

ELECTRONIC SPECTRA OF QUADRATE CHROMIUM(III) COMPLEXES

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(Received July 5th, 1968)

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ABBREVIATIONS

en = ethylenediamine
phen = *o*-phenanthroline
dipy = dipyrityl
ox = oxalate
das = *o*-phenylenebisdimethylarsine
 ζ = spin orbit coupling coefficient

etren = tetraethylenepentamine
trien = triethylenetetramine
pn = propylenediamine
ibn = isobutylenediamine
DMSO = dimethylsulfoxide

A. INTRODUCTION

Our understanding of the electronic structures of transition metal compounds has rapidly gained momentum in the past decade and a half with the advent of ligand field theory. Various physicochemical observations such as the stereochemistry, magnetism, and spectroscopic behavior of a variety of systems have been satisfactorily interpreted by recent bonding theories¹⁻⁵. This has been particularly true in the case of compounds of cubic symmetry. Even in systems of non-cubic symmetry, some successful interpretations of electronic spectra have been reported⁶⁻³⁵. In order to make further progress on these non-cubic compounds not only do the theories have to be systematically extended but more precise and exact experimental spectroscopic measurements have to be made. These experimental studies have to be carried out with the aims of locating the exact band positions, of achieving better resolution of the band components, and of uncovering bands

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of low intensity. Until recently most of the spectroscopic data available on the known non-cubic transition metal compounds have been obtained only in connection with synthetic, kinetic, and photolytic studies and not with the sole aim of making intensive spectroscopic investigations. As a result, much needs to be done in the area of visible and ultraviolet electronic spectroscopy of transition metal compounds.

In this report we will limit our survey and discussion to complexes of chromium(III) belonging mainly to quadrate symmetry. The aim of this review is to summarize briefly the theory of cubic and non-cubic ligand fields with special emphasis on the effect of quadrate fields on d^3 configuration, to survey all the available spectroscopic data, the band positions and the intensities of all the known mono and disubstituted octahedral complexes of chromium(III), and to attempt to systematize and interpret the data as much as possible by the theory developed. The result of such a survey should bring into focus appropriate systems for further studies and provide guidelines to extending both experimental and theoretical investigations on non-cubic compounds of transition metals in general.

B. THEORY

The theory of cubic compounds is well-known. Figure 1 shows the Tanabe-Sugano energy plot for the d^3 configuration in octahedral fields. This energy diagram is plotted somewhat differently in the sense³⁶ that the ordinate is the absolute energy with the ground state being zero, varied as a function of Dq from 0 to 4000 cm^{-1} . The B and C values are chosen to be suitable to the hexaquo-chromium(III) complex cation *i.e.*, $B = 700\text{ cm}^{-1}$ and $C/B = 4$. The optical spectrum of the hexaquo ion fits very well at a Dq value of 1740 cm^{-1} . With a slight variation of B and C/B such energy plots can be used to explain the spectra of a variety of octahedral chromium(III) complexes. Thus the spectra of hexacyano ($Dq = 2650\text{ cm}^{-1}$, $B = 500\text{ to }550\text{ cm}^{-1}$), trisethylenediamine ($Dq = 2185\text{ cm}^{-1}$, $B = 625\text{ cm}^{-1}$), hexaammine ($Dq = 2155\text{ cm}^{-1}$, $B = 650\text{ cm}^{-1}$), hexaisothiocyanato ($Dq = 1765\text{ cm}^{-1}$, $B = 575\text{ cm}^{-1}$), hexafluoro ($Dq \cong 1600\text{ cm}^{-1}$, $B = 750\text{ cm}^{-1}$) and of many other systems can be interpreted. In both chromium(III) and nickel(II) octahedral complexes the lowest energy spin-allowed band directly gives $10 Dq$ (or Δ), and the evaluation of B can be made by the use of any of the following formulae³⁷.

$$B = (2\nu_1^2 + \nu_2^2 - 3\nu_1\nu_2)/(15\nu_2 - 27\nu_1) \quad (\text{fitting the second band})$$

$$B = (2\nu_1^2 + \nu_3^2 - 3\nu_1\nu_3)/(15\nu_3 - 27\nu_1) \quad (\text{fitting the third band})$$

$$B = (\nu_2 + \nu_3 - 3\nu_1)/15 \quad (\text{fitting the sum of the second and the third band maxima})$$

$$B = 1/75\{3v_1 + [25(v_3 - v_2)^2 - 16v_1^2]^{\frac{1}{2}}\} \quad (\text{fitting the difference of the third and the second band maxima})$$

In the above equations v_1 , v_2 , and v_3 are the first, second, and the third spin-allowed transitions in the order of increasing energy, respectively.

Thus in cubic fields only one ligand field parameter, Dq , is needed to describe the spectra. On the other hand, in quadrate fields, two more ligand field parameters, Dt and Ds , are introduced because of the added axial fields. The axial ligand field parameter, Dt , is very similar to Dq in that both are matrix elements of the fourth order harmonic potential, whereas Ds is the matrix element of the second order harmonic potential^{21a}. In the limit of crystal field formalism it can be shown that $Dt = -2/7 (Dq_x - Dq_y)$ for an octahedral complex of the formula MX_5Y and twice this for *trans*- MX_4Y_2 . Although more general symmetry arguments require ten electron correlation parameters in cubic fields and twenty three in quadrate fields these can be averaged to three both in quadrate and cubic fields^{21a} if the differences among these parameters are assumed small. They are the usual Racah parameters A, B, and C (or the related Slater-Condon-Shortley parameters F_0 , F_2 , and F_4). Since the parameter A occurs in all energy levels and since our interest is in energy differences, we are concerned with only B and C, which depend upon the positions of the spin-allowed and spin-forbidden bands, respectively. Spin-orbit perturbation is not included in the present report.

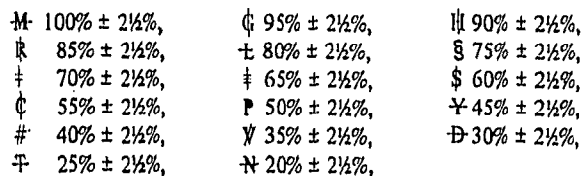
In the limit of zero spin-orbit interaction the quadrate theory can be developed on the basis of either of the representations that axial fields being perturbative additions to the cubic fields or that they are large enough being included along with the cubic fields to start with^{21a}. The latter scheme would be more appropriate to describe systems of pentacoordinate square pyramidal, tetraordinate square planar, and highly tetragonally distorted octahedral geometry. On the other hand, mono- and *trans*-disubstituted hexacoordinate octahedral systems which are under present study can be conveniently described by the former scheme, *i.e.* these systems would be treated as slightly deviated from cubic symmetry. The symmetry adapted wave functions in this representation are simply the cubic wave functions but properly decomposed in going to quadrate symmetry. The decomposition of the representations of cubic symmetry relative to quadrate is as follows: $A_{1g}^C \rightarrow A_{1g}^Q$, $A_{2g}^C \rightarrow B_1^Q$, $E_{ga}^C \rightarrow A_1^Q$, $E_{gb}^C \rightarrow B_1^Q$, $T_{1ga}^C \rightarrow A_2^Q$, $T_{1gb,c}^C \rightarrow E_{a,b}^Q$, $T_{2ga}^C \rightarrow B_2^Q$, and $T_{2gb,c}^C \rightarrow E_{a,b}^Q$. These symmetry adapted strong-field d^3 quadrate wave functions are listed in Appendix A. Using the same decomposition it is, of course, possible to carry out the perturbation of axial fields over the octahedral weak-field representation. Since it is the strong-field functions that more aptly describe the real systems we chose to carry out our calculations in strong-field formalism. The structure of the energy matrices is obvious from the decomposition of representations described above. The matrix elements in cubic fields, *i.e.*, cubic ligand field and electron correlation terms, would stand as they are. Now in addition to the added axial

field parameters in the diagonal elements, the A_{1g}^C and $E_{g,1}^C$ representations both being transformed to A_1^Q representation in quadrate would be connected by axial ligand field off-diagonal elements. Similarly the A_{2g}^C and $E_{g,2}^C$, the $T_{1g,b,c}^C$ and $T_{2g,b,c}^C$ representations will have non zero off-diagonal elements in axial ligand field parameters, Dt and Ds . The energy matrices of d^3 configuration in quadrate fields are listed in Appendix B*.

The splitting of the octahedral energy levels in quadrate fields is shown in Figure 2 which has been constructed with the parametric values $B = 650 \text{ cm}^{-1}$, $C/B = 4$, $Dt = +300 \text{ cm}^{-1}$ and $\kappa \equiv Ds/Dt = 2$. Such a plot is applicable to systems where an octahedral complex is either monosubstituted or *trans*-disubstituted by a ligand whose Dq value is larger than the Dq value of the parent complex. Note that this diagram is also appropriate to describe the energy levels of an elongated tetrahedral complex of d^7 configuration. In this diagram Dq is varied from 0 to 4000 cm^{-1} . At zero Dq value, we have linear symmetry with $Dt = +300 \text{ cm}^{-1}$ and $\kappa = 2$. The energy levels on this line correspond to those of cylindrical labels. At the right hand side of the diagram are given the strong-field labels for the quadrate representation. Each of the orbitally doubly and triply degenerate octahedral levels split into two quadrate levels as expected. Considering only the diagonal elements the doublets of (t_{2g}^3) configuration do not split but they do so when configuration interaction is included. Our primary interest in this energy plot is the splittings of the three excited spin quartet levels. In the first approximation it can be seen from the diagonal elements of the energy matrices that these are given by $+35/4 Dt$ (${}^4E - {}^4B_2$), $+6Ds - 5/4 Dt$ (${}^4A_2 - {}^4E$), and $+3Ds - 5Dt$ (${}^4E - {}^4A_2$). For the parameters chosen here the splitting of the third quartet cannot be observed in this diagram. If configuration interaction is included the 4E levels repel each other so that the splittings of the first two quartets would be actually lower than given by these formulae. For negative values of Dt the quartet levels will be reversed so that configuration interaction actually enhances the splitting of these quartets. The effects of configuration interaction can be seen very nicely in the energy diagrams displayed in Figures 3 and 4. The 4B_2 component of the first excited quartet is placed at an energy of $10 Dq$ from the 4B_1 ground state even when configuration interaction is included. The value of $10 Dq$ is fixed in these energy plots and Dt is varied so that such plots will be applicable for a series of mono and *trans*-disubstituted derivatives of given parent octahedral complex^{21b}. The Dq value chosen in Figures 3 and 4 is 1740 cm^{-1} which is that of an hexaquo complex cation. As pointed out above these diagrams reveal that the splitting of the first excited quartet depends not only upon the magnitude of Dt but also upon its sign. In fact, in Fig. 3 for positive Dt the splitting of the first quartet band becomes smaller as the Dt value is increased as a consequence of the non-crossing of the 4E levels. Another interesting observation that can be made in

* Appendices A and B which have been deposited with the ADI as part of ref. 21a are reproduced here by permission from *J. Phys. Chem.*

