few cases, such an evaluation has been carried out<sup>5</sup> using hydrogenic, Slater, and Hartree-Fock functions with the result that their ratio comes out to be 4 to 5. On the other hand, they can be obtained as empirical parameters by fitting the experimental spectral data where it is possible. This has been attempted in the case of copper(II) complexes where this ratio has been found to be<sup>6</sup> approximately unity. A value of unity can be obtained by a theoretical calculation if a reduced bond distance is used.<sup>5c,d</sup> With this value of unity,  $\kappa$  turns out to be 3. As already noted, we shall adjust these parameters empirically.

**Energy Diagrams.** We have shown previously<sup>2</sup> that in quadrate fields the transition energy  ${}^4B_1^Q[{}^4A_{2g}^C(t_{2g}^3)] \rightarrow {}^4B_2^Q[{}^4T_{2g}^C(t_{2g}^2e_g)]$  is given by  $10Dq$  including configuration interaction. This means that the  ${}^4B_2$  component in both mono- and *trans*-disubstituted systems should remain positioned at the frequency of the parent octahedral  ${}^4T_{2g}$  band. The  ${}^4E^Q$  component would then be placed either on the higher or on the

lower energy side of the  ${}^4B_2$  band depending upon whether the substituting ligand is of higher or of lower ligand field strength than that of the original ligand. Accordingly, it is possible to fix the value of  $Dq$  appropriate to an octahedral complex and to construct an energy diagram as a function of  $Dt$  parameter. Such plots are useful for the interpretation of the optical spectra of the substituted tetragonal derivatives of the parent complex. Figures 1 and 2 show the energy level diagrams<sup>7</sup> in the range of  $Dt$ , 0 to  $\pm 2000 \text{ cm}^{-1}$ . We have chosen a  $Dq$  value of  $2155 \text{ cm}^{-1}$  which corresponds to that of the hexaammine Cr(III) complex so that these diagrams can be employed for the interpretation of the spectra of acidopentaammines and *trans*-diacidobisethylenediammines<sup>8</sup> of Cr(III). Note that these diagrams are also appropriate to describe the energy levels of a quadrately distorted (compressed or elongated) tetrahedral  $d^7$  complex of  $Dq = 2155 \text{ cm}^{-1}$ .

Several points may be noted from these energy diagrams. As expected, the  ${}^4B_2^Q$  component of  ${}^4T_{2g}$  is a parallel level to the  ${}^4B_1^Q({}^4A_{2g})$  state separated by  $10Dq$ . The energy levels at zero  $Dt$  value correspond to levels of parent cubic complex (hexaammine); i.e., they correspond to a one-dimensional cross section of Tanabe-Sugano octahedral plot at a  $Dq$  value of  $2155 \text{ cm}^{-1}$ . At both ends of the diagrams are given the quadrate labels with no  $g$  subscripts along with their octahedral parentage. These are true as given for  $C_{4v}$ , but they are to be supplemented with  $g$  subscripts for

(4) From these definitions, some simple relations among these parameters can be derived for  $C_{4v}$  and  $D_{4h}$  systems in the limit of crystalline field formalism. If the parent octahedral complex is  $MX_6$ , for the case of  $MX_5Y$  and  $MX_5$  belonging to  $C_{4v}$ , we may write the axial field as that due to  $(-X + Y)$  and  $(-X)$ , respectively. Substitution of the corresponding charges in the definitions give rise to  $Dt = 1/21(-q_x + q_y)e\langle R_4(r) \rangle = -2/7(Dq_x - Dq_y)$  for mono-substituted and  $Dt = 1/21(-q_x)e\langle R_4(r) \rangle = -2/7Dq_x$  for penta-coordinate square pyramid. Similar relations for *trans*-disubstituted  $MX_4Y_2$  and square planar  $MX_4$  systems can be found. These are:  $Dt = -4/7(Dq_x - Dq_y)$  and  $Dt = -4/7Dq_x$ , respectively. (Note that in the derivation of these formulas, substitution of  $eq\langle R_4(r) \rangle = 6Dq$  implies the assumption that the  $Dq$  of an octahedral complex is made up of six equal contributions from its six ligands.)

(5) (a) D. S. McClure, *J. Chem. Phys.*, **36**, 2757 (1962); (b) H. A. Weakliem, *ibid.*, **36**, 2117 (1962); (c) T. S. Piper and R. L. Carlin, *ibid.*, **33**, 1208 (1960); (d) J. R. Perumareddi, unpublished results.

(6) (a) W. E. Hatfield and T. S. Piper, *Inorg. Chem.*, **3**, 841 (1964); (b) P. Day, *Proc. Chem. Soc.*, 18 (1964).

(7) All of our energy matrices were solved and energy levels were plotted on the IBM 7090 computer at the University of Pittsburgh Computer Center. Energy diagrams have been plotted on a Calcomp Plotter through IBM 1401, which is fed by a magnetic tape from IBM 7090. For the sake of simplicity, only the quartet and the lower energy doublet states are shown in these energy diagrams.

(8) Although the  $Dq$  value of trisethylenediammine complex is  $2185 \text{ cm}^{-1}$ , we have not constructed energy diagrams suitable for this value, since it does not differ much from  $2155 \text{ cm}^{-1}$ . On the other hand, the energy diagrams of this paper have been used to estimate the transition energies only for the acidopentaammines, whereas special runs have been made for particular sets of parameters for *trans*-diacidobisethylenediammines and other miscellaneous systems.

Figure 1. Energy level diagram for  $d^3$  configuration in quadrate fields:  $\zeta = 0$ ,  $B = 500 \text{ cm}^{-1}$ ,  $C/B = 7$ ,  $Dq = 2155 \text{ cm}^{-1}$ ,  $\kappa = 3$ . At both ends of the diagram are given the strong-field configurational labels. At the center of the diagram,  $Dt = 0$  refers to octahedral levels. The quadrate designations as given are true for  $C_4v$  symmetry. They have to be supplemented with  $g$  subscripts for  $D_{4h}$  symmetry. Quartets are drawn in solid lines and the doublets are distinguished by various kinds of broken lines. The superscripts on the energy labels refer to the per cent of that eigenvector component of the eigenfunction. The various symbols have the following meaning:  $\$$ ,  $75 \pm 2.5\%$ ;  $\mp$ ,  $70 \pm 2.5\%$ ;  $\mp\mp$ ,  $65 \pm 2.5\%$ ;  $\$$ ,  $60 \pm 2.5\%$ ;  $\epsilon$ ,  $55 \pm 2.5\%$ ;  $P$ ,  $50 \pm 2.5\%$ ;  $\text{Y}$ ,  $45 \pm 2.5\%$ ;  $\#$ ,  $40 \pm 2.5\%$ ;  $N$ ,  $35 \pm 2.5\%$ .



extreme end of the negative side of the energy plot with  $\kappa = 3$  is due to change in the ground state; *i.e.*, for large negative  $Dt$  values,  $(10Dq + 12B)$  becomes less than  $\sim |(4Ds + 5Dt)|$  so that the  ${}^4A_2^Q[{}^4T_{1g}(t_{2g}^2e_g)]$  level assumes the ground state. This situation is similar to the change of the magnetic ground state in cubic compounds of  $d^4$ ,  $d^5$ ,  $d^6$ , and  $d^7$  configurations.<sup>10</sup>

