Contribution from the Institute of Physical Chemistry II, University of Erlangen-Nürnberg, D-8520 Erlangen, Germany

Theory of Spin Triplet Ground States in d^6 Transition Metal Compounds of D_{4h} and D_{3d} Symmetries. I. Ground State Boundary Delineation

E. König and R. Schnakig

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The formation of spin triplet ground states in the $3d^6$ configuration of transition metal complexes is investigated within D_{4h} and D_{3d} symmetries. Employing as a basis the state functions resulting from the cubic $^5T_{2g}(t_{2g}{}^4e_g{}^2)$, $^1A_{1g}(t_{2g}{}^6)$, $^3T_{1g}(t_{2g}{}^5e_g)$, and $^3T_{2g}(t_{2g}{}^5e_g)$ terms it is demonstrated that, in D_{4h} symmetry, the triplet states $^3A_2$, $^3B_2$, $^3E(^3T_1)$, and $^3E(^3T_2)$ may be stabilized as ground states. On the other hand, only the $^3E(^3T_1)$ state may become ground state if the symmetry is D_{3d}. Diagrams showing the ground state boundaries, in D_{4h} symmetry, as function of the parameters Dq, Dt, and $x = Ds/Dt$ are presented. In D_{3d} symmetry, Dq, Dτ, and $x = D\sigma/D\tau$ are equally employed. The relevance of the present calculations to available experimental data is discussed.

1. Introduction

In the electronic configurations d^4, d^5, d^6, and d^7 within octahedral symmetry, one of two possible electronic ground states may be stabilized, depending on the strength of the field set up by the ligands. These states which are known as high-spin and low-spin states are characterized by a different symmetry transformation property and a different value of the total spin S.[1] The configurations d^4, d^5, and d^6 are remarkable in that states of an additional, third, spin multiplicity are formed. As long as O_h symmetry is strictly preserved, it is only certain excited states to which the total spin $S = 0$, $S = 3/2$, and $S = 1$ may be assigned in d^4, d^5, and d^6, respectively.

In the d^6 configuration, in particular, the possible ground terms within a field of octahedral symmetry are $^5T_{2g}(t_{2g}{}^4e_g{}^2)$ and $^1A_{1g}(t_{2g}{}^6)$ and complexes of these ground states are well documented. In addition, there are numerous spin triplet excited states, although only two, *viz.* $^3T_{1g}(t_{2g}{}^5e_g)$ and $^3T_{2g}(t_{2g}{}^5e_g)$,, have reasonably low energies. Recently, the question has been raised, whether spin triplet ground states may be formed, provided the symmetry of the field is lower than cubic. The $S = 1$ ground states expected would then possibly arise from the excited $^3T_{1g}(t_{2g}{}^5e_g)$ and $^3T_{2g}(t_{2g}{}^5e_g)$ terms of the octahedral field. The problem is stimulated by experimental magnetic and spectroscopic results in certain complex compounds of iron(II) and cobalt(III). These data which will be briefly discussed below justify a theoretical study. Therefore, in this paper, we will investigate the conditions for spin triplet ground state formation within a limited basis set of the d^6 configuration assuming that the effective ligand field is of tetragonal (D_{4h}) or trigonal (D_{3d}) symmetry.

(1) E. König, S. Kremer, *Theoret. Chim. Acta* (Berlin) 23, 12 (1971).

2. Single d Electron Eigenfunctions and Energies

In the ligand field model of a transition metal complex, the complete Hamiltonian considered may be written as

$$H=\sum_i\left(-\frac{\nabla_i^2}{2m_i}-\frac{Ze^2}{r_i}\right)+V_{Lig}+\sum_{i>j}\frac{e^2}{r_{ij}}+\sum_i\zeta l_i\cdot s_i \quad (1)$$