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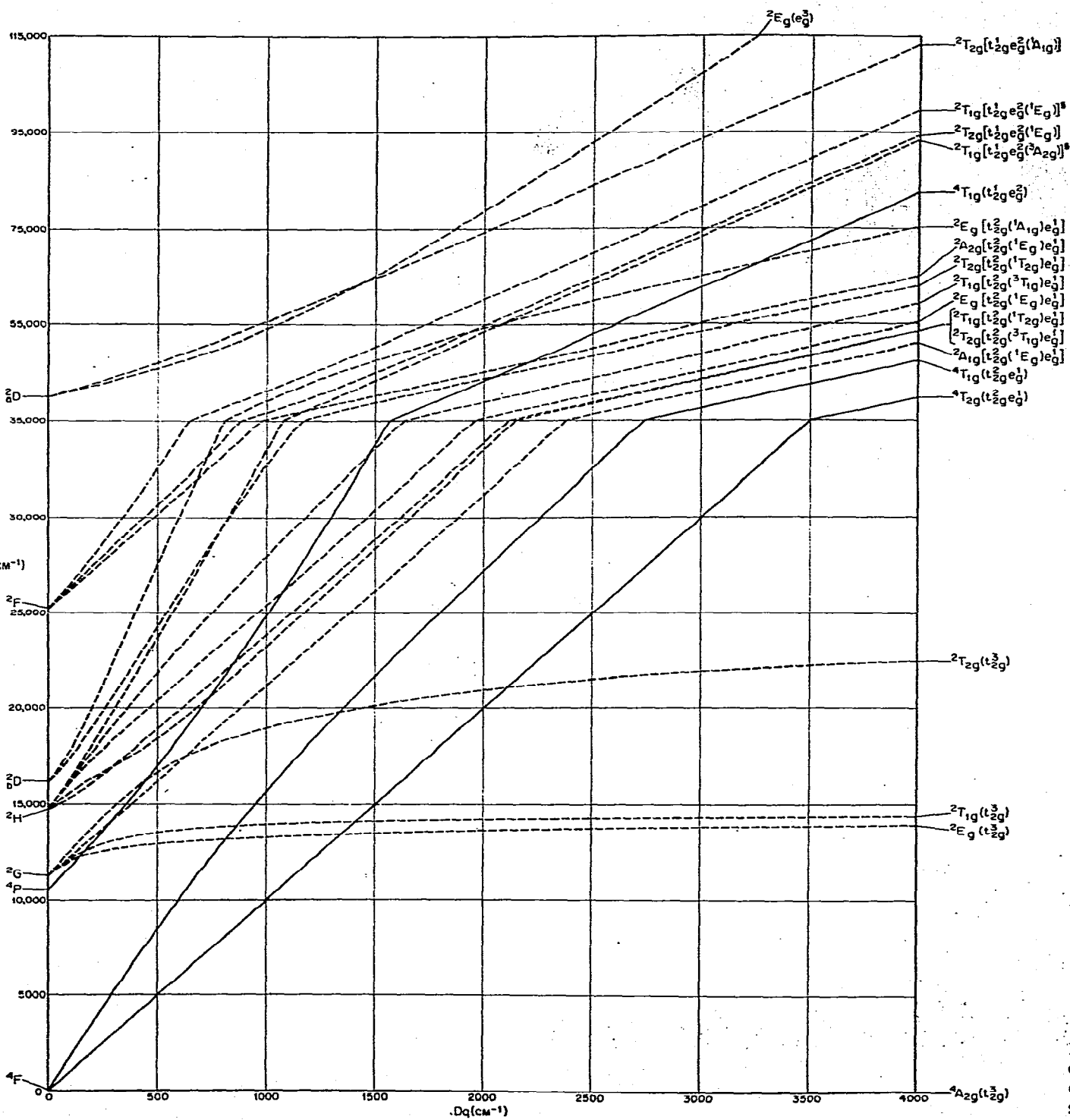


Fig. 1. Energy level diagram for d^3 configuration in octahedral fields: $\zeta = 0$, $B = 700 \text{ cm}^{-1}$, $C/B = 4$. (See the caption of Fig. 2 for the meaning of the superscript symbols of the energy labels.)

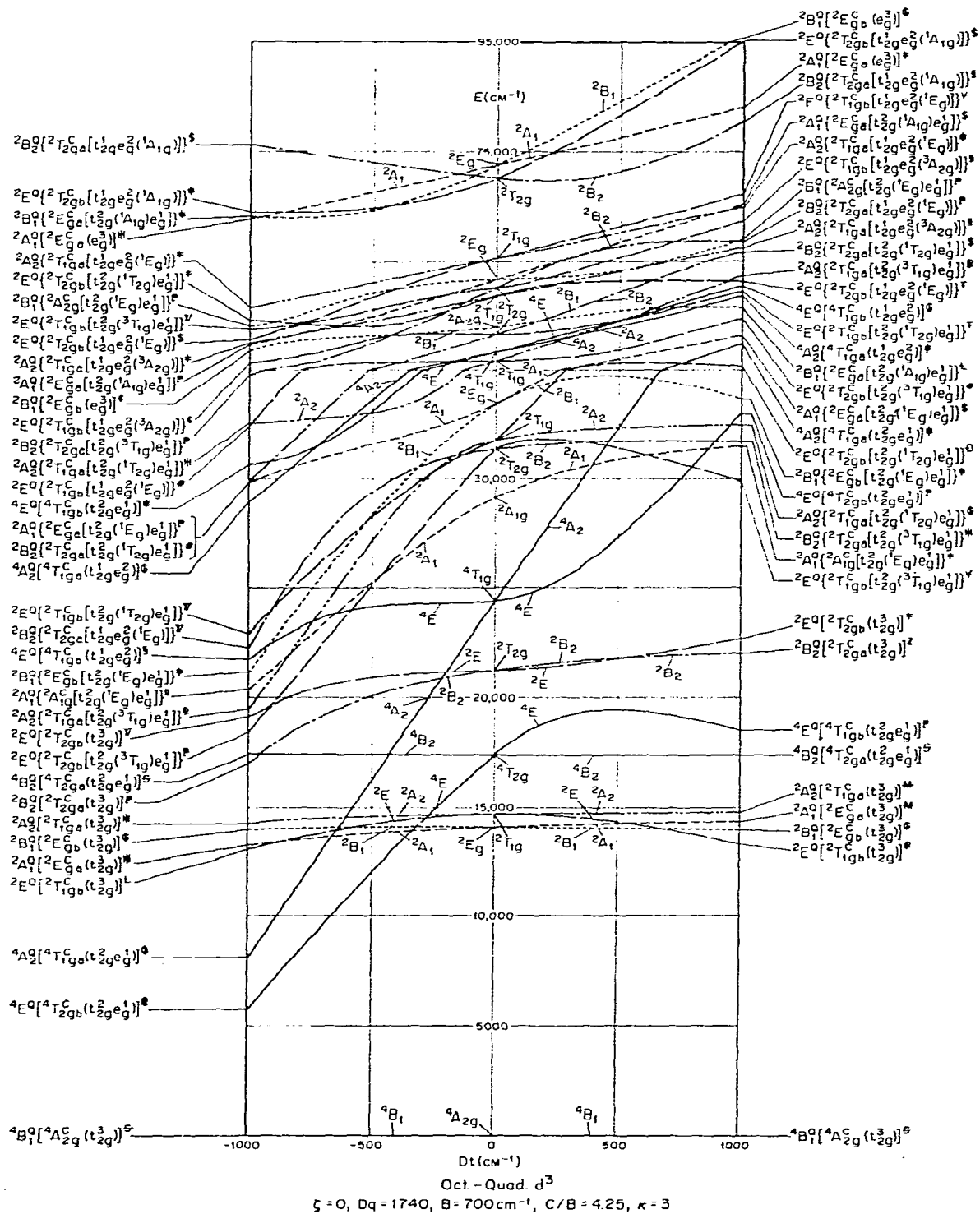


Fig. 3. Energy level diagram for d^3 configuration in quadrate fields (varying Dt) $\zeta = 0$, $Dq = 1740 \text{ cm}^{-1}$, $B = 700 \text{ cm}^{-1}$, $C/B = 4.25$, $\kappa = 3$ (see the caption of Fig. 2 for the meaning of the superscript symbols on the energy labels).

this same plot is that for negative values of Dt around 400 cm^{-1} the 4A_2 and 4B_2 levels are so close to each other so that in systems which can be described by this set of parameters, only three transitions may be observed instead of the more general four component structure of the two cubic quartet transitions.

There is no definitive answer at present as to whether κ is a constant or whether it varies from system to system. Further extensive investigations, in particular polarized spectroscopic measurements by which definitive assignments can be given for the observed transitions are required. Until then we use alternate values of κ resulting in alternate assignments for the second cubic quartet components.

Figures 5 and 6 are the quadrate energy diagrams with $Dq = 2650\text{ cm}^{-1}$ applicable to substituted cyanocomplexes of chromium(III). Since cyanide is at the extreme strong-field end of the spectrochemical series most of the substituted cyano complexes would have negative Dt values, so the energy levels are not derived for positive values of Dt in these diagrams. Energy plots appropriate to substituted ammine and ethylenediamine systems have been constructed earlier by the author^{21b}.

The theory described above rigorously applies to monosubstituted and *trans* disubstituted derivatives of parent O_h complexes belonging to C_{4v} and D_{4h} symmetries, respectively. Although the *cis*-disubstituted complexes strictly belong to C_{2v} or lower symmetry, they can be treated as approximately belonging to D_{4h} symmetry if each of the *trans* ligand pairs can be averaged in considering the ligand fields^{3,22}. The *cis*-disubstituted compound MX_4Y_2 would then become pseudo *trans*- MZ_4X_2 where Z is a ligand intermediate in ligand field strength to X and Y . The Dt for such a *cis*- MX_4Y_2 is then $-4/7 (Dq_Z - Dq_X)$ and since $Dq_Z = 1/2 (Dq_X + Dq_Y)$, $Dt = -2/7 (Dq_Y - Dq_X)$ which is the same as the value for a monosubstituted C_{4v} complex but of opposite sign. This is in harmony with the fact that the *cis* compounds MX_4Y_2 or MX_2Y_4 can be considered as monosubstituted derivatives of 1, 2, 3 or *cis* MX_3Y_3 . If $Dq_X > Dq_Y$ then $Dq_Z \equiv 1/2 (Dq_X + Dq_Y) > Dq_Y$ so that Dt for *cis*- MX_4Y_2 is positive in contrast to the negative Dt for the corresponding *trans* compound. Similarly if $Dq_X < Dq_Y$ then $Dq_Z \equiv 1/2 (Dq_X + Dq_Y) < Dq_Y$ so that Dt for *cis*- MX_4Y_2 is negative in contrast to the positive Dt for the corresponding *trans* compound.

Neglecting configuration interaction these Dt relations can be substituted in the energy equations for the first quadrate quartet components. Schematic spectral profiles in this region for mono, *cis* and corresponding *trans* disubstituted compounds are displayed in Figure 7 which also includes the above derivations pictorially. Two points are of significance in the spectroscopic relationships between *cis* and *trans* for the cases MX_4Y_2 where $Dq_X > Dq_Y$ and $Dq_X < Dq_Y$. Comparing the two cases for *trans* only, we would expect a larger splitting of the first cubic band for the $Dq_X > Dq_Y$ because of configuration interaction. Similar wider splitting, though not to the same extent, can be expected in the *cis* case for the reverse

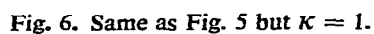


Fig. 6. Same as Fig. 5 but $\kappa = 1$.