Another important point to be noted is on the positive side of  $Dt$ . Because of the occurrence of levels of same symmetry designation in sequence, namely the  ${}^4E$  components of the first two quartets, these two levels do not cross (the so-called noncrossing rule) and because of configuration interaction, the lower  ${}^4E$  is depressed and the upper  ${}^4E$  is raised in energy. So, for the systems which are represented by this region of the diagrams, one should not use diagonal elements only and conclude that the splitting of the first quartet is given by  ${}^{35}/4Dt$  and that of the second quartet by  $(6Ls - {}^{5}/4Dt)$ . Indeed, it follows from the above reasoning as an obvious corollary that for the same negative and positive values of  $Dt$ , the same amount of splitting of the first two quartets may not be expected. Because of configuration interaction, larger splittings are expected for a system of negative  $Dt$  than for a system of same positive  $Dt$ . Finally, for large values of  $Dt$ , both positive and negative, the representation used here, *i.e.*, the octahedral orientation, is not pure. For more on this, see part I.<sup>2</sup>

Although the doublets  ${}^2E_g$ ,  ${}^2T_{1g}$ , and  ${}^2T_{2g}$  of  $(t_{2g}^3)$  configuration do not appear to be split (from the diagonal elements of the energy matrices), they do so by a few tens of wavenumbers when configuration interaction is included. It is interesting to note that none of these doublets arising from the strong-field configuration  $(t_{2g}^3)$  split in the first order as we go to lower symmetry such as quadrate (or trigonal). Thus, the  ${}^2A_1^Q$  and  ${}^2B_1^Q$  of  ${}^2E_g^C(t_{2g}^3)$  and the  ${}^2A_2^Q$  and  ${}^2E^Q$  of  ${}^2T_{1g}^C(t_{2g}^3)$  and  ${}^2B_2^Q$  and  ${}^2E^Q$  of  ${}^2T_{2g}^C(t_{2g}^3)$  are all degenerate pairs, just as the  ${}^2E_g^C$  and  ${}^2T_{1g}^C$  of  $(t_{2g}^3)$  configuration are in cubic fields. [Indeed because of this latter degeneracy in cubic fields, the  ${}^2A_1^Q({}^2E_g)$ ,  ${}^2B_1^Q({}^2E_g)$ ,  ${}^2A_2^Q({}^2T_{1g})$ , and  ${}^2E^Q({}^2T_{1g})$  states are all degenerate in the first-order, their energy separation from the ground level being  $(9B + 3C)$ . The transition energy to the  ${}^2B_2^Q({}^2T_{2g})$  and  ${}^2E^Q({}^2T_{2g})$  levels from the ground state is  $(15B + 5C)$ . It is the configuration interaction that can lift the otherwise first-order degeneracy of these doublet levels both in cubic and noncubic fields.<sup>11</sup>

### III. Applications

**Acidopentaammines.** The spectra of chloro- and bromopentaammines were studied by diffuse reflectance

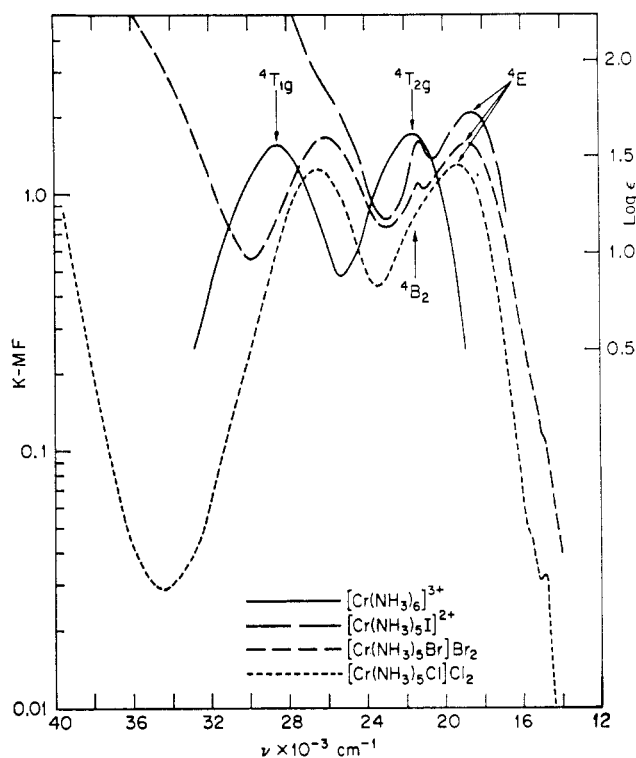


Figure 3. Spectra of hexaammine and acidopentaammines of Cr(III). [Extinction coefficient scale on the right of the figure refers to the hexaammine and iodopentaammine (ref 12). The K-M F on the left is Kubelka-Munk function which is given by a function of reflectance,  $f(R) = (1 - R)^2/2R$ , where  $R$  is the fraction reflectance and is roughly proportional to the extinction coefficient. The K-M F scale refers to the reflectance spectra of bromo- and chloropentaammines measured against LiF as white standard.]

measurements of pressed powders at room temperature against LiF as white standard on a Carl Zeiss PMQ II spectrophotometer. These spectra are given in Figure 3 along with the solution absorption spectra of iodopentaammine and hexaammine obtained by Linhard and Weigel.<sup>12</sup> These workers have also studied the solution absorption spectra of chloro- and bromopentaammines which agree with ours presented in the figure. We have achieved better resolution of the two-component system of the first cubic spin-allowed band in the bromopentaammine complex than that observed in its solution absorption spectrum. Such resolution was not achieved, however, in the spectrum of chloropenta-

(10) See, for instance, the corresponding Tanabe-Sugano plots: Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **9**, 766 (1954).

(11) See also (a) S. Sugano and Y. Tanabe, *Discussions Faraday Soc.*, **26**, 43 (1958); (b) Y. Tanabe and H. Kamimura, *J. Phys. Soc. Japan*, **13**, 394 (1958).

(12) M. Linhard and M. Weigel, *Z. Anorg. Allgem. Chem.*, **266**, 49 (1951).

**Table I:** Spectral Data of  $\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$ 

| Obsd   |                                   | Calcd $\nu_{\text{max}}$ ; assignment<br>$Dq = 2155 \text{ cm}^{-1}$ , $Dt = -225 \text{ cm}^{-1}$   |  |
|--|-----------------------------------|--|--|
| $\nu_{\text{max}}$ (log $\epsilon$ )<br>(Ref 12) | $\nu_{\text{max}}$<br>(This work) | $B = 600 \text{ cm}^{-1}$<br>$C/B = 5.5$ , $\kappa = 1$  | $B = 500 \text{ cm}^{-1}$<br>$C/B = 7$ , $\kappa = 3$  |
|  | 14,800                            | $\{14,478; {}^2A_1({}^2E_g)$<br>$14,496; {}^2B_1({}^2E_g)$<br>$14,921; {}^2E({}^2T_{1g})$<br>$14,958; {}^2A_2({}^2T_{1g})$<br>$22,143; {}^2B_2({}^2T_{2g})$<br>$22,280; {}^2E({}^2T_{2g})$<br>$19,482; {}^4E({}^4T_{2g})$<br>$21,550; {}^4B_2({}^4T_{2g})$ | $\{14,377; {}^2A_1({}^2E_g)$<br>$14,434; {}^2B_1({}^2E_g)$<br>$14,660; {}^2E({}^2T_{1g})$<br>$14,749; {}^2A_2({}^2T_{1g})$<br>$21,960; {}^2B_2({}^2T_{2g})$<br>$22,152; {}^2E({}^2T_{2g})$<br>$19,232; {}^4E({}^4T_{2g})$<br>$\{21,550; {}^4B_2({}^4T_{2g})$<br>$23,259; {}^4A_2({}^4T_{1g})$<br>$27,229; {}^4E({}^4T_{1g})$ |
| 19,400 (1.58)<br>(22,100) (0.90)                 | 19,200<br>$\sim 21,400$           |  |  |
| 26,600 (1.64)                                    | 26,400                            | $\{25,918; {}^4A_2({}^4T_{1g})$<br>$27,054; {}^4E({}^4T_{1g})$<br>$42,782; {}^4A_2({}^4T_{1g})$<br>$43,264; {}^4E({}^4T_{1g})$   | $\{42,288; {}^4E({}^4T_{1g})$<br>$43,041; {}^4A_2({}^4T_{1g})$   |