If it is assumed that a central field solution to the first two terms of H has been obtained, the remaining three terms may be accounted for by a perturbation calculation. In what follows, we will employ the so-called strong-field approximation, *i.e.*

$$V_{Lig}>\sum_{i>j}\frac{e^2}{r_{ij}}>\sum\zeta l_i\cdot s_i \quad (2)$$

The ligand field potential V_{Lig} may be expanded into spherical harmonics and is frequently expressed as a cubic term and a perturbing term due to lower symmetry. Below, we will always use the combined potential which may be written, in D_{4h} symmetry.[2],

$$V_{tetr}=A(r)C_0^{(2)}(\theta,\varphi)+B(r)\{C_0^{(4)}(\theta,\varphi)-\\ -\sqrt{\frac{7}{10}}[C_4^{(4)}(\theta,\varphi)+C_{-4}^{(4)}(\theta,\varphi)]\} \quad (3)$$

where

$$C_m^{(k)}(\theta,\varphi)=\left(\frac{4\pi}{2k+1}\right)^{1/2}Y_{km}(\theta,\varphi) \quad (4)$$

(2) S. Sugano, Y. Tanabe, H. Kamimura, Multiplets of Transition-Metal Ions in Crystals, Academic Press, New York, 1970.
(3) B.R. Judd, Operator Techniques in Atomic Spectroscopy, McGraw-Hill, New York, 1963.

are Racah's rationalized spherical harmonics.[3] On the other hand, in D_{3d} symmetry, it is

$$V_{trig} = A(r)C_0^{(2)}(\theta,\varphi) + D(r)\{C_0^{(4)}(\theta,\varphi) - \\ -\frac{1}{2}\sqrt{\frac{7}{10}}[C_3^{(4)}(\theta,\varphi) - C_{-3}^{(4)}(\theta,\varphi)]\} \quad (5)$$

In D_{4h} symmetry, the cubic single d electron orbitals

$$e\theta = |20\rangle = d_{z^2}$$

$$e\varepsilon = \frac{1}{\sqrt{2}}[|22\rangle + |2-2\rangle] = d_{x^2-y^2}$$

$$t_2\eta = -\frac{1}{\sqrt{2}}[|21\rangle - |2-1\rangle] = d_{xz} \quad (6)$$

$$t_2\xi = \frac{i}{\sqrt{2}}[|21\rangle + |2-1\rangle] = d_{yz}$$

$$t_2\zeta = -\frac{i}{\sqrt{2}}[|22\rangle - |2-|2-2\rangle] = d_{yx}$$

may be employed. These orbitals transform now, in the above sequence, according to a_1, b_1, e_a, e_b, and b_2, respectively. The corresponding single electron energies may be expressed in terms of the splitting parameters for $Y_{20}(\theta,\varphi)$ and $Y_{40}(\theta,\varphi)$, Ds and Dt respectively, according to the definition of Ballhausen[*4]

$$E(a_{1g}) = \langle e\theta|V_{tetr}|e\theta\rangle = 6Dq - 2Ds - 6Dt$$
$$E(b_{1g}) = \langle e\varepsilon|V_{tetr}|e\varepsilon\rangle = 6Dq + 2Ds - Dt \quad (7)$$
$$E(e_g) = \langle t_2\xi|V_{tetr}|t_2\xi\rangle = \langle t_2\eta|V_{tetr}|t_2\eta\rangle = -4Dq - Ds + 4Dt$$
$$E(b_{2g}) = \langle t_2\zeta|V_{tetr}|t_2\zeta\rangle = -4Dq + 2Ds - Dt$$

The resulting orbital energies are depicted in Figure 1. As is well known, the center of gravity holds for the Ds terms within the e_g and t_{2g} orbitals separately, while for the Dt terms this is true for the whole configuration only.

In D_{3d} symmetry, the trigonally oriented single d electron orbitals

$$eu_+ = -\frac{1}{\sqrt{3}}[|2-2\rangle - \sqrt{2}|21\rangle]$$

$$eu_- = \frac{1}{\sqrt{3}}[|22\rangle + \sqrt{2}|2-1\rangle] \quad (8)$$

$$t_2x_+ = -\frac{1}{\sqrt{3}}[\sqrt{2}|2-2\rangle + |21\rangle]$$

$$t_2x_- = \frac{1}{\sqrt{3}}[\sqrt{2}|22\rangle - |2-1\rangle]$$

$$t_2x_0 = |20\rangle$$

are used to advantage. In Eq. (8), the first two orbitals transform now according to e(e), the following

(*) It should be observed that Ds and Dt parameters (and $D\sigma$ and $D\tau$ as well) differing in sign from those used here [4] have been defined by Perumareddi [5,6].
(4) J.C. Ballhausen, Introduction to Ligand Field Theory, McGraw-Hill, New York, 1962.
(5) J.R. Perumareddi, *J. Phys. Chem.*, *71*, 3144 (1967).
(6) J.R. Perumareddi, *Coord. Chem. Rev.*, *4*, 73 (1969).