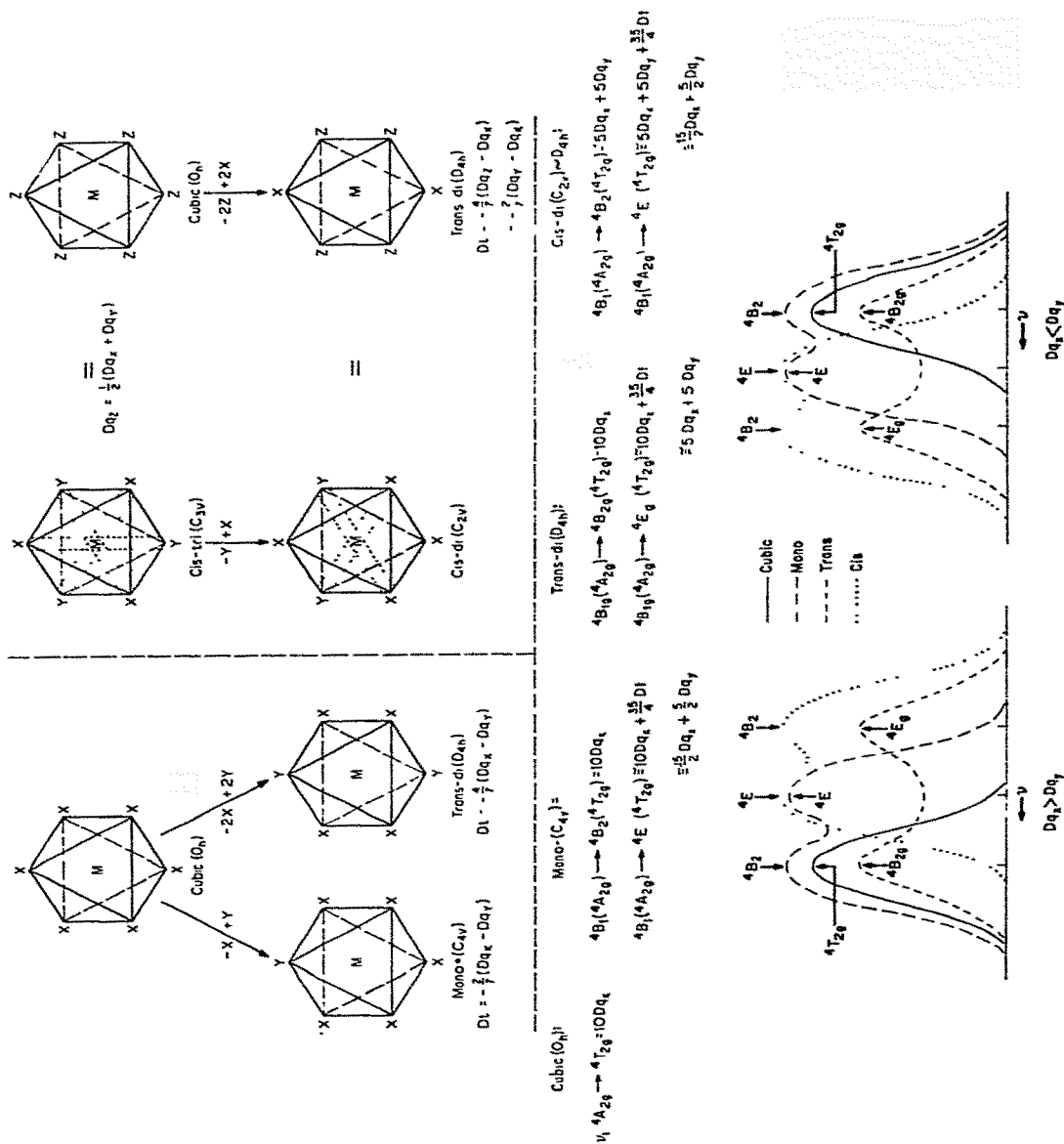


Fig. 7. Schematic spectroscopic relationships between MX_6Y_2 , MX_6Y ; and cis and trans isomers of MX_4Y_2 . (The upper part of this diagram is reproduced from ref. 22 by permission from *Inorg. Chem.*)

systems, *i.e.* $Dq_x < Dq_y$. Another interesting observation is that the 4B_2 level of a *cis* compound is predicted to be positioned roughly at the same energy as the 4E_g level of the corresponding *trans* compound and the 4E level of a *cis* compound to be roughly placed in the middle of 4E_g and ${}^4B_{2g}$ levels of the corresponding *trans* complex, which is also the approximate frequency maximum of the 4E component of the monosubstituted complex. Thus the 4B_2 levels of *cis* and *mono* derivatives are mirror images to each other with the 4E level of both forming the mirror plane. These predictions along with the fact that greater intensities are expected in the *cis* compounds because of lower symmetry should aid as spectroscopic criteria in distinguishing the *cis* and *trans* disubstituted derivatives of octahedral complexes²².

C. APPLICATIONS

While it is not our intention here to calculate and compare the transition energies with the observed bands, we intend to give quadrate assignments where definitive, remark on the derived values of the parameters, in particular Dt and finally predict the band positions of some hitherto uncharacterized substituted complexes.

Table 1 collects the data of all the known monosubstituted complexes of chromium(III). Among the acidopentaammines only the halopentaammines show splitting of the ${}^4T_{2g}$ band. Resolution has not been achieved in the others which are expected to show a splitting of about 1000 cm^{-1} . Among the pentaquo systems definite splitting has been observed in the iodo and chloro systems whilst an asymmetric appearance of the ${}^4T_{2g}$ band suggests the presence of a second component in the bromo and other complexes. Precise measurements should certainly resolve this band; a definite component should appear at about $17,400\text{ cm}^{-1}$ corresponding to the 4B_2 transition. There are only two complexes of positive Dt in this list. Resolution has not been achieved in the aquopentaammine itself so that the pentaquoammine with the corresponding positive Dt does not show any splitting of the ${}^4T_{2g}$ band. The cyanopentaquo system displays a second component upon gaussian analysis. The splitting of the second cubic quartet band ${}^4T_{1g}$ into two components has only been observed in two or three systems and the third cubic spin-allowed band which has been uncovered in only two systems, the fluoropentaquo and the aquopentafluoro, does not split at all.

Most of the *trans* disubstituted systems show splitting of the ${}^4T_{2g}$ band as can be seen from Table 2. This is because Dt in these systems is twice that of the corresponding monosubstituted derivatives resulting in a larger splitting of the ${}^4T_{2g}$ level. In contrast to the C_{4v} systems splitting of the second band has been observed in many D_{4h} compounds. Once again the third cubic quartet was uncovered in only two systems, the *trans*-difluoro and the dichlorotetraquo, and in both cases does not show any splitting. For the reasons already noted only a few

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TABLE 1

SPECTROSCOPIC DATA OF MONOSUBSTITUTED COMPLEXES (C_{4v})

(Absorption maxima in cm^{-1} followed by extinction coefficients in $1 \text{ mole}^{-1} \text{ cm}^{-1}$ in parentheses are given in this and following Tables. The maxima in parentheses are from diffuse reflectance spectroscopic studies.)

Complex	${}^2A_1, {}^2B_1({}^2E_g); {}^2A_2, {}^2E({}^2T_{1g})$	${}^4E({}^4T_{1g})$	${}^4B_2({}^4T_{2g})$	${}^4A_2({}^4T_{1g}); {}^4E({}^4T_{1g})$	${}^4A_2({}^4T_{1g}); {}^4E({}^4T_{1g})$	References
$[\text{Cr}(\text{NH}_3)_5\text{I}]^{2+}$	18,500 (53.7)		21,250 (38.9)	$\sim 26,000$ (50.0)		38
$[\text{Cr}(\text{NH}_3)_5\text{Br}]^{2+}$	19,050 (38.0)		21,770 (27.5)	26,490 (45.7)		38
	(14,800)		(21,300)	(26,000)		21b
$[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$	14,858 (0.7)		22,100 (27.5)	26,600 (43.6)		38
	(14,800)		(21,400)	(26,400)		21b
$[\text{Cr}(\text{NH}_3)_5(\text{OH})]^{2+}$	(15,500)			25,500 (36.7)	29,800 (13.3)	39, 40, 41
$[\text{Cr}(\text{NH}_3)_5\text{F}]^{2+}$				27,030 (22.0)		42, 43, 44
$[\text{Cr}(\text{NH}_3)_5(\text{N}_3)]^{2+}$				26,180 (93.4)		42, 45
$[\text{Cr}(\text{NH}_3)_5(\text{NCS})]^{2+}$	14,600 (0.15) $\sim 15,385$			27,548 (51.8)		46, 47, 48,
						49, 42, 45
$[\text{Cr}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$	15,267 (0.25)			27,777 (29.0)		39, 40, 50,
						41, 42, 48,
						51, 44
						48, 42, 45
$[\text{Cr}(\text{NH}_3)_5(\text{ONO})]^{2+}$						52
$\alpha\text{-}[\text{Cr}(\text{teiren})\text{Cl}]^{2+}$				28,089 (79.4)		53
$\alpha\text{-}[\text{Cr}(\text{teiren})(\text{NCS})]^{2+}$				26,666 (82.0)		54, 55, 56
$[\text{Cr}(\text{H}_2\text{O})_5\text{I}]^{2+}$				25,773 (63.2)		55, 56
$[\text{Cr}(\text{H}_2\text{O})_5\text{Br}]^{2+}$	$\sim 14,814$ (~ 12.0)			21,097 (32.6)		55, 57, 58,
$[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$	$\sim 14,836$ (7.5)			$\sim 21,277$ (~ 15.0)	23,148(23.7)	56, 54
				23,364 (21.9)		55, 54, 59
$[\text{Cr}(\text{H}_2\text{O})_5\text{F}]^{2+}$	14,992 (~ 5.1)			23,980 (12.4)		60
	(14,930)			(22,940)		61
$[\text{Cr}(\text{H}_2\text{O})_5(\text{SO}_4)]^{+}$	$\sim 14,903$ (5.3)			23,980 (18.8)		62, 63
$[\text{Cr}(\text{H}_2\text{O})_5(\text{NO}_3)]^{2+}$				24,271 (18.9)		46
$[\text{Cr}(\text{H}_2\text{O})_5(\text{NCS})]^{2+}$	15,598			24,390 (32.8)		50, 51, 64
$[\text{Cr}(\text{H}_2\text{O})_5(\text{NH}_3)]^{3+}$	15,152 (2.0)			25,000 (17.3)		22
$[\text{Cr}(\text{H}_2\text{O})_5(\text{CN})]^{2+}$	$\sim 14,700$			25,500 (20.5)		22
$[\text{Cr}(\text{CN})_5(\text{H}_2\text{O})]^{2-}$				29,000 (45.0)	32,100 (50.0)	60
$[\text{CrF}_5(\text{H}_2\text{O})]^{2-}$	(15,130)			(23,310)	(35,490)	

* The extinction coefficients reported in reference 42 for this complex are incorrect.