**Table II:** Spectral Data of  $\text{Cr}(\text{NH}_3)_5\text{Br}^{2+}$ 

| Obsd   |                                   | Calcd $\nu_{\text{max}}$ ; assignment<br>$Dq = 2155 \text{ cm}^{-1}$ , $Dt = -275 \text{ cm}^{-1}$   |  |
|--|-----------------------------------|--|--|
| $\nu_{\text{max}}$ (log $\epsilon$ )<br>(Ref 12) | $\nu_{\text{max}}$<br>(This work) | $B = 600 \text{ cm}^{-1}$<br>$C/B = 5.5$ , $\kappa = 1$  | $B = 500 \text{ cm}^{-1}$<br>$C/B = 7$ , $\kappa = 3$  |
|  | 14,800                            | $\{14,469; {}^2A_1({}^2E_g)$<br>$14,491; {}^2B_1({}^2E_g)$<br>$14,902; {}^2E({}^2T_{1g})$<br>$14,954; {}^2A_2({}^2T_{1g})$<br>$22,096; {}^2B_2({}^2T_{2g})$<br>$22,175; {}^2E({}^2T_{2g})$<br>$19,000; {}^4E({}^4T_{2g})$<br>$21,550; {}^4B_2({}^4T_{2g})$ | $\{14,364; {}^2A_1({}^2E_g)$<br>$14,435; {}^2B_1({}^2E_g)$<br>$14,612; {}^2E({}^2T_{1g})$<br>$14,745; {}^2A_2({}^2T_{1g})$<br>$21,889; {}^2B_2({}^2T_{2g})$<br>$22,150; {}^2E({}^2T_{2g})$<br>$18,657; {}^4E({}^4T_{2g})$<br>$\{21,550; {}^4B_2({}^4T_{2g})$<br>$22,418; {}^4A_2({}^4T_{1g})$<br>$27,325; {}^4E({}^4T_{1g})$ |
| 19,050 (1.58)<br>21,770 (1.07)                   | 18,800<br>21,300                  |  |  |
| 26,490 (1.66)                                    | 26,000                            | $\{25,458; {}^4A_2({}^4T_{1g})$<br>$26,866; {}^4E({}^4T_{1g})$<br>$42,142; {}^4A_2({}^4T_{1g})$<br>$42,733; {}^4E({}^4T_{1g})$   | $\{41,668; {}^4E({}^4T_{1g})$<br>$42,582; {}^4A_2({}^4T_{1g})$   |

ammine complex. Note that the low intensity doublets have also been discovered in both the chloropentaammine and bromopentaammine spectra. The doublet in the chloropentaammine spectrum is actually split into two components.

Tables I and II collect our spectral data on chloro- and bromopentaammines along with those obtained by Linhard and Weigel. The spectral data on iodopentaammine are given in Table III. These tables also contain tentative assignments. All the complexes have absorption maxima around  $\sim 22,000 \text{ cm}^{-1}$ , which is roughly the band maximum ( $21,550 \text{ cm}^{-1}$ ) of the  ${}^4T_{2g}$  transition in the parent cubic hexaammine complex. This may be immediately assigned to the  ${}^4B_2$  component so that the component on the low-energy side of this transition is the  ${}^4E$ . From these two transitions, the

$Dt$  value can be derived by an exact fitting. These  $Dt$  values are also given in the tables. It may be noted that they are in the expected order.<sup>13</sup> Now the non-splitting (or nonobservable splitting) of the second band can be explained on the basis of two values; *i.e.*,  $\kappa = 1$  where the splitting is not observable in solution and  $\kappa = 3$ , where the  ${}^4A_2^Q$  component of  ${}^4T_{1g}(t_2^2e_g)$  is placed close to  ${}^4B_2^Q$  so that only one spin-allowed transition may still be seen at higher energy in solution spectrum. Both choices of assignments are included in

(13) Because of the similarity of the harmonic terms appearing in the definitions of  $Dq$  and  $Dt$  (as against  $Dq$  and  $Ds$ ), it may be expected that a smooth relation may exist between  $Dq$  and  $Dt$ . Such a relation has been shown in the limit of crystalline field model (*cf.* footnote 4). Although this relation may not be exact, it seems to be a very good guideline in an *a priori* estimate of  $Dt$ , at least in the case of  $\text{Cr}(\text{III})$  complexes. (See Addendum.)

**Table III:** Spectral Data of  $\text{Cr}(\text{NH}_3)_5\text{I}^{2+}$ 

| Obsd<br>$\nu_{\text{max}}$ (log $\epsilon$ )<br>(Ref 12) | Calcd $\nu_{\text{max}}$ ; assignment   |   |
|--|---|---|
|  | $Dq = 2155 \text{ cm}^{-1}$ , $Dt = -325 \text{ cm}^{-1}$   |   |
|  | $B = 600 \text{ cm}^{-1}$<br>$C/B = 5.5$ , $\kappa = 1$   | $B = 500 \text{ cm}^{-1}$<br>$C/B = 7$ , $\kappa = 3$   |
|  | $\left\{ \begin{array}{l} 14,461; {}^2A_1({}^2E_g) \\ 14,487; {}^2B_1({}^2E_g) \\ 14,879; {}^2E({}^2T_{1g}) \\ 14,951; {}^2A_2({}^2T_{1g}) \end{array} \right.$ | $\left\{ \begin{array}{l} 14,349; {}^2A_1({}^2E_g) \\ 14,435; {}^2B_1({}^2E_g) \\ 14,556; {}^2E({}^2T_{1g}) \\ 14,741; {}^2A_2({}^2T_{1g}) \end{array} \right.$ |
|  | $\left\{ \begin{array}{l} 22,047; {}^2B_2({}^2T_{2g}) \\ 22,151; {}^2E({}^2T_{2g}) \end{array} \right.$   | $\left\{ \begin{array}{l} 21,811; {}^2B_2({}^2T_{2g}) \\ 22,151; {}^2E({}^2T_{2g}) \end{array} \right.$   |
| 18,500 (1.73)  | 18,513; ${}^4E({}^4T_{2g})$   | 18,070; ${}^4E({}^4T_{2g})$   |
| 21,250 (1.43)  | 21,550; ${}^4B_2({}^4T_{2g})$   | $\left\{ \begin{array}{l} 21,550; {}^4B_2({}^4T_{2g}) \\ 21,577; {}^4A_2({}^4T_{1g}) \end{array} \right.$   |
| $\sim 26,000$ (1.70)?                                    | $\left\{ \begin{array}{l} 24,998; {}^4A_2({}^4T_{1g}) \\ 26,685; {}^4E({}^4T_{1g}) \end{array} \right.$   | $\left\{ \begin{array}{l} 27,430; {}^4E({}^4T_{1g}) \\ 27,430; {}^4E({}^4T_{1g}) \end{array} \right.$   |
|  | $\left\{ \begin{array}{l} 41,502; {}^4A_2({}^4T_{1g}) \\ 42,203; {}^4E({}^4T_{1g}) \end{array} \right.$   | $\left\{ \begin{array}{l} 41,050; {}^4E({}^4T_{1g}) \\ 42,123; {}^4A_2({}^4T_{1g}) \end{array} \right.$   |

the tables. The third spin-allowed absorption of weak intensity at still higher energies has not been uncovered in these complexes.