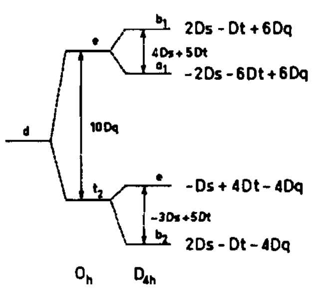

Figure 1. Single electron orbital energies in D_{4h} symmetry in terms of Dq, Ds, and Dt.

two as $e(t_2)$, and t_2x_0 according to a_1. In terms of the parameters $D\sigma$ and $D\tau$ of the D_{3d} field,[4] the corresponding single electron energies result as

$$E[e(e)] = \langle eu_\pm|V_{trig}|eu_\pm\rangle = 6Dq + \frac{7}{3}D\tau$$

$$E[e(t_2)] = \langle t_2x_\pm|V_{trig}|t_2x_\pm\rangle = -4Dq + D\sigma + \frac{2}{3}D\tau \quad (9)$$

$$E(a_1) = \langle t_2x_0|V_{trig}|t_2x_0\rangle = -4Dq - 2D\sigma - 6D\tau$$

However, in contrast to the situation in a D_{4h} field, the trigonal field mixes the two e orbitals by way of the off-diagonal matrix element

$$\langle eu_\pm|V_{trig}|t_2x_\pm\rangle = \frac{\sqrt{2}}{3}(3D\sigma - 5D\tau) \quad (10)$$

which has to be taken into account in calculating E[e] according to Eq. (9).

3. Total Six-Electron States

Total d^6 electron states transforming according to the irreducible representation Γ (in one of the point groups considered, D_{4h} or D_{3d}), component γ, and possessing a total spin S with z component M_S may be constructed from the one-electron orbitals Eq. (6) and (8) by the application of

$$|^{2S+1}\Gamma M_S\gamma\rangle = \sum_{\substack{m_{s1}m_{s2}\\ \gamma_1\gamma_2}} |\Gamma_1 m_{s1}\gamma_1\rangle|\Gamma_2 m_{s2}\gamma_2\rangle\langle s_1 m_{s1} s_2 m_{s2}|SM_S\rangle \times \\ \langle\Gamma_1\gamma_1\Gamma_2\gamma_2|\Gamma\gamma\rangle \quad (11)$$

taking two orbitals at one time. In Eq. (11), $\langle s_1 m_{s1} s_2 m_{s2}|SM_S\rangle$ are Wigner coefficients for the electron spin and $\langle\Gamma_1\gamma_1\Gamma_2\gamma_2|\Gamma\gamma\rangle$ are coupling coefficients for the symmetry group concerned. In fact, only total wavefunctions of the d^4 electron problem are required, if the equivalency between electrons and holes is utilized. Previous calculations indicate that it is essentially only the lowest multiplets which provide a major contribution to the elecronic ground state. Therefore, we limit our calculations, in the present study, to those states arising from the octahedral terms $^5T_{2g}(t_{2g}^4e_g^2)$, $^1A_{1g}(t_{2g}^6)$, $^3T_{1g}(t_{2g}^5e_g)$, and $^3T_{2g}(t_{2g}^5e_g)$ comprising altogether 34 electron levels. In this case, the interelectronic repulsion energies are diagonal to first order and may thus be written as

$$E_{Coulomb}(^5T_{2g}) = 0$$
$$E_{Coulomb}(^3T_{1g}) = 5B + 5C$$
$$E_{Coulomb}(^3T_{2g}) = 13B + 5C \quad (12)$$
$$E_{Coulomb}(^1A_{1g}) = 5B + 8C$$