TABLE 2

SPECTROSCOPIC DATA OF *TRANS*-DISUBSTITUTED COMPLEXES (D_{4h})

Complex	${}^2A_{1g}$, ${}^2B_{1g}$ (2E_g); ${}^2A_{2g}$, 2E_g (${}^2T_{1g}$); ${}^4A_{1g}$, 4E_g (${}^4T_{1g}$); ${}^4A_{2g}$ (${}^4T_{2g}$)	4E_g (${}^4T_{2g}$)	${}^4B_{3g}$ (${}^4T_{2g}$)	${}^4A_{2g}$ (${}^4T_{1g}$); 4E_g (${}^4T_{1g}$)	${}^4A_{2g}$ (${}^4T_{1g}$); 4E_g (${}^4T_{1g}$)	References
$[\text{Cr}(\text{en})_2(\text{O})_2]^+$		16,350	21,000			27
$[\text{Cr}(\text{en})_2(\text{Br})_2]^+$		16,474 (34.7)	$\sim 21,739$ (24.0)		24,630 (30.9)	65
$[\text{Cr}(\text{en})_2(\text{Cl})_2]^+$		17,300 (24.5)	22,075 (22.9)		25,252 (33.9) 27,250 (22.9)	66, 67, 68, 69a, 69b
$[\text{Cr}(\text{en})_2(\text{OH})_2]^+$	14,598 (1.4)		19,900 (31.8)		25,250 (28.9) 29,000 (11.0)?	70, 71
$[\text{Cr}(\text{en})_2(\text{F})_2]^+$		19,047 (19.0)	21,459 (24.0)		25,000 (16.1) 28,571 (18.0)	72
$[\text{Cr}(\text{en})_2(\text{H}_2\text{O})_2]^{3+}$		19,700 (22.4)	22,600 (29.5)		27,700 (38.9)	73, 74, 65, 67, 70
$[\text{Cr}(\text{en})_2(\text{ONO})_2]^+$	$\sim 15,000$		20,964		30,487	75
$[\text{Cr}(\text{en})_2(\text{NCS})_2]^+$			20,700 (93.0)		27,470 (67.0)	27, 76
$[\text{Cr}(\text{en})_2(\text{H}_2\text{O})\text{Br}]^{2+}$		17,825 (23.4)	21,978 (25.1)		26,041 (44.6)	65
$[\text{Cr}(\text{en})_2(\text{H}_2\text{O})\text{Cl}]^{2+}$		18,315 (20.4)	22,321 (24.5)		26,315 (47.9)	67
$[\text{Cr}(\text{en})_2(\text{H}_2\text{O})(\text{OH})]^{2+}$	14,706 (2.1)		20,200 (38.0)		25,125 (49.0) 29,000 (24.0)?	71
$[\text{Cr}(\text{en})_2(\text{H}_2\text{O})\text{F}]^{2+}$		19,267 (24.2)	22,026 (25.6)		26,954 (31.2)	72
$[\text{Cr}(\text{en})_2(\text{H}_2\text{O})(\text{NCS})]^{2+}$		$\sim 19,000$ (72.0)			$\sim 25,500$ (45.0)	77
$[\text{Cr}(\text{en})_2(\text{OH})\text{Cl}]^+$		18,796 (35.0)			25,125 (39.0)	78
$[\text{Cr}(\text{H}_2\text{O})_4(\text{Cl})_2]^+$	15,000	15,750			22,200	57, 58
$[\text{Cr}(\text{H}_2\text{O})_4(\text{F})_2]^+$	14,800	16,300			22,700	59
$[\text{Cr}(\text{H}_2\text{O})_4(\text{NCS})_2]^+$			17,540 (31.6)		23,810 (31.6)	82
$[\text{Cr}(\text{H}_2\text{O})_4(\text{NH}_3)_2]^{3+}$		$\sim 19,230$ (~ 21.0)			$\sim 25,500$ (~ 24.5)	51
$[\text{Cr}(\text{NCS})_4(\text{NH}_3)_2]^-$	13,400; 13,800; 14,250; 14,550 (13,800)	19,230 (105.0) $\sim 17,600$ (60.2)			$\sim 25,640$ (77.6)	83, 84
$[\text{Cr}(\text{ox})_2(\text{H}_2\text{O})_2]^-$			18,520 (20.5)		24,635 (24.2)	21b
$[\text{Cr}(\text{dipy})_2(\text{Cl})_2]^+$		18,020 (46.0)	22,470		24,100	79, 80, 81
$[\text{Cr}(\text{dipy})_2(\text{OH})_2]^+$		$\sim 19,000$ (43.0)			25,510	27
$[\text{Cr}(\text{dipy})_2(\text{H}_2\text{O})_2]^{3+}$		20,410 (42.8)				85
$[\text{Cr}(\text{phen})_2(\text{OH})_2]^+$		$\sim 19,000$ (40.0)				85
$[\text{Cr}(\text{phen})_2(\text{H}_2\text{O})_2]^{3+}$		20,200 (40.7)				85
$[\text{Cr}(\text{das})_2(\text{O})_2]^+$	(13,300)	15,400 (100.0)				86
$[\text{Cr}(\text{das})_2(\text{Br})_2]^+$	(13,300)	16,300 (140.0) $\sim 20,000$ (180.0)			22,600 (1150) $\sim 24,500$ (680)	86
$[\text{Cr}(\text{das})_2(\text{Cl})_2]^+$	(13,300)	17,000 (80.0) $\sim 20,800$ (270.0)			23,600 (1300) $\sim 25,500$ (900)	86

TABLE 3

SPECTROSCOPIC DATA OF *cis*-DISUBSTITUTED COMPLEXES (C_{2v})

Complex	2A_1 , 2B_1 (2E_g); 2A_2 , 2E (${}^2T_{1g}$)	4E (${}^4T_{2g}$)	4B_1 (${}^4T_{2g}$)	4A_2 (${}^4T_{1g}$)	4E (${}^4T_{1g}$)	4A_2 (${}^4T_{1g}$); 4E (${}^4T_{1g}$)	References
$[\text{Cr(en)}_2(\text{Br})_2]^+$		18,382 (89.4)			24,096 (83.0)		65
$[\text{Cr(en)}_2(\text{Cl})_2]^+$		18,939 (70.6)			24,875 (68.5)		68, 66, 69a
		19,400					69b
$[\text{Cr(en)}_2(\text{OH})_2]^+$			18,100				71, 70
$[\text{Cr(en)}_2(\text{F})_2]^+$	14,450 (1.4)		18,939 (65.0)				87, 88
			$\sim 19,380$ (75.0)				89, 27
$[\text{Cr(en)}_2(\text{N}_3)_2]^+$			19,417 (224.0)				71, 70, 90,
$[\text{Cr(en)}_2(\text{H}_2\text{O})_2]^{3+}$	15,037 (0.5); 15,503 (0.35); 15,748 (0.4)	20,608 (67.6)			27,322 (43.6)		74
$[\text{Cr(en)}_2(\text{ox})]^+$		20,202 (97.0)			27,027 (87.0)		91
$[\text{Cr(en)}_2(\text{ONO})_2]^+$		20,790 (90.0)			28,011 (152.0)		75
$[\text{Cr(en)}_2(\text{NCS})_2]^+$	$\sim 15,000$ (split)	20,408 (148.0)			27,027 (91.0)		27, 92
$[\text{Cr(en)}_2(\text{H}_2\text{O})\text{Br}]^{2+}$		19,267 (72.2)			25,839 (60.5)		65
$[\text{Cr(en)}_2(\text{H}_2\text{O})\text{Cl}]^{2+}$		19,608 (71.4)			25,974 (55.7)		68
$[\text{Cr(en)}_2(\text{H}_2\text{O})(\text{OH})]^{2+}$			19,417 (72.0)		28,530 (30.0) 25,510 (47.0)		71
$[\text{Cr(en)}_2(\text{OH})\text{Cl}]^+$	14,684 (1.4)	18,484 (74.0)			26,455 (51.0)		78
$[\text{Cr(en)}_2(\text{F})\text{Br}]^+$		19,531 (61.2)			26,246 (37.6)		72
$[\text{Cr(en)}_2(\text{F})\text{Cl}]^+$		19,305 (62.4)			25,839 (42.8)		72
$[\text{Cr(en)}_2(\text{F})(\text{NCS})]^+$		20,000 (85.1)			26,667 (52.0)		72
$[\text{Cr(Pn)}_2(\text{F})_2]^+$		19,157 (55.1)			26,316 (31.5)		88
$[\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})]^{3+}$		$\sim 20,400$ (~ 36.0)	18,870 (25)?		27,200 (~ 24.5)		51
$[\text{Cr}(\text{NH}_3)_4(\text{ox})]^+$		20,000 (57.5)			26,670 (70.8)		42, 93
$[\text{Cr}(\text{NH}_3)_4(\text{ONO})_2]^+$		20,240 (79.4)			27,680 (126.0)		42
$[\text{Cr}(\text{NH}_3)_4(\text{NCS})_2]^+$		20,160 (83.2)			26,880 (55.0)		42

TABLE 3 (continued)

Complex	${}^2A_1, {}^2B_1({}^2E_g); {}^2A_2, {}^2E({}^2T_{1g})$	${}^4E({}^2T_{2g})$	${}^4B_2({}^4T_{2g})$	${}^4A_2({}^4T_{1g})$	${}^4E({}^4T_{1g})$	${}^4A_2({}^4T_{1g}); {}^4E({}^4T_{1g})$	References
$[\text{Cr}(\text{trien})(\text{Cl})_2]^+$	$\sim 14,388 (5.5)$	19,011 (95.5)	17,544 (77.6)	25,380 (87.1)			94, 95, 96
$[\text{Cr}(\text{trien})(\text{N}_3)_2]^+$		19,305 (185.0)		24,875 (106.0)			95
$[\text{Cr}(\text{trien})(\text{ox})]^+$		20,000 (139.0)		26,881 (96.5)			95
$[\text{Cr}(\text{trien})(\text{NCS})_2]^+$		20,491 (15.70)		26,881 (86.7)			95
$[\text{Cr}(\text{H}_2\text{O})_4(\text{Cl})_2]^+$	(14,493)	15,750 (24.0) (15,385)		22,220 (28.2)			57
$[\text{Cr}(\text{H}_2\text{O})_4(\text{OX})]^+$		18,018 (34.2)		23,980 (39.6)			97
$[\text{Cr}(\text{H}_2\text{O})_4(\text{NCS})_2]^+$		18,180 (35.5)		23,810 (39.8)			82
$[\text{Cr}(\text{H}_2\text{O})_4(\text{en})]^{3+}$		19,342 (32.0)		25,839 (22.0)			98, 90, 99
$[\text{Cr}(\text{H}_2\text{O})_4(\text{pn})]^{3+}$		19,417 (36.0)		26,109 (24.4)			100
$[\text{Cr}(\text{H}_2\text{O})_4(\text{fiba})_2]^{3+}$		19,305 (29.0)		25,641 (11.9)			100
$[\text{Cr}(\text{H}_2\text{O})_4(\text{CN})_2]^+$		18,518 (18.0)	21,433 (45.0)	26,455 (20.0)			22
$[\text{Cr}(\text{ox})_2(\text{H}_2\text{O})_2]^-$	14,534 (3.3)	17,730 (52.0)		24,096 (69.0)			79, 80, 81
$[\text{Cr}(\text{ox})_2(\text{NH}_3)_2]^-$		18,690 (77.6)		26,670 (70.8)			42
$[\text{Cr}(\text{ox})_2(\text{en})]^-$	14,493 (2.1)	18,868 (88.0)		25,316 (94.4)			91, 101
$[\text{Cr}(\text{ox})_2(\text{dipy})]^-$		18,865 (100.0)		$\sim 25,320 (\sim 205.0)$			102 107
$[\text{Cr}(\text{ox})_2(\text{phen})]^-$		18,520 (~ 80.0)		$\sim 25,000 (\sim 140.0)$			102 107
$[\text{Cr}(\text{DMSO})_4(\text{Cl})_2]^{2+}$		14,814 (50.1)	14,184 (45.7)	20,618 (38.0)			103, 104
$[\text{Cr}(\text{F})_4(\text{en})]^-$	15,050 (14,970)	17,450 (34.0)		24,390 (18.5)		37,310 (37,580)	105
$[\text{Cr}(\text{CN})_4(\text{H}_2\text{O})_2]^-$		(17,270)		(23,870)			60
$[\text{Cr}(\text{phen})_2(\text{H}_2\text{O})_2]^{3+}$		23,420 (110.0)	19,600 (60.0)	30,120 (50.0)			22
$[\text{Cr}(\text{phen})_2(\text{ox})]^+$		23,810 (126)	19,920 (62)	28,490 (1810) ?	28,810 (126)		85
$[\text{Cr}(\text{dipy})_2(\text{ox})]^+$		22,380 (90)	19,610 (60)	25,510 (364)	23,980 (220)		108

* $Dq = 1587 \text{ cm}^{-1}$.