The reflectance spectrum of chloropentaammine shows two weak absorptions at 14,800 and 15,500  $\text{cm}^{-1}$ , whereas the bromopentaammine spectrum contains only one at 14,800  $\text{cm}^{-1}$ . These are the spin-forbidden doublet transitions. Although the two cubic doublets in this region, namely the  ${}^2E_g$  and  ${}^2T_{1g}$  of  $(t_{2g})^3$  configuration, split into four quadrupole doublets by configuration interaction, it can be seen from Table I that the splitting of the quadrupole components of these doublets is only of the order of 20 to 30  $\text{cm}^{-1}$  (or 60 to 90  $\text{cm}^{-1}$  for alternative assignment) which cannot be resolved in the room temperature reflectance spectra. Thus, in the spectrum of chloropentaammine, the 14,800- $\text{cm}^{-1}$  band is assigned to both  ${}^2A_1$  and  ${}^2B_1$  levels, and the 15,500- $\text{cm}^{-1}$  band to both  ${}^2A_2$  and  ${}^2E$  levels. The agreement of the observed transitions with the calculated can be brought still closer than shown in the table if the  $C$  value is slightly increased, probably by another 100  $\text{cm}^{-1}$ . Since only one band at 14,800  $\text{cm}^{-1}$  is observed in the bromopentaammine spectrum, this is assigned to all the four quadrupole transitions, *i.e.*,  ${}^2A_1$ ,  ${}^2B_2$ ,  ${}^2A_2$ , and  ${}^2E$ . The resolution of these sharp doublets which are only separated by a few hundred wavenumbers in the room temperature spectra of some of the systems, but not in all, seems to depend on how far are they removed in energy from the first broad and more intense spin-allowed band. The farther they are removed, the better they seem to be resolved.

*trans-Diacidobisethylenediammines.* Since the  $Dq$  value of trisethylenediammine complex is almost the same as that of the hexaammine complex, it may be expected

that in the case of the *trans*-diacidobisethylenediammine complexes, the  $Dt$  values be correspondingly roughly twice that of the acidopentaammines. This is shown in Tables IV–VIII, where the spectral data for these systems are collected from the papers of Linhard and Weigel,<sup>14</sup> Garner and co-workers,<sup>15</sup> and also from the work of Woldbye.<sup>16</sup> Figure 4 summarizes the observed transition energies in all these compounds.

All these complexes show well-resolved splitting of the first cubic band ( ${}^4T_{2g}$ ), but no such splitting has

**Table IV:** Spectral Data of *trans*- $\text{Cr}(\text{en})_2(\text{H}_2\text{O})_2^{3+}$ 

| Obsd<br>$\nu_{\text{max}}$ (log $\epsilon$ )<br>(Ref 15, 16) | Calcd $\nu_{\text{max}}$ ; assignment   |   |
|--|---|---|
|  | $Dq = 2185 \text{ cm}^{-1}$ , $Dt = -225 \text{ cm}^{-1}$   |   |
|  | $B = 650 \text{ cm}^{-1}$<br>$C/B = 5$ , $\kappa = 1$   | $B = 500 \text{ cm}^{-1}$<br>$C/B = 7$ , $\kappa = 4$   |
|  | $\left\{ \begin{array}{l} 14,666; {}^2A_1({}^2E_g) \\ 14,686; {}^2B_1({}^2E_g) \\ 15,172; {}^2E({}^2T_{1g}) \\ 15,209; {}^2A_2({}^2T_{1g}) \end{array} \right.$ | $\left\{ \begin{array}{l} 14,369; {}^2A_1({}^2E_g) \\ 14,447; {}^2B_1({}^2E_g) \\ 14,474; {}^2E({}^2T_{1g}) \\ 14,749; {}^2A_2({}^2T_{1g}) \end{array} \right.$ |
|  | $\left\{ \begin{array}{l} 22,434; {}^2B_2({}^2T_{2g}) \\ 22,489; {}^2E({}^2T_{2g}) \end{array} \right.$   | $\left\{ \begin{array}{l} 21,954; {}^2B_2({}^2T_{2g}) \\ 22,363; {}^2E({}^2T_{2g}) \end{array} \right.$   |
| 19,700 (1.35)  | 19,788; ${}^4E({}^4T_{2g})$   | 19,386; ${}^4E({}^4T_{2g})$   |
| 22,600 (1.47)  | 21,850; ${}^4B_2({}^4T_{2g})$   | $\left\{ \begin{array}{l} 21,850; {}^4B_2({}^4T_{2g}) \\ 22,695; {}^4A_2({}^4T_{1g}) \end{array} \right.$   |
| 27,700 (1.59)  | $\left\{ \begin{array}{l} 26,677; {}^4A_2({}^4T_{1g}) \\ 27,801; {}^4E({}^4T_{1g}) \end{array} \right.$   | $\left\{ \begin{array}{l} 28,107; {}^4E({}^4T_{1g}) \\ 28,107; {}^4E({}^4T_{1g}) \end{array} \right.$   |
|  | $\left\{ \begin{array}{l} 43,673; {}^4E({}^4T_{1g}) \\ 43,928; {}^4A_2({}^4T_{1g}) \end{array} \right.$   | $\left\{ \begin{array}{l} 42,681; {}^4E({}^4T_{1g}) \\ 44,055; {}^4A_2({}^4T_{1g}) \end{array} \right.$   |

**Table V:** Spectral Data of *trans*- $\text{Cr}(\text{en})_2\text{Cl}_2^+$ 

| Obsd<br>$\nu_{\text{max}}$ (log $\epsilon$ )<br>(Ref 14, 15a) | Calcd $\nu_{\text{max}}$ ; assignment   |  |
|---|---|--|
|   | $Dq = 2185 \text{ cm}^{-1}$ , $Dt = -475 \text{ cm}^{-1}$   |  |
|   | $B = 700 \text{ cm}^{-1}$ , $C/B = 4.5$ , $\kappa = 1$  |  |
|   | $\left\{ \begin{array}{l} 14,635; {}^2A_1({}^2E_g) \\ 14,686; {}^2B_1({}^2E_g) \\ 15,125; {}^2E({}^2T_{1g}) \\ 15,282; {}^2A_2({}^2T_{1g}) \\ 22,201; {}^2B_2({}^2T_{2g}) \\ 22,396; {}^2E({}^2T_{2g}) \end{array} \right.$ |  |
| 17,301 (1.39)   | 17,355; ${}^4E({}^4T_{2g})$   |  |
| 22,075 (1.36)   | 21,850; ${}^4B_2({}^4T_{2g})$   |  |
| 25,252 (1.53)   | 24,786; ${}^4A_2({}^4T_{1g})$   |  |
| $\sim 27,250$ ( $\sim 1.36$ )                                 | $\left\{ \begin{array}{l} 27,264; {}^4E({}^4T_{1g}) \\ 40,814; {}^4A_2({}^4T_{1g}) \\ 41,881; {}^4E({}^4T_{1g}) \end{array} \right.$  |  |

(14) M. Linhard and M. Weigel, *Z. Physik. Chem.* (Frankfurt), **5**, 20 (1955).

(15) (a) C. S. Garner and D. J. MacDonald in "Advances in the Chemistry of Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, pp 266–275; (b) L. P. Quinn and C. S. Garner, *Inorg. Chem.*, **3**, 1348 (1964).

(16) F. Woldbye, *Acta Chem. Scand.*, **12**, 1079 (1958).

**Table VI:** Spectral Data of  $\text{trans-Cr(en)}_2\text{Br}_2^+$ 

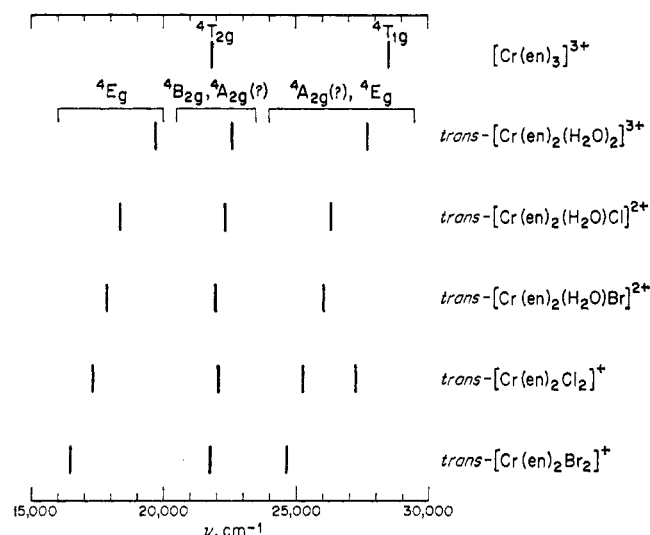
| Obsd<br>$\nu_{\text{max}}$ (log $\epsilon$ )<br>(Ref 15b) | Calcd $\nu_{\text{max}}$ ; assignment                     |  |
|---|---|--|
|   | $Dq = 2185 \text{ cm}^{-1}$ ; $Dt = -575 \text{ cm}^{-1}$ |  |
|   | $B = 500 \text{ cm}^{-1}$<br>$C/B = 7, \kappa = 1$        | $B = 600 \text{ cm}^{-1}$<br>$C/B = 5.5, \kappa = 1/3$ |
|   | 14,358; ${}^2A_1({}^2E_g)$                                | 14,261; ${}^2E({}^2T_{1g})$                            |
|   | 14,394; ${}^2B_1({}^2E_g)$                                | 14,442; ${}^2B_1({}^2E_g)$                             |
|   | 14,597; ${}^2E({}^2T_{1g})$                               | 14,449; ${}^2A_1({}^2E_g)$                             |
|   | 14,739; ${}^2A_2({}^2T_{1g})$                             | 14,944; ${}^2A_2({}^2T_{1g})$                          |
|   | 21,719; ${}^2B_2({}^2T_{2g})$                             | 21,907; ${}^2B_2({}^2T_{2g})$                          |
|   | 22,004; ${}^2E({}^2T_{2g})$                               | 22,538; ${}^2E({}^2T_{2g})$                            |
| 16,474 (1.54)   | 16,246; ${}^4E({}^4T_{2g})$                               | 16,534; ${}^4E({}^4T_{2g})$                            |
| $\sim 21,739$ ( $\sim 1.38$ )                             | 21,850; ${}^4B_2({}^4T_{2g})$                             | 21,850; ${}^4B_2({}^4T_{2g})$                          |
|   | 22,099; ${}^4A_2({}^4T_{1g})$                             |  |
| 24,630 (1.49)   | 25,332; ${}^4E({}^4T_{1g})$                               | 24,400; ${}^4A_2({}^4T_{1g})$                          |
|   |   | 25,231; ${}^4E({}^4T_{1g})$                            |
|   | 38,301; ${}^4A_2({}^4T_{1g})$                             | 38,266; ${}^4A_2({}^4T_{1g})$                          |
|   | 39,523; ${}^4E({}^4T_{1g})$                               | 40,452; ${}^4E({}^4T_{1g})$                            |

**Table VII:** Spectral Data of  $\text{trans-Cr(en)}_2(\text{H}_2\text{O})\text{Cl}_2^{2+}$ 

| Obsd<br>$\nu_{\text{max}}$ (log $\epsilon$ )<br>(Ref 15a) | Calcd $\nu_{\text{max}}$ ; assignment                     |  |
|---|---|--|
|   | $Dq = 2185 \text{ cm}^{-1}$ ; $Dt = -350 \text{ cm}^{-1}$ |  |
|   | $B = 500 \text{ cm}^{-1}$<br>$C/B = 7, \kappa = 2$        | $B = 600 \text{ cm}^{-1}$<br>$C/B = 5.5, \kappa = 1/3$ |
|   | 14,370; ${}^2A_1({}^2E_g)$                                | 14,476; ${}^2B_1({}^2E_g)$                             |
|   | 14,426; ${}^2B_1({}^2E_g)$                                | 14,479; ${}^2A_1({}^2E_g)$                             |
|   | 14,733; ${}^2E({}^2T_{1g})$                               | 14,690; ${}^2E({}^2T_{1g})$                            |
|   | 14,747; ${}^2A_2({}^2T_{1g})$                             | 14,957; ${}^2A_2({}^2T_{1g})$                          |
|   | 21,895; ${}^2B_2({}^2T_{2g})$                             | 22,110; ${}^2B_2({}^2T_{2g})$                          |
|   | 22,044; ${}^2E({}^2T_{2g})$                               | 22,347; ${}^2E({}^2T_{2g})$                            |
| 18,315 (1.31)   | 18,322; ${}^4E({}^4T_{2g})$                               | 18,670; ${}^4E({}^4T_{2g})$                            |
| 22,321 (1.39)   | 21,850; ${}^4B_2({}^4T_{2g})$                             | 21,850; ${}^4B_2({}^4T_{2g})$                          |
|   | 22,814; ${}^4A_2({}^4T_{1g})$                             |  |
| 26,315 (1.68)   | 26,902; ${}^4E({}^4T_{1g})$                               | 25,942; ${}^4A_2({}^4T_{1g})$                          |
|   |   | 26,381; ${}^4E({}^4T_{1g})$                            |
|   | 41,625; ${}^4E({}^4T_{1g})$                               | 41,375; ${}^4A_2({}^4T_{1g})$                          |
|   | 41,836; ${}^4A_2({}^4T_{1g})$                             | 42,715; ${}^4E({}^4T_{1g})$                            |