TABLE 4

Dt VALUES IN cm^{-1} FOR COMPLEXES OF THE FORMULA $[\text{Cr}(\text{X})_5\text{Y}]^a$ (The *Dt* values for *trans*- $[\text{Cr}(\text{X})_4(\text{Y})_2]$ are twice and for *cis*- $[\text{Cr}(\text{X})_4(\text{Y})_2]$ are the same but of opposite sign.)

$\text{Y} \backslash \text{X}$	CN^-	NH_3	NCS^-	H_2O	N_3^-	F^-	OH^-	Cl^-	Br^-	I^-
CN^-	—	+141	+253	+260	+291	+297	+339	+380	+416	+466
NH_3	-141	—	+111	+119	+150	+156	+197	+239	+275	+325
NCS^-	-253	-111	—	+7	+39	+44	+86	+127	+163	+213
H_2O	-260	-119	-7	—	+31	+37	+79	+120	+156	+206
N_3^-	-291	-150	-39	-31	—	+6	+47	+89	+125	+175
F^-	-297	-156	-44	-37	-6	—	+41	+83	+119	+169
OH^-	-339	-197	-86	-79	-47	-41	—	+41	+78	+128
Cl^-	-380	-239	-127	-120	-89	-83	-41	—	+36	+86
Br^-	-416	-275	-163	-156	-125	-119	-78	-36	—	+50
I^-	-466	-325	-213	-206	-175	-169	-128	-86	-50	—

^a *Dq* values: $\text{CN}^- = 2650$, $\text{NH}_3 = 2155$, $\text{NCS}^- = 1765$, $\text{H}_2\text{O} = 1740$, $\text{N}_3^- = 1630$, $\text{F}^- = 1610$, $\text{OH}^- = 1465$, $\text{Cl}^- = 1320$, $\text{Br}^- = 1193$, $\text{I}^- = 1018 \text{ cm}^{-1}$.^a Thus the observed ${}^4T_{1g}$ components can best be fitted by the following κ values (with slightly varying *B* values): $[\text{Cr}(\text{NH}_3)_5(\text{OH})]^{2+}$ $\kappa = 7/2$; $[\text{Cr}(\text{H}_2\text{O})_5\text{Br}]^{2+}$, $[\text{Cr}(\text{CN})_5(\text{H}_2\text{O})]^{2-}$ $\kappa = 2$.*trans*- $[\text{Cr}(\text{en})_2(\text{OH})_2]^{2+}$, $[\text{Cr}(\text{en})_2\text{F}_2]^{+}$, $[\text{Cr}(\text{en})_2(\text{H}_2\text{O})(\text{OH})]^{2+}$ $\kappa = 2$; $[\text{Cr}(\text{en})_2\text{Cl}_2]^{+}$ $\kappa = 1$; $[\text{Cr}(\text{H}_2\text{O})_4\text{F}_2]^{+}$ $\kappa = 5$; $[\text{Cr}(\text{dipy})_2\text{Cl}_2]^{+}$, $[\text{Cr}(\text{das})_2\text{Cl}_2]^{+}$, $[\text{Cr}(\text{das})_2\text{Br}_2]^{+}$ $\kappa = 3/4$.*cis*- $[\text{Cr}(\text{en})_2(\text{H}_2\text{O})(\text{OH})]^{2+}$ $\kappa = 7/2$, $[\text{Cr}(\text{dipy})_2(\text{ox})]^{+}$ $\kappa = 2$. Note that the corresponding negative κ values would also predict the observed splittings but reverse quadrate assignments. Definitive assignments may probably be arrived at by further polarized spectroscopic studies.

It should be added that the negative κ value not only reverses the quadrate assignments (for the modulus $\kappa > 5/3$) but gives rise to the prediction of a much enhanced splitting (for all values of κ) of the third spin-allowed cubic band, ${}^4T_{1g}$, compared with the corresponding positive κ for both positive and negative *Dt*. This enhanced splitting which increases with the increasing value of *Dt* is due to the energy difference of the two quadrate components, ($3Ds-5Dt$). The configuration interaction effects are expected to be similar on both the quadrate components since both 4A_2 and 4E , respectively, being the second and third energy levels (both being highest) of the same symmetry designations in the order of increasing energy will be raised in energy although may not be to the same extent. Thus the magnitude of splitting of the third band in conjunction with a knowledge of the *Dt* value can be used indirectly to derive the sign of the κ parameter. Unfortunately, the third band which is usually buried under intense charge transfer absorption itself has been uncovered only in very few systems and in no case has been found to be split.

Based on the possibility that the *Dt*, *Ds* parameters can be regarded as symmetry parameters in ligand field and molecular orbital theories, it has been suggested earlier (ref. 21b) that κ may also assume negative values. However, the corresponding assignments have not been given either in ref. 21b or here only to restrict the alternative choices of assignments until further studies, particularly polarized spectral measurements, are carried out. Using an empirical molecular orbital approach^{23,24} with certain assumptions on the σ and π bonding characteristics of ligands, references 27, 30, and 106 discuss and give the reverse assignments for the quadrate components of the second quartet (and the third) in the spectra of some of the *trans* complexes listed in Table 2. It is interesting to note that the recent polarized spectral measurements of Yamada (ref. 69b) on *trans*- $[\text{Cr}(\text{en})_2\text{Cl}_2]^{+}$, the only such study to date on any chromium(III) complex, confirms our earlier and present assignment, but not the reverse assignments based on negative κ .

of the *cis* disubstituted systems listed in Table 3, show splitting of the ${}^4T_{2g}$ band. The second band has not been found to split in any of these except the hydroxy-aquo(bisethylenediamine) and the oxalato(bisdipyridyl) systems; the third band which has been revealed only in the tetrafluoro ethylenediamine system does not show any splitting.

The Dt values calculated from the simple crystal field assumptions seem to agree with the observations and are noted for some of the systems in Table 4. Using appropriate Dt values from this Table, the predicted positions of the quadrate components in the spectra of the mono- and disubstituted ammine, aquo and cyano complexes of chromium(III) are calculated and listed in Tables 5, 6 and 7. In these Tables the quadrate components of the ${}^4T_{2g}$ and ${}^4T_{1g}$ cubic bands are given for the mono and *trans*-disubstituted derivatives whereas only the ${}^4T_{2g}$ components are listed for the *cis*-disubstituted compounds. Although the predicted maxima of the ${}^4T_{2g}$ components in these systems are expected to be accurate the ${}^4T_{1g}$ components may be found to be somewhat different from the values given here, since these are obtained with constant B and κ values. The B and κ values may be different for different derivatives of a parent octahedral complex^a. The transition energies for C_{4v} and D_{4h} systems are derived exactly from the energy matrices for the same set of parameters as in the appropriate energy diagrams of $\kappa = 1$. [It may be pointed out here that the author had directly read the transition energies from the energy diagrams and found that they are within about $\pm 50 \text{ cm}^{-1}$ of the actual computed values and the discrepancy is usually very close to $\pm 10 \text{ cm}^{-1}$ and in no case exceeded 100 cm^{-1}]. Those of the *cis* disubstituted are obtained by the use of the formulae of Figure 7 and do not include configuration interaction. Although the 4B_2 values are exact, including configuration interaction, the 4E values will probably be reduced by about 100 to 500 cm^{-1} for these *cis* systems. The spectroscopic predictions of these Tables agree well with those bands observed in systems which are well characterized, if it is assumed that whenever the expected splitting is of the order of 2000 cm^{-1} or less, only one band is observed at either of the predicted positions or some mean value of them (see also the footnote on p. 92). It appears that the resolution of the quadrate components depends not only on the extent of splitting but also on the widths of the bands and their intensities. Another factor is their position relative to the electronically allowed transitions. It is rather difficult to achieve resolution if they appear as humps on the intense charge transfer bands.

D. CONCLUSIONS

Definitive quadrate assignments have been given only for those systems where resolutions of the cubic quartets has been observed. Such resolution in most of these systems has only been found for the components of the ${}^4T_{2g}$ band. Alternate

TABLE 5

PREDICTED SPECTRA OF SUBSTITUTED AMMINE COMPLEXES ($B = 600 \text{ cm}^{-1}$, $\kappa = 1$)^a

X	[Cr(NH ₃) ₅ X]			<i>trans</i> -[Cr(NH ₃) ₄ X ₂]			<i>cis</i> -[Cr(NH ₃) ₄ X ₂]		
	⁴ E(⁴ T _{2g})	⁴ B ₂ (⁴ T _{2g})	⁴ A ₂ (⁴ T _{1g})	⁴ E(⁴ T _{1g})	⁴ E _g (⁴ T _{2g})	⁴ B _{2g} (⁴ T _{2g})	⁴ A _{2g} (⁴ T _{1g})	⁴ E _g (⁴ T _{1g})	⁴ B ₂ (⁴ T _{2g})
CN ⁻	22,734	21,550	29,277	28,672	23,802	21,550	30,568	29,471	22,788
NCS ⁻	20,553	21,550	26,965	27,504	19,511	21,550	25,945	27,065	20,575
H ₂ O	20,479	21,550	26,892	27,471	19,357	21,550	25,798	27,004	20,513
N ₃ ⁻	20,191	21,550	26,607	27,346	18,757	21,550	25,228	26,775	20,238
F ⁻	20,135	21,550	26,552	27,322	18,640	21,550	25,118	26,731	20,188
OH ⁻	19,749	21,550	26,175	27,161	17,831	21,550	24,363	26,441	19,825
Cl ⁻	19,348	21,550	25,789	27,001	16,989	21,550	23,590	26,153	19,463
Br ⁻	19,000	21,550	25,458	26,866	16,258	21,550	22,926	25,912	19,145
I ⁻	18,513	21,550	24,998	26,685	15,232	21,550	22,003	25,583	18,208
NH ₃	21,550		27,966		21,550		27,966		21,550

^a Spectra of the *trans*- and *cis*-[Cr(en)₂X₂] will be expected to be similar to the corresponding *trans* and *cis*-[Cr(NH₃)₄X₂] since the 10 *Dq* of the ethylenediamine complex (21,850 cm⁻¹) is very close to that of the ammine complex (21,550 cm⁻¹).