**Table VIII:** Spectral Data of  $\text{trans-Cr(en)}_2(\text{H}_2\text{O})\text{Br}_2^{2+}$ 

| Obsd<br>$\nu_{\text{max}}$ (log $\epsilon$ )<br>(Ref 15b) | Calcd $\nu_{\text{max}}$ ; assignment                     |  |
|---|---|--|
|   | $Dq = 2185 \text{ cm}^{-1}$ ; $Dt = -400 \text{ cm}^{-1}$ |  |
|   | $B = 500 \text{ cm}^{-1}$<br>$C/B = 7, \kappa = 2$        | $B = 600 \text{ cm}^{-1}$<br>$C/B = 5.5, \kappa = 1/3$ |
|   | 14,360; ${}^2A_1({}^2E_g)$                                | 14,469; ${}^2B_1({}^2E_g)$                             |
|   | 14,425; ${}^2B_1({}^2E_g)$                                | 14,473; ${}^2A_1({}^2E_g)$                             |
|   | 14,726; ${}^2E({}^2T_{1g})$                               | 14,609; ${}^2E({}^2T_{1g})$                            |
|   | 14,744; ${}^2A_2({}^2T_{1g})$                             | 14,954; ${}^2A_2({}^2T_{1g})$                          |
|   | 21,830; ${}^2B_2({}^2T_{2g})$                             | 22,068; ${}^2B_2({}^2T_{2g})$                          |
|   | 21,972; ${}^2E({}^2T_{2g})$                               | 22,378; ${}^2E({}^2T_{2g})$                            |
| 17,825 (1.37)   | 17,773; ${}^4E({}^4T_{2g})$                               | 18,201; ${}^4E({}^4T_{2g})$                            |
| 21,978 (1.40)   | 21,850; ${}^4B_2({}^4T_{2g})$                             | 21,850; ${}^4B_2({}^4T_{2g})$                          |
|   | 22,167; ${}^4A_2({}^4T_{1g})$                             |  |
| 26,041 (1.65)   | 26,879; ${}^4E({}^4T_{1g})$                               | 25,602; ${}^4A_2({}^4T_{1g})$                          |
|   |   | 26,121; ${}^4E({}^4T_{1g})$                            |
|   | 41,049; ${}^4E({}^4T_{1g})$                               | 40,682; ${}^4A_2({}^4T_{1g})$                          |
|   | 41,283; ${}^4A_2({}^4T_{1g})$                             | 42,211; ${}^4E({}^4T_{1g})$                            |

**Figure 4.** Observed absorption maxima in the spectra of trisethylenediammine and  $\text{trans-diacidobisethylenediamminechromium(III)}$  complex cations.

been observed for the second cubic band ( ${}^4T_{1g}$ ) in any of these systems except the dichloro, in which there seems to be a well-defined shoulder on the high-energy side of the second band. The two components of the first band were fitted in the way described for the acidopentaammines, and the derived  $Dt$  values of all the systems are reported in the respective tables of spectral data. Since in the case of the dichloro spectrum the second band is also split, the ratio of the  $Ds$  to  $Dt$  parameters can be exactly derived by fitting the two components. This has been found to be unity.

Once again in the case of the diaquo complex, two different values of  $\kappa$  have been used to interpret the spectral data, whereas in the other  $\text{trans}$  systems the  $Dt$  values are large enough so that for even a smaller value of 1 or 2 for  $\kappa$ , the  ${}^4A_2$  component of the second cubic band already is positioned in proximity to the  ${}^4B_2$  component of the first band. Thus, if it is supposed that the second band is not split to a considerable extent in these cases, a still smaller value of  $\kappa$  such as  $1/3$  or less is to be used. The third spin-allowed absorption of weak intensity at high energy has not been found in any of the complexes. The spin-forbidden doublet transitions also have not been observed.

It is to be noted that in the case of aquochloro and aquobromo systems (Tables VII and VIII), the  $Dt$  value is found to be the average of the  $Dt$  values of the diaquo and dichloro, and, diaquo and dibromo, respectively. In other words, the fields of the two axial ligands are averaged even if these two ligands are not identical. If this argument is extended, the  $\text{cis-disub-}$



stituted systems can be treated as though belonging to quadrate fields in the sense that they are derived from the *cis*-symmetrically trisubstituted parent compound. This situation is more fully explained elsewhere.<sup>17</sup>

**Miscellaneous Systems.** Finally, Tables IX, X, and XI have spectral data of three different complexes. The *trans*-difluorotetraaquo system of King and co-workers<sup>18</sup> shows no splitting of the first band, which is in agreement with the fact that the fluoro ligand stands very close to the aquo group in spectrochemical series, so that the  $Dt$  value for the system under consideration is very small. In fact, the  $Dt$  value of about  $-100\text{ cm}^{-1}$  predicts a splitting of  $1000\text{ cm}^{-1}$  which may not be resolved in the solution absorption spectrum. Interestingly, there is wide splitting of the second band which could be explained by a  $\kappa$  value of 5. It is worthwhile to note that cubic fluoro complexes are examples of where the  $B$  values are closer to the free-ion  $B$  values and once again fluoro substitution seems to require a larger value of  $\kappa$  compared to other systems. Another interesting feature of this spectrum is the finding of the third spin-allowed band at  $37,000\text{ cm}^{-1}$ , which is one of the few systems in which such a third band has been uncovered. This band has not been found to be split, which is in agreement with the calculated splitting of  $530\text{ cm}^{-1}$  (*cf.* Table IX) not being observable in the solution spectrum. This system also has a weak absorption at  $14,800\text{ cm}^{-1}$  which has been assigned to all the four quadrate doublets  ${}^2A_1$ ,  ${}^2B_1$ ,  ${}^2A_2$ , and  ${}^2E$  of  ${}^2E_g$  and  ${}^2T_{1g}$  cubic levels. The doublets are not resolved in the room temperature spectrum probably because they are placed close to the first spin-allowed transition at  $16,300\text{ cm}^{-1}$ .

The two other complexes that are included in Tables X and XI are of special interest. It may have been noted already that in all the systems that are described

**Table IX:** Spectral Data of *trans*-Cr(H<sub>2</sub>O)<sub>4</sub>F<sub>2</sub><sup>+</sup>

| Obsd<br>$\nu_{\max}$ (log $\epsilon$ )<br>(Ref 18) | Calcd $\nu_{\max}$ ; assignment<br>$Dq = 1740$ , $Dt = -100$ , $B = 750\text{ cm}^{-1}$<br>$C/B = 4$ , $\kappa = 5$   |
|--|---|
| 14,800   | $\left\{ \begin{array}{l} 14,403; {}^2A_1({}^2E_g) \\ 14,498; {}^2B_1({}^2E_g) \\ 15,039; {}^2E({}^2T_{1g}) \\ 15,147; {}^2A_2({}^2T_{1g}) \end{array} \right.$ |
| 16,300   | $\left\{ \begin{array}{l} 21,554; {}^2B_2({}^2T_{2g}) \\ 21,835; {}^2E({}^2T_{2g}) \end{array} \right.$   |
| 22,700   | $\left\{ \begin{array}{l} 16,399; {}^4E({}^4T_{2g}) \\ 17,400; {}^4B_2({}^4T_{2g}) \end{array} \right.$   |
| 25,500   | $\left\{ \begin{array}{l} 22,463; {}^4A_2({}^4T_{1g}) \\ 24,995; {}^4E({}^4T_{1g}) \end{array} \right.$   |
| 37,000   | $\left\{ \begin{array}{l} 37,456; {}^4E({}^4T_{1g}) \\ 37,987; {}^4A_2({}^4T_{1g}) \end{array} \right.$   |