TABLE 6

PREDICTED SPECTRA OF SUBSTITUTED AQUO COMPLEXES ($B = 700 \text{ cm}^{-1}$, $\kappa = 1$)^a

X	[Cr(H ₂ O) ₅ X]			<i>trans</i> -[Cr(H ₂ O) ₄ X ₂]			<i>cis</i> -[Cr(H ₂ O) ₄ X ₂]		
	⁴ E(⁴ T _{2g})	⁴ B ₂ (⁴ T _{2g})	⁴ A ₂ (⁴ T _{1g})	⁴ E(⁴ T _{1g})	⁴ E _g (⁴ T _{2g})	⁴ B _{2g} (⁴ T _{2g})	⁴ A _{2g} (⁴ T _{1g})	⁴ E _g (⁴ T _{1g})	⁴ B ₂ (⁴ T _{2g})
CN ⁻	19,517	17,400	26,829	25,808	21,257	17,400	29,255	27,569	19,675
NH ₃	18,411	17,400	25,507	25,003	19,351	17,400	26,623	25,676	18,438
NCS ⁻	17,461	17,400	24,456	24,425	17,522	17,400	24,522	24,459	17,464
N ₃ ⁻	17,127	17,400	24,098	24,239	16,850	17,400	23,806	24,090	17,125
F ⁻	17,074	17,400	24,042	24,210	16,742	17,400	23,693	24,033	17,075
OH ⁻	16,697	17,400	23,646	24,010	15,971	17,400	22,901	23,646	16,713
Cl ⁻	16,323	17,400	23,260	23,819	15,199	17,400	22,126	23,283	16,350
Br ⁻	15,990	17,400	22,920	23,655	14,506	17,400	21,445	22,972	16,033
I ⁻	15,522	17,400	22,448	23,432	13,526	17,400	20,495	22,547	15,095
H ₂ O	17,400		24,345		17,400		24,345		17,400

^a Spectra of the corresponding isothiocyanato complexes will be expected to be similar since the *Dq* of the isothiocyanato complex is very close to that of the aquo complex (cf. Table 4).

TABLE 7

PREDICTED SPECTRA OF SUBSTITUTED CYANO COMPLEXES ($B = 550 \text{ cm}^{-1}$, $\kappa = 1$)

X	[Cr(CN) ₅ X]		<i>trans</i> -[Cr(CN) ₄ X ₂]				<i>cis</i> -[Cr(CN) ₄ X ₂]	
	${}^4E(^4T_{2g})$	${}^4B_1(^4T_{2g})$	${}^4A_2(^4T_{1g})$	${}^4E(^4T_{1g})$	${}^4E_1(^4T_{2g})$	${}^4B_2(^4T_{2g})$	${}^4E(^4T_{2g})$	${}^4B_2(^4T_{2g})$
NH ₃	25,222	26,500	31,324	32,029	23,874	26,500	25,263	24,025
NCS ⁻	24,156	26,500	30,306	31,619	21,636	26,500	24,288	22,075
H ₂ O	24,088	26,500	30,242	31,595	21,494	26,500	24,425	21,950
N ₃ ⁻	23,786	26,500	29,960	31,488	20,859	26,500	23,950	21,400
F ⁻	23,728	26,500	29,906	31,468	20,735	26,500	23,900	21,300
OH ⁻	23,314	26,500	29,523	31,327	19,866	26,500	23,538	20,575
Cl ⁻	22,907	26,500	29,150	31,194	19,011	26,500	23,175	19,850
Br ⁻	22,547	26,500	28,823	31,079	18,256	26,500	22,858	19,215
I ⁻	22,043	26,500	28,368	30,922	17,202	26,500	21,920	18,340
CN ⁻	26,500		32,560		26,500		32,560	26,500

assignments based on alternate choices of B and κ values are possible for the observed transitions in the higher energy region because of lack of resolution of the $^4T_{1g}$ cubic quartets. In most of the systems surveyed, spin-forbidden bands have not been uncovered let alone the observation of their splitting. Thus more and precise experimental data are needed in the area of the spectra of quadrate chromium(III) complexes. Of particular interest would be polarized spectra of single crystals at low temperatures in the hope of achieving better resolution and definitive assignments. The detection of low intensity spin-forbidden bands will aid in evaluating more definitive values for the electron correlation parameters B and C and thus in understanding the covalency effects in these compounds. The energy diagrams presented in this report and earlier^{21b} would be valuable in the interpretation of the spectra of a variety of substituted ammine, aquo, and cyano compounds. Similar energy diagrams can be constructed for appropriate sets of parameters from the energy matrices of Appendix B. Finally, when more precise and abundant data become available on the band positions and intensities spin-orbit perturbation can be included in these calculations.

ACKNOWLEDGMENTS

The author wishes 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 Mr. E. L. Helgerman, also of the Mellon Institute Research Drafting Department, for their expert aid in the preparation of the figures.

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APPENDIX A

SYMMETRY ADAPTED STRONG FIELD WAVE FUNCTIONS: QUADRATE FIELDS

(Q = quadrate, C = cubic)

Spin quartets:

$${}^4B_1^Q[{}^4A_{2g}^C(t_{2g}^3)] : | (xy) (zx) (yz) |$$

$${}^4B_2^Q[{}^4T_{2g}^C(t_{2g}^2e_g)] : | (zx) (yz) (x^2-y^2) |$$

 ${}^4A_2^Q$:

$$[{}^4T_{1g}^C(t_{2g}^2e_g)] : | (zx) (yz) (z^2) |$$

$$[{}^4T_{1g}^C(t_{2g}e_g^2)] : | (xy) (z^2) (x^2-y^2) |$$

 ${}^4E_g^Q$:

$$[{}^4T_{2g}^C(t_{2g}^2e_g)] : [-\frac{1}{2} | (yz) (xy) (x^2-y^2) | + \frac{\sqrt{3}}{2} | (yz) (xy) (z^2) |]$$

$$[{}^4T_{1g}^C(t_{2g}^2e_g)] : [-\frac{1}{2} | (yz) (xy) (z^2) | - \frac{\sqrt{3}}{2} | (yz) (xy) (x^2-y^2) |]$$

$$[{}^4T_{1g}^C(t_{2g}e_g^2)] : | (zx) (z^2) (x^2-y^2) |$$

 ${}^4E_g^Q$:

$$[{}^4T_{2g}^C(t_{2g}^2e_g)] : [-\frac{1}{2} | (xy) (zx) (x^2-y^2) | - \frac{\sqrt{3}}{2} | (xy) (zx) (z^2) |]$$

$$[{}^4T_{1g}^C(t_{2g}^2e_g)] : [-\frac{1}{2} | (xy) (zx) (z^2) | + \frac{\sqrt{3}}{2} | (xy) (zx) (x^2-y^2) |]$$

$$[{}^4T_{1g}^C(t_{2g}e_g^2)] : | (yz) (z^2) (x^2-y^2) |$$

Spin Doublets: (Bar indicates negative spin)

 ${}^2A_1^Q$:

$${}^2A_{1g}^C[t_{2g}^2({}^1E_g)e_g] : \sqrt{\frac{1}{2}} \{ \sqrt{\frac{1}{2}} [-2 | (xy) (\overline{xy}) (z^2) | + | (yz) (\overline{yz}) (z^2) | + | (zx) (\overline{zx}) (z^2) |] + \sqrt{\frac{1}{2}} [| (zx) (\overline{zx}) (x^2-y^2) | - | (yz) (\overline{yz}) (x^2-y^2) |] \}$$

$${}^2E_{g}^C(t_{2g}^3) : \sqrt{\frac{1}{2}} [| (xy) (zx) (\overline{yz}) | - | (xy) (\overline{zx}) (yz) |]$$

$${}^2E_{g}^C[t_{2g}^2({}^1A_1)e_g] : \sqrt{\frac{1}{2}} [| (xy) (\overline{xy}) (z^2) | + | (zx) (\overline{zx}) (z^2) | + | (yz) (\overline{yz}) (z^2) |]$$

$${}^2E_{g}^C[t_{2g}^2({}^1E_g)e_g] : \sqrt{\frac{1}{2}} \{ \sqrt{\frac{1}{2}} [-2 | (xy) (\overline{xy}) (z^2) | + | (zx) (\overline{zx}) (z^2) | + | (yz) (\overline{yz}) (z^2) |] - \sqrt{\frac{1}{2}} [| (zx) (\overline{zx}) (x^2-y^2) | - | (yz) (\overline{yz}) (x^2-y^2) |] \}$$

$${}^2E_{g}^C(e_g^3) : | (z^2) (x^2-y^2) (\overline{x^2-y^2}) |$$

 ${}^2A_2^Q$:

$${}^2T_{1g}^C(t_{2g}^3) : \sqrt{\frac{1}{2}} [| (zx) (\overline{zx}) (xy) | - | (yz) (\overline{yz}) (xy) |]$$

$${}^2T_{1g}^C[t_{2g}^2({}^3T_{1g})e_g] : \sqrt{\frac{1}{2}} [-2 | (zx) (yz) (\overline{z^2}) | + | (zx) (\overline{yz}) (z^2) | + | (zx) (yz) (z^2) |]$$

$${}^2T_{1g}^C[t_{2g}^2({}^1T_{2g})e_g] : \sqrt{\frac{1}{2}} [| (zx) (\overline{yz}) (x^2-y^2) | - | (zx) (yz) (x^2-y^2) |]$$

$${}^2T_{1g}^C[t_{2g}e_g^2({}^3A_2)] : \sqrt{\frac{1}{2}} [-2 | (xy) (z^2) (\overline{x^2-y^2}) | + | (xy) (z^2) (\overline{x^2-y^2}) | + | (xy) (\overline{z^2}) (x^2-y^2) |]$$

$${}^2T_{1g}^C[t_{2g}e_g^2({}^1E_g)] : \sqrt{\frac{1}{2}} [- | (xy) (z^2) (\overline{x^2-y^2}) | + | (xy) (\overline{z^2}) (x^2-y^2) |]$$