**Table X:** Spectral Data of *trans*-Cr(NCS)<sub>4</sub>(NH<sub>3</sub>)<sub>2</sub><sup>-</sup>

| Obsd                                       |                             | Calcd $\nu_{\max}$ ; assignment<br>$Dq = 1765\text{ cm}^{-1}$ ,<br>$Dt = 200\text{ cm}^{-1}$ ,<br>$B = 600\text{ cm}^{-1}$ ,<br>$C/B = 5$ , $\kappa = 1$ |
|--|-----------------------------|--|
| $\nu_{\max}$ (log $\epsilon$ )<br>(Ref 19) | $\nu_{\max}$<br>(This work) |  |
| 13,400                                     |                             | 13,535; ${}^2B_1({}^2E_g)$   |
| 13,800                                     |                             | 13,553; ${}^2A_1({}^2E_g)$   |
| 14,250                                     | $\sim 13,800$               | 14,009; ${}^2E({}^2T_{1g})$  |
| 14,550                                     |                             | 14,026; ${}^2A_2({}^2T_{1g})$  |
|  |                             | 20,719; ${}^2B_2({}^2T_{2g})$  |
|  |                             | 20,724; ${}^2E({}^2T_{2g})$  |
| $\sim 17,600$ (1.78)?                      |                             | 17,650; ${}^4B_2({}^4T_{2g})$  |
| 19,230 (2.02)                              |                             | 19,294; ${}^4E({}^4T_{2g})$  |
| $\sim 25,000$ (1.98)                       |                             | $\left\{ \begin{array}{l} 24,910; {}^4E({}^4T_{1g}) \\ 25,723; {}^4A_2({}^4T_{1g}) \end{array} \right.$  |
|  |                             | 40,196; ${}^4E({}^4T_{1g})$  |
|  |                             | 40,627; ${}^4A_2({}^4T_{1g})$  |

**Table XI:** Spectral Data of Cr(H<sub>2</sub>O)<sub>5</sub>CN<sup>2+</sup>

| Obsd<br>$\nu_{\max}$ (log $\epsilon$ )<br>(Ref 17) | Calcd $\nu_{\max}$ ; assignment<br>$Dq = 1740\text{ cm}^{-1}$ , $Dt = 250\text{ cm}^{-1}$<br>$B = 600\text{ cm}^{-1}$ , $C/B = 5.5$ , $\kappa = 1$              |
|--|---|
| $\sim 14,700$                                      | $\left\{ \begin{array}{l} 14,446; {}^2B_1({}^2E_g) \\ 14,466; {}^2A_1({}^2E_g) \\ 14,899; {}^2E({}^2T_{1g}) \\ 14,925; {}^2A_2({}^2T_{1g}) \end{array} \right.$ |
|  | $\left\{ \begin{array}{l} 21,955; {}^2E({}^2T_{2g}) \\ 21,988; {}^2B_2({}^2T_{2g}) \end{array} \right.$   |
| $\sim 17,500$ ( $\sim 0.70$ )                      | 17,400; ${}^4B_2({}^4T_{2g})$   |
| 19,200 (1.42)                                      | 19,418; ${}^4E({}^4T_{2g})$   |
| 25,500 (1.32)                                      | $\left\{ \begin{array}{l} 24,940; {}^4E({}^4T_{1g}) \\ 25,920; {}^4A_2({}^4T_{1g}) \end{array} \right.$   |
|  | 40,242; ${}^4E({}^4T_{1g})$   |
|  | 40,780; ${}^4A_2({}^4T_{1g})$   |

above, the  $Dt$  values are negative. Examples where the  $Dt$  values are positive seem to be very few. The cyanopentaaquo complex cation which has been recently prepared<sup>17</sup> is one and the other is Reinecke's salt<sup>19</sup> which is a *trans*-diamminotetraisoithiocyanatochromium(III) complex. On the basis of the  $Dt$  values estimated for the above systems, the  $Dt$  values of these two complexes may be expected to be around  $200\text{ cm}^{-1}$ . As has been pointed out earlier, if the  $Dt$  is positive,

(17) (a) W. B. Schaap, R. Krishnamurty, D. K. Wakefield, and J. R. Perumareddi, Abstracts, IXth International Conference on Coordination Chemistry, Switzerland, Sept 1966; (b) R. Krishnamurty, W. B. Schaap, and J. R. Perumareddi, *Inorg. Chem.*, **6**, 1338 (1967).

(18) T. Y. Chia and E. L. King, *Discussions Faraday Soc.*, **29**, 109 (1960).

(19) The spectral data of this system can be found in (a) E. E. Wegner and A. W. Adamson, *J. Am. Chem. Soc.*, **88**, 394 (1966); (b) A. W. Adamson, *ibid.*, **80**, 3183 (1958).

the splittings of the first two quartets may not be the same as is expected for systems of same negative  $Dt$ . For this reason, no well-resolved splitting of the first band is observed in either system. Since it is the  ${}^4B_2$  component which is not resolved,  $Dt$  values could still be evaluated by fitting the corresponding  ${}^4E$  components and the energies of the  ${}^4T_{2g}$  transitions in the parent octahedral complexes, namely the hexaaquo<sup>20</sup> and hexaisothiocyanato<sup>21</sup> complex ions. For the second band, only the lower ratio of  $\kappa$  resulting in nonobservable splitting is reasonable in these systems because it is never possible to bring down the  ${}^4E$  component of the second quartet close to that of the first quartet for any reasonable value of  $B$ . Thus the data of these two systems are best interpreted by assigning  $\kappa$  a value of unity.

The third spin-allowed band has not been uncovered in either of these systems, probably because it is buried under charge-transfer absorption. Both complexes show the weak intensity transitions in the low energy region. Only one such transition is observed at 14,700  $\text{cm}^{-1}$  in the spectrum of the cyanopentaaquo complex cation which has been ascribed once again to the four quadrate doublets expected at this energy. However, in the case of the Reinecke salt, although only one weak intensity absorption has been found in the reflectance spectrum, four well-defined weak intensity absorptions, in the form of humps, have been observed in its room temperature solution absorption spectrum.<sup>19a</sup> It is rather difficult to evaluate exactly the absorption maxima of these humps from the published spectrum. Our estimate as given in Table X shows that all four are almost equally separated, although the calculated values show that they should occur as two pairs separated by about 450  $\text{cm}^{-1}$ , each pair in turn splitting into 20  $\text{cm}^{-1}$ . If our estimate of equal separation of these four doublets from the published spectrum is correct, in order to obtain better agreement of the calculated levels with the observed, either a completely different set of all parameters must be used or spin-orbit interaction should be included in the calculations.

#### IV. Conclusions

We have made an attempt to apply our calculations on  $d^3$  configuration in quadrate fields for the interpretation of the spectra of substituted octahedral chromium(III) compounds. Although the two components of the first cubic quartet band can be definitely assigned, it is clear that, at the present time, the two components of the second cubic quartet band cannot be uniquely assigned because of the low resolution and large band widths of the spectra. Many of the spectral data can be interpreted by a consistent set of parameters<sup>22</sup> of

$B$ ,  $C/B$ ,  $Dq$ ,  $Dt$ , and two different values<sup>23</sup> of  $\kappa$ . In the case of the spectra of *trans*-difluorotetraaquo-chromium(III), *trans*-dichlorobisethylenediammine-chromium(III) and of systems of positive  $Dt$  even one value of  $\kappa$  is sufficient. The exact choice of the  $\kappa$  value can only be decided by making further spectral measurements on single crystals by means of polarized light and at low temperatures, hoping to narrow the widths of the absorption bands and to attain greater resolution, which in turn would permit the choice of the assignments of the absorption bands proposed in this paper. Further studies on solution absorption spectra at room temperature of the same systems discussed in this work are not likely to provide any better understanding than is already presented here.