 ${}^2B_1^Q$:

$${}^2A_{2g}^C[t_{2g}^2({}^1E_g)e_g] : \sqrt{\frac{1}{2}} \{ \sqrt{\frac{1}{2}} [-2 | (xy) (\overline{xy}) (x^2-y^2) | + | (zx) (\overline{zx}) (x^2-y^2) |$$

$$+ | (yz) (\overline{yz}) (x^2-y^2) |] + \sqrt{\frac{1}{2}} [| (zx) (\overline{zx}) (x^2-y^2) |$$

$$- | (yz) (\overline{yz}) (x^2-y^2) |] \}$$

$${}^2E_{g}^C(t_{2g}^3) : \sqrt{\frac{1}{2}} [-2 | (\overline{xy}) (zx) (yz) | + | (xy) (\overline{zx}) (yz) | + | (xy) (zx) (\overline{yz}) |]$$

$${}^2E_{g}^C[t_{2g}^2({}^1A_1)e_g] : \sqrt{\frac{1}{2}} [| (xy) (\overline{xy}) (x^2-y^2) | + | (zx) (\overline{zx}) (x^2-y^2) | + | (yz) (\overline{yz}) (x^2-y^2) |]$$

$$\begin{aligned}
{}^2E_{gb}^C[t_{2g}^2({}^1E_g)e_g] : & \sqrt{\frac{1}{2}}\{\sqrt{\frac{1}{3}}[-2|(xy)(\overline{xy})(x^2-y^2)|+|(zx)(\overline{zx})(x^2-y^2)| \\
& +|(yz)(\overline{yz})(x^2-y^2)|+1+\sqrt{\frac{1}{2}}[|(zx)(\overline{zx})(z^2)|-|(yz)(\overline{yz})(z^2)|]\} \\
{}^2E_{gb}^C(e_g^3) : & |(z^2)(\overline{z^2})(x^2-y^2)| \\
{}^2B_2^Q : & \\
{}^2T_{2ga}^C(t_{2g}^3) : & \sqrt{\frac{1}{2}}[|(zx)(\overline{zx})(xy)|+|(yz)(\overline{yz})(xy)|] \\
{}^2T_{2ga}^C[t_{2g}^2({}^3T_{1g})e_g] : & \sqrt{\frac{1}{6}}[-2|(zx)(\overline{yz})(x^2-y^2)|+|(zx)(\overline{yz})(x^2-y^2)| \\
& +|(\overline{zx})(yz)(x^2-y^2)|] \\
{}^2T_{2ga}^C[t_{2g}^2({}^1T_{2g})e_g] : & \sqrt{\frac{1}{2}}[|(zx)(\overline{yz})(z^2)|-|(\overline{zx})(yz)(z^2)|] \\
{}^2T_{2ga}^C[t_{2g}e_g^2({}^1A_{1g})] : & \sqrt{\frac{1}{2}}[|(xy)(z^2)(\overline{z^2})|+|(xy)(x^2-y^2)(\overline{x^2-y^2})|] \\
{}^2T_{2ga}^C[t_{2g}e_g^2({}^1E_g)] : & \sqrt{\frac{1}{2}}[|(xy)(z^2)(\overline{z^2})|-|(xy)(x^2-y^2)(\overline{x^2-y^2})|] \\
{}^2E_a^Q : & \\
{}^2T_{1gb}^C(t_{2g}^3) : & \sqrt{\frac{1}{2}}[|(yz)(\overline{yz})(zx)|-|(xy)(\overline{xy})(zx)|] \\
{}^2T_{1gb}^C[t_{2g}^2({}^3T_{1g})e_g] : & \sqrt{\frac{1}{6}}\{\frac{1}{2}[2|(yz)(\overline{xy})(z^2)|-|(yz)(\overline{xy})(z^2)|-|(\overline{yz})(xy)(z^2)|] \\
& +\frac{\sqrt{3}}{2}[2|(yz)(\overline{xy})(x^2-y^2)|-|(yz)(\overline{xy})(x^2-y^2)| \\
& -|(\overline{yz})(xy)(x^2-y^2)|]\} \\
{}^2T_{1gb}^C[t_{2g}^2({}^1T_{2g})e_g] : & \sqrt{\frac{1}{2}}\{\frac{1}{2}[-|(yz)(\overline{xy})(x^2-y^2)|+|(\overline{yz})(xy)(x^2-y^2)|] \\
& +\frac{\sqrt{3}}{2}[|(yz)(\overline{xy})(z^2)|-|(\overline{yz})(xy)(z^2)|]\} \\
{}^2T_{1gb}^C[t_{2g}e_g^2({}^3A_{2g})] : & \sqrt{\frac{1}{6}}[-2|(\overline{zx})(z^2)(x^2-y^2)|+|(zx)(z^2)(\overline{x^2-y^2})|+|(zx)(\overline{z^2})(x^2-y^2)|] \\
{}^2T_{1gb}^C[t_{2g}e_g^2({}^1E_g)] : & \sqrt{\frac{1}{2}}\{\frac{1}{2}[|(zx)(z^2)(\overline{x^2-y^2})|-|(zx)(z^2)(x^2-y^2)|] \\
& +\frac{\sqrt{3}}{2}[|(zx)(z^2)(\overline{z^2})|-|(zx)(x^2-y^2)(\overline{x^2-y^2})|]\} \\
{}^2T_{2gb}^C(t_{2g}^3) : & \sqrt{\frac{1}{2}}[|(yz)(\overline{yz})(zx)|+|(xy)(\overline{xy})(zx)|] \\
{}^2T_{2gb}^C[t_{2g}^2({}^3T_{1g})e_g] : & \sqrt{\frac{1}{6}}\{\frac{1}{2}[2|(yz)(\overline{xy})(x^2-y^2)|-|(yz)(\overline{xy})(x^2-y^2)| \\
& -|(\overline{yz})(xy)(x^2-y^2)|]+ \frac{\sqrt{3}}{2}[-2|(yz)(\overline{xy})(z^2)| \\
& +|(yz)(\overline{xy})(z^2)|+|(\overline{yz})(xy)(z^2)|]\} \\
{}^2T_{2gb}^C[t_{2g}^2({}^1T_{2g})e_g] : & \sqrt{\frac{1}{2}}\{\frac{1}{2}[-|(yz)(\overline{xy})(z^2)|+|(\overline{yz})(xy)(z^2)|] \\
& +\frac{\sqrt{3}}{2}[-|(yz)(\overline{xy})(x^2-y^2)|+|(\overline{yz})(xy)(x^2-y^2)|]\} \\
{}^2T_{2gb}^C[t_{2g}e_g^2({}^1A_{1g})] : & \sqrt{\frac{1}{2}}[|(zx)(z^2)(\overline{z^2})|+|(zx)(x^2-y^2)(\overline{x^2-y^2})|] \\
{}^2T_{2gb}^C[t_{2g}e_g^2({}^1E_g)] : & \sqrt{\frac{1}{2}}\{\frac{1}{2}[-|(zx)(z^2)(\overline{z^2})|+|(zx)(x^2-y^2)(\overline{x^2-y^2})|] \\
& +\frac{\sqrt{3}}{2}[|(zx)(z^2)(\overline{x^2-y^2})|-|(zx)(\overline{z^2})(x^2-y^2)|]\} \\
{}^2E_b^Q : & \\
{}^2T_{1gc}^C(t_{2g}^3) : & \sqrt{\frac{1}{2}}[|(xy)(\overline{xy})(yz)|-|(zx)(\overline{zx})(yz)|] \\
{}^2T_{1gc}^C[t_{2g}^2({}^3T_{1g})e_g] : & \sqrt{\frac{1}{6}}\{\frac{1}{2}[2|(xy)(\overline{zx})(z^2)|-|(xy)(\overline{zx})(z^2)| \\
& -|(\overline{xy})(zx)(z^2)|]+ \frac{\sqrt{3}}{2}[-2|(xy)(\overline{zx})(x^2-y^2)| \\
& +|(xy)(\overline{zx})(x^2-y^2)|+|(\overline{xy})(zx)(x^2-y^2)|]\}
\end{aligned}$$

$$\begin{aligned}
{}^2T_{1gc}^c[t_{2g}^2({}^1T_{2g})e_g] &: \sqrt{\frac{1}{2}}\left\{\frac{1}{2}\left[-|\langle xy \rangle \overline{\langle zx \rangle} (x^2-y^2)| + |\langle xy \rangle \overline{\langle zx \rangle} (x^2-y^2)|\right] \right. \\
&\quad \left. + \frac{\sqrt{3}}{2}\left[|\langle xy \rangle \overline{\langle zx \rangle} (z^2)| - |\langle xy \rangle \overline{\langle zx \rangle} (z^2)|\right]\right\} \\
{}^2T_{1gc}^c[t_{2g}e_g^2({}^3A_{2g})] &: \sqrt{\frac{1}{6}}\left\{-2|\langle yz \rangle \overline{\langle z^2 \rangle} (x^2-y^2)| + |\langle yz \rangle \overline{\langle z^2 \rangle} (x^2-y^2)| \right. \\
&\quad \left. + |\langle yz \rangle \overline{\langle z^2 \rangle} (x^2-y^2)|\right\} \\
{}^2T_{1gc}^c[t_{2g}e_g^2({}^1E_g)] &: \sqrt{\frac{1}{2}}\left\{\frac{1}{2}\left[|\langle yz \rangle \overline{\langle z^2 \rangle} (x^2-y^2)| - |\langle yz \rangle \overline{\langle z^2 \rangle} (x^2-y^2)|\right] \right. \\
&\quad \left. + \sqrt{\frac{3}{2}}\left[|\langle yz \rangle \overline{\langle x^2-y^2 \rangle} (x^2-y^2)| - |\langle yz \rangle \overline{\langle z^2 \rangle} (z^2)|\right]\right\} \\
{}^2T_{2gc}^c(t_{2g}^3) &: \sqrt{\frac{1}{2}}\left[|\langle xy \rangle \overline{\langle xy \rangle} \langle yz \rangle| + |\langle zx \rangle \overline{\langle zx \rangle} \langle yz \rangle|\right] \\
{}^2T_{2gc}^c[t_{2g}^2({}^3T_{1g})e_g] &: \sqrt{\frac{1}{6}}\left\{\frac{1}{2}\left[2|\langle xy \rangle \overline{\langle zx \rangle} (x^2-y^2)| - |\langle xy \rangle \overline{\langle zx \rangle} (x^2-y^2)| \right. \right. \\
&\quad \left. - |\langle xy \rangle \overline{\langle zx \rangle} (x^2-y^2)| + \frac{\sqrt{3}}{2}\left[2|\langle xy \rangle \overline{\langle zx \rangle} (z^2)| \right. \right. \\
&\quad \left. \left. - |\langle xy \rangle \overline{\langle zx \rangle} (z^2)| - |\langle xy \rangle \overline{\langle zx \rangle} (z^2)|\right]\right\} \\
{}^2T_{2gc}^c[t_{2g}^2({}^1T_{2g})e_g] &: \sqrt{\frac{1}{2}}\left\{\frac{1}{2}\left[-|\langle xy \rangle \overline{\langle zx \rangle} (z^2)| + |\langle xy \rangle \overline{\langle zx \rangle} (z^2)|\right] \right. \\
&\quad \left. + \frac{\sqrt{3}}{2}\left[|\langle xy \rangle \overline{\langle zx \rangle} (x^2-y^2)| - |\langle xy \rangle \overline{\langle zx \rangle} (x^2-y^2)|\right]\right\} \\
{}^2T_{2gc}^c[t_{2g}e_g^2({}^1A_{1g})] &: \sqrt{\frac{1}{2}}\left[|\langle yz \rangle \overline{\langle z^2 \rangle} (z^2)| + |\langle yz \rangle \overline{\langle x^2-y^2 \rangle} (x^2-y^2)|\right] \\
{}^2T_{2gc}^c[t_{2g}e_g^2({}^1E_g)] &: \sqrt{\frac{1}{2}}\left\{\frac{1}{2}\left[|\langle yz \rangle \overline{\langle x^2-y^2 \rangle} (x^2-y^2)| - |\langle yz \rangle \overline{\langle z^2 \rangle} (z^2)|\right] \right. \\
&\quad \left. + \frac{\sqrt{3}}{2}\left[-|\langle yz \rangle \overline{\langle z^2 \rangle} (x^2-y^2)| + |\langle yz \rangle \overline{\langle z^2 \rangle} (x^2-y^2)|\right]\right\}
\end{aligned}$$

APPENDIX B

ENERGY MATRICES OF THE d^3 CONFIGURATION: QUADRATE FIELDS

(All matrices are symmetric.)

${}^4B_1^Q$	${}^4A_{2g}^c(t_{2g}^3)$	${}^4B_2^Q$	${}^4T_{2g}^c(t_{2g}^2e_g)$
${}^4A_2^c(t_{2g}^3)$	$-12Dq-7Dt$ $+3A-15B-E$	${}^4T_{2g}^c(t_{2g}^2e_g)$	$-2Dq-7Dt$ $+3A-15B-E$
${}^4A_2^Q$	${}^4T_{1g}^c(t_{2g}^2e_g)$	${}^4T_{1g}^c(t_{2g}e_g^2)$	
${}^4T_{1g}^c(t_{2g}^2e_g)$	$-2Dq+4Ds-2Dt$ $+3A-3B-E$	$+6B$	
${}^4T_{1g}^c(t_{2g}e_g^2)$		$8Dq-2Ds+8Dt$ $+3A-12B-E$	
${}^4E^Q$	${}^4T_{2g}^c(t_{2g}^2e_g)$	${}^4T_{1g}^c(t_{2g}^2e_g)$	${}^4T_{1g}^c(t_{2g}e_g^2)$
${}^4T_{2g}^c(t_{2g}^2e_g)$	$-2Dq+\frac{1}{3}Dt$ $+3A-15B-E$	$-\frac{\sqrt{3}}{4}(4Ds+5Dt)$	0
${}^4T_{1g}^c(t_{2g}^2e_g)$		$-2Dq-2Ds-\frac{2}{3}Dt$ $+3A-3B-E$	$+6B$
${}^4T_{1g}^c(t_{2g}e_g^2)$			$8Dq+Ds+3Dt$ $+3A-12B-E$

${}^2A_1^0$	${}^2A_{1g}^0 [t_{2g}^{-2}({}^1E_g)e_g]$	${}^2E_{2g}^0(t_{2g}^{-3})$	${}^2E_{2g}^0[t_{2g}^{-2}({}^1A_{1g})e_g]$	${}^2E_{2g}^0[t_{2g}^{-2}({}^1E_g)e_g]$	${}^2E_{2g}^0(e_g^{-3})$
${}^2A_{1g}^0 [t_{2g}^{-2}({}^1E_g)e_g]$	$-\frac{1}{3}(12Dq+7Dt)$ $+3A-11B+3C$ $-E$	0	$\frac{1}{3}(3Ds-5Dt)$	$5\frac{1}{3}Dt$	0
${}^2E_{2g}^0(t_{2g}^{-3})$		$-12Dq-7Dt$ $+3A-6B+3C$ $-E$	$-6\sqrt{2}B$	$-3\sqrt{2}B$	0
${}^2E_{2g}^0[t_{2g}^{-2}({}^1A_{1g})e_g]$			$\frac{1}{3}(-3Dq+3Ds+2Dt)$ $+3A+8B+6C$ $-E$	$\frac{1}{3}(3Ds-5Dt)$ $+10B$	$\sqrt{3}(2B+C)$
${}^2E_{2g}^0[t_{2g}^{-2}({}^1E_g)e_g]$			$-\frac{1}{3}(12Dq+7Dt)$ $+3A-B+3C$ $-E$	$2\sqrt{3}B$	
${}^2E_{2g}^0(e_g^{-3})$				$18Dq-2Ds+8Dt$ $+3A-8B+4C$ $-E$	
${}^2A_2^0$	${}^2T_{1g}^0(t_{2g}^{-3})$	${}^2T_{1g}^0[t_{2g}^{-2}({}^3T_{1g})e_g]$	${}^2T_{1g}^0[t_{2g}^{-2}({}^1T_{2g})e_g]$	${}^2T_{1g}^0[t_{2g}^{-2}({}^3A_{2g})e_g]$	${}^2T_{1g}^0[t_{2g}^{-2}({}^1E_g)e_g]$
${}^2T_{1g}^0(t_{2g}^{-3})$	$-12Dq-7Dt$ $+3A-6B+3C$ $-E$	3B	-3B	0	$-2\sqrt{3}B$
${}^2T_{1g}^0[t_{2g}^{-2}({}^3T_{1g})e_g]$		$-2Dq+4Ds-2Dt$ $+3A+3C$ $-E$	-3B	-3B	$-3\sqrt{3}B$
${}^2T_{1g}^0[t_{2g}^{-2}({}^1T_{2g})e_g]$			$-2Dq-7Dt$ $+3A-6B+3C$ $-E$	+3B	$\sqrt{3}B$
${}^2T_{1g}^0[t_{2g}^{-2}({}^3A_{2g})e_g]$				$8Dq-2Ds+8Dt$ $+3A-6B+3C$ $-E$	$2\sqrt{3}B$
${}^2T_{1g}^0[t_{2g}^{-2}({}^1E_g)e_g]$					$8Dq-2Ds+8Dt$ $+3A-2B+3C$ $-E$

${}^2B_1^0$	${}^2A_{2g}^C[t_{2g}^2({}^1E_g)e_g]$	${}^2E_{g0}^C(t_{2g}^3)$	${}^2E_{g0}^C[t_{2g}^2({}^1A_{1g})e_g]$	${}^2E_{g0}^C[t_{2g}^2({}^1E_g)e_g]$	${}^2E_{g0}^C(e_g^3)$
${}^2A_{2g}^C[t_{2g}^2({}^1E_g)e_g]$	$-\frac{1}{3}(12Dq+7Dt)$ $+3A+9B+3C$ $-E$	0	$\frac{1}{3}(3Ds-5Dt)$	$-\frac{1}{3}(-24Ds+5Dt)$	0
${}^2E_{g0}^C(t_{2g}^3)$		$-12Dq-7Dt$ $+3A-6B+3C$ $-E$	$-6\sqrt{2}B$	$-3\sqrt{2}B$	0
${}^2E_{g0}^C[t_{2g}^2({}^1A_{1g})e_g]$			$-\frac{1}{3}(6Dq+6Ds+11Dt)$ $+3A+8B+6C$ $-E$	$-\frac{1}{3}(3Ds-5Dt)$ $+10B$	$\sqrt{3}(2B+C)$
${}^4E_{g0}^C[t_{2g}^2({}^1E_g)e_g]$				$-\frac{1}{3}(12Dq+7Dt)$ $+3A-B+3C$ $-E$	$2\sqrt{3}B$
${}^2E_{g0}^C(e_g^3)$					$18Dq+2Ds+13Dt$ $+3A-8B+4C$ $-E$
${}^2B_2^0$	${}^2T_{2g0}^C(t_{2g}^3)$	${}^2T_{2g0}^C[t_{2g}^2({}^3T_{1g})e_g]$	${}^2T_{2g0}^C[t_{2g}^2({}^1T_{2g})e_g]$	${}^2T_{2g0}^C[t_{2g}^2({}^1A_{1g})]$	${}^2T_{2g0}^C[t_{2g}^2({}^1E_g)]$
${}^2T_{2g0}^C(t_{2g}^3)$	$-12Dq-7Dt$ $+3A+5C$ $-E$	$3\sqrt{3}B$	$-5\sqrt{3}B$	$4B+2C$	$-2B$
${}^2T_{2g0}^C[t_{2g}^2({}^3T_{1g})e_g]$		$-2Dq-7Dt$ $+3A-6B+3C$ $-E$	$-3B$	$3\sqrt{3}B$	$-3\sqrt{3}B$
${}^2T_{2g0}^C[t_{2g}^2({}^1T_{2g})e_g]$			$-2Dq+4Ds-2Dt$ $+3A+4B+3C$ $-E$	$-\sqrt{3}B$	$-\sqrt{3}B$
${}^2T_{2g0}^C[t_{2g}^2({}^1A_{1g})]$				$8Dq-2Ds+8Dt$ $+3A+6B+5C$ $-E$	$4Ds+5Dt$ $-10B$
${}^2T_{2g0}^C[t_{2g}^2({}^1E_g)]$					$8Dq-2Ds+8Dt$ $+3A-2B+3C$ $-E$

${}^2E^Q$	${}^2T_{1gb}^C(t_{2g}^3)$	${}^2T_{1gb}^C[t_{2g}^2({}^3T_{1g})e_g]$	${}^2T_{1gb}^C[t_{2g}^2({}^1T_{2g})e_g]$	${}^2T_{1gb}^C[t_{2g}e_g^2({}^3A_{2g})]$
${}^2T_{1gb}^C(t_{2g}^3)$	$-12Dq-7Dt$ $+3A-6B+3C$ $-E$	$3B$	$-3B$	0
${}^2T_{1gb}^C[t_{2g}^2({}^3T_{1g})e_g]$		$-\frac{1}{4}(8Dq+8Ds+3Dt)$ $+3A+3C$ $-E$	$-3B$	$-3B$
${}^2T_{1gb}^C[t_{2g}^2({}^1T_{2g})e_g]$			$\frac{1}{4}(-8Dq+7Dt)$ $+3A-6B+3C$ $-E$	$3B$
${}^2T_{1gb}^C[t_{2g}e_g^2({}^3A_{2g})]$				$8Dq+Ds+3Dt$ $+3A-6B+3C$ $-E$
${}^2T_{1gb}^C[t_{2g}e_g^2({}^1E_g)]$				
${}^2T_{2gb}^C(t_{2g}^3)$				
${}^2T_{2gb}^C[t_{2g}^2({}^3T_{1g})e_g]$				
${}^2T_{2gb}^C[t_{2g}^2({}^1T_{2g})e_g]$				
${}^2T_{2gb}^C[t_{2g}e_g^2({}^1A_{1g})]$				
${}^2T_{2gb}^C[t_{2g}e_g^2({}^1E_g)]$				

${}^2T_{1g}{}^C[t_{2g}e_g^2({}^1E_g)]$	${}^2T_{2g}{}^C(t_{2g}^3)$	${}^2T_{2g}{}^C[t_{2g}^2({}^3T_{1g})e_g]$	${}^2T_{2g}{}^C[t_{2g}^2({}^1T_{2g})e_g]$	${}^2T_{2g}{}^C[t_{2g}e_g^2({}^1A_{1g})]$	${}^2T_{2g}{}^C[t_{2g}e_g^2({}^1E_g)]$
$-2\sqrt{3} B$	$3Ds-5Dt$	0	0	0	0
$-3\sqrt{3} B$	0	$-\frac{\sqrt{3}}{4}(4Ds+5Dt)$	0	0	0
$\sqrt{3} B$	0	0	$-\frac{\sqrt{3}}{4}(4Ds+5Dt)$	0	0
$2\sqrt{3} B$	0	0	0	0	0
$8Dq+Ds+3Dt$ $+3A-2B+3C$ $-E$	0	0	0	$\frac{\sqrt{3}}{2}(4Ds+5Dt)$	0
	$-12Dq-7Dt$ $+3A+5C$ $-E$	$3\sqrt{3} B$	$-5\sqrt{3} B$	$4B+2C$	$-2B$
		$\frac{1}{4}(-8Dq+7Dt)$ $+3A-6B+3C$ $-E$	$-3B$	$3\sqrt{3} B$	$-3\sqrt{3} B$
			$-\frac{1}{4}(8Dq+8Ds+3Dt)$ $+3A+4B+3C$ $-E$	$-\sqrt{3} B$	$-\sqrt{3} B$
				$8Dq+Ds+3Dt$ $+3A+6B+5C$ $-E$	$-\frac{1}{4}(4Ds+5Dt)$ $-10B$
					$8Dq+Ds+3Dt$ $+3A-2B+3C$ $-E$