It should be added that similar energy diagrams applicable to tetragonally distorted tetrahedral chromium(III) and other compounds of  $d^3$  configuration and octahedral and tetrahedral cobalt(II) and other compounds of  $d^7$  configuration can be constructed with an appropriate set of parametric values from the energy matrices given in part I.<sup>2</sup>

Finally, we have attempted to show that within the limits of ligand field or crystalline field theory, a complete theory with full configuration interaction can be

(20) R. Tsuchida and M. Kobayashi, *Bull. Chem. Soc. Japan*, **13**, 471 (1938). See also ref 17b.

(21) J. Bjerrum, A. W. Adamson, and O. Bostrup, *Acta Chem. Scand.*, **10**, 329 (1956); see also ref 19a.

(22) The  $B$ ,  $C$  values used for all the systems discussed in this report are very reasonable in the sense that they are below the Cr(III) free-ion values of 920 and 3680  $\text{cm}^{-1}$ , respectively [A. D. Liehr, *J. Phys. Chem.*, **67**, 1314 (1963)]. In addition, the  $B$  value of a quadrate complex has been chosen to be similar to that of the either of the ligands, original or substituting, of the corresponding octahedral complex. As the assignments of some of the bands in the spectra of these quadrate systems are at present not definitive, the  $B$  values quoted in the assignment tables are only tentative. Exact  $B$  values can be derived when the assignments are given on a definitive basis by further experiments, such as polarized spectral studies. It is premature to attempt suggesting theories to explain the variational trends of  $B$  values of the quadrate complexes at this time. It may be pointed out here that in the cubic series, although the  $B$  value varies from 60% (hexacyanide) to 82.5% (hexafluoride) of the free-ion value, corresponding  $C$  value varies only from 78% (hexacyanide) to 82% (hexafluoride) of the free-ion value. In other words, the  $C$  value remains almost constant in a series of cubic complexes. This trend seems to be true in the case of quadrate complexes also.

(23) Strictly speaking, still alternative assignments are possible in terms of ligand field theory, particularly for the components of the second cubic quartet band until further experimental resolution of the spectra is achieved and polarization properties of the bands are measured. The alternative assignments arise from the fact that the ratio of the axial parameters can be negative. If this be so, for positive values of  $Dt$  and negative values of  $\kappa$ , the present sequence of the two components of the second quartet will be reversed placing  ${}^4A_2$  below in energy to  ${}^4E$  in which two values of  $\kappa$  smaller or larger result in nonobservable splitting or near coincidence of the  ${}^4A_2$  energy with that of the  ${}^4E$  component of the  ${}^4T_{2g}$  transition. For negative values of  $Dt$  and  $\kappa$ , the  ${}^4E$  will be placed lower in energy to  ${}^4A_2$  so that only one alternative assignment is possible because of configuration interaction (*cf.* the case of positive  $Dt$  and  $\kappa$ ).

developed and applied with ease wherever suitable systems exist, and thus there is no need for applications with any approximations or restricted calculations.

## V. Addendum

We wish to make one final remark on the applicability of crystal field model for quadrate chromium(III) complexes insofar as the values of  $Dt$  are concerned. Since the  $Dt$  values have been fairly definitely established in this work by fitting the experimental spectral data, it is interesting to compare these values with those that can be calculated on the basis of crystal field model as has been pointed out earlier. The results of such calculations<sup>24</sup> using the formulas of footnote 4 are given in Table XII where the observed  $Dt$  values as extracted from the spectra<sup>25</sup> are also included for com-

parison. The predicted values of  $Dt$  can be seen to be remarkably close to the observed values for all the systems studied in this report, thus suggesting that  $Dt$  values indeed can be calculated by crystal fields assumptions at least in the case of quadrate chromium(III) complexes. This then should permit one to estimate from the knowledge of  $Dq$  values of the ligands in a quadrate Cr(III) complex, a rough value of  $Dt$  and, hence, the extent of splitting of the first cubic quartet band.

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**Table XII:** Comparison of Observed  $Dt$  Values with Those Calculated by Crystal Field Model

| Complex <sup>a</sup>                                       | Obsd $Dt$ , $\text{cm}^{-1}$<br>(by spectral fitting) <sup>b</sup> | Calcd $Dt$ , $\text{cm}^{-1}$<br>(by crystal field model;<br>see footnote 4) <sup>c</sup> |
|--|--|---|
| $\text{Cr}(\text{NH}_3)_6\text{Cl}^{2+}$                   | -225   | -239  |
| $\text{Cr}(\text{NH}_3)_6\text{Br}^{2+}$                   | -275   | -275 <sup>c</sup>   |
| $\text{Cr}(\text{NH}_3)_6\text{I}^{2+}$                    | -325   | -325 <sup>c</sup>   |
| $\text{Cr}(\text{en})_2(\text{H}_2\text{O})_2^{3+}$        | -225   | -254  |
| $\text{Cr}(\text{en})_2\text{Cl}_2^+$                      | -475   | -494  |
| $\text{Cr}(\text{en})_2\text{Br}_2^+$                      | -575   | -567  |
| $\text{Cr}(\text{en})_2(\text{H}_2\text{O})\text{Cl}^{2+}$ | -350   | -374  |
| $\text{Cr}(\text{en})_2(\text{H}_2\text{O})\text{Br}^{2+}$ | -400   | -401  |
| $\text{Cr}(\text{H}_2\text{O})_6\text{F}_2^+$              | -100   | -74   |
| $\text{Cr}(\text{NCS})_4(\text{NH}_3)_2^-$                 | 200  | 223   |
| $\text{Cr}(\text{H}_2\text{O})_6\text{CN}^{2+}$            | 250  | 260   |

<sup>a</sup> All the disubstituted complexes are *trans*-geometrical isomers.

<sup>b</sup> See footnote 25. <sup>c</sup> See footnote 24.

(24) The  $Dq$  values for six-coordinate bromo and iodo complexes are not known, and hence these  $Dt$  values are fitted with the observed values. By such a fitting, the  $10Dq$  of a bromo complex is 11,925  $\text{cm}^{-1}$  and that of an iodo complex is 10,175  $\text{cm}^{-1}$ . These values in turn are used to calculate the  $Dt$  values of the corresponding *trans* systems. The  $Dq$  values of the other complexes used are as follows:  $\text{NH}_3 = 2155 \text{ cm}^{-1}$ ,  $\text{en} = 2185 \text{ cm}^{-1}$ ,  $\text{H}_2\text{O} = 1740 \text{ cm}^{-1}$ ,  $\text{NCS}^- = 1765 \text{ cm}^{-1}$ ,  $\text{Cl}^- = 1320 \text{ cm}^{-1}$ ,  $\text{F}^- = 1610 \text{ cm}^{-1}$ ,  $\text{CN}^- = 2650 \text{ cm}^{-1}$ .

(25) These values are subject to minor changes to allow for an exact fitting and configuration interaction effects when the other parameters are also exactly evaluated by definitive assignments.