(a) *Tetragonal Symmetry Case.* In D_{4h} symmetry, the splitting of the parent octahedral terms is according to $^5T_{2g} \rightarrow {}^5B_2 + {}^5E$, $^3T_{1g} \rightarrow {}^3A_2 + {}^3E$, and $^3T_{2g} \rightarrow {}^3B_2 + {}^3E$, all resulting states being g on the basis of parity. In addition, the $^1A_{1g}$ state is not affected by the change of symmetry. Since there is a one-to-one correspondence of states in O_h and D_{4h}, the required d^4 state functions may be easily set up as[7]

$$|^1A_10a_1\rangle = |\theta^2\varepsilon^2\rangle$$
$$|^5B_22b_2\rangle = |^5T_22\zeta\rangle = |\theta^+\varepsilon^+\xi^+\eta^+\rangle$$
$$|^5E2e_a(e_b)\rangle = |^5T_22\eta(\xi)\rangle = |\theta^+\varepsilon^+\zeta^+\eta^+(\xi^+)\rangle$$
$$|^3A_21a_2\rangle = |^3T_11z\rangle = |\theta^2\varepsilon^+\zeta^+\rangle \quad (13)$$
$$|^3E1e_a(e_b)\rangle = |^3T_11y(x)\rangle = -\frac{1}{2}\,\theta^2\varepsilon^+\eta^+(\xi^+)\rangle \pm \frac{\sqrt{3}}{2}|\theta^+\varepsilon^2\eta^+(\xi^+)\rangle$$
$$|^3B_21b_2\rangle = |^3T_21\zeta\rangle = |\theta^+\varepsilon^2\zeta^+\rangle$$
$$|^3E1e_a(e_b)\rangle = |^3T_21\eta(\xi)\rangle = \mp\frac{\sqrt{3}}{2}|\theta^2\varepsilon^+\eta^+(\xi^+)\rangle - \frac{1}{2}|\theta^+\varepsilon^2\eta^+(\xi^+)\rangle$$

In Eq. (13), only functions characterized by the maximum M_S value are listed. The remaining functions may be easily generated by application of the step-down operator S_-. These functions, however, are needed in calculations including spin-orbit interaction, although complex functions may be prefered for convenience.

It should be observed that, due to the use of d^4 functions Eq. (13), the sign of the ligand field parameters Dq, Ds, and Dt (as well as that of the spin-orbit coupling constant ζ to be introduced below) has to be changed. The calculation of matrix elements of the ligand field potential V_{tetr} of Eq. (3) then yields the term energies

$$E(^1A_1) = -24Dq + 14Dt + 5B + 8C$$
$$E(^3A_2) = -14Dq + 14Dt + 5B + 5C$$
$$E(^31E(^3T_1)) = -14Dq + Ds + \frac{13}{2}Dt - 9B + 5C - R_1$$
$$E(^3B_2) = -14Dq - 4Ds + 9Dt + 13B + 5C \quad (14)$$
$$E(^32E(^3T_2)) = -14Dq + Ds + \frac{13}{2}Dt + 9B + 5C + R_1$$
$$E(^5B_2) = -4Dq + 2Ds - Dt$$
$$E(^5E) = -4Dq - Ds + 4Dt$$

where

$$R_1 = \frac{1}{2}\{(2Ds + \frac{10}{4}Dt + 8B)^2 + \frac{3}{4}(4Ds + 5Dt)^2\}^{1/2} \quad (15)$$

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

In Eq. (14), the appropriate interelectronic repulsion energies of Eq. (12) have been included which are not affected by a lowering of symmetry. The square root Eq. (15) results from a non-zero ligand field interaction between the ^3E states, *viz.*

	$^3E(^3T_1)$	$^3E(^3T_2)$
$^3E(^3T_1)$	$-14Dq + \frac{21}{4}Dt + 5B + 5C$	$\frac{\sqrt{3}}{4}(4Ds + 5Dt)$
$^3E(^3T_2)$		$-14Dq + 2Ds + \frac{31}{4}Dt + 13B + 5C$

(16)

Spin-orbit matrix elements have been calculated by application of the operator $\Sigma_i\zeta \mathbf{l}_i \cdot \mathbf{s}_i$ to the complex functions corresponding to Eq. (13) as well as to the functions of lower M_S values.* The resulting 34×34 spin-orbit interaction matrix then factors into a matrix of dimension 10 and three 8×8 matrices, two of which are identical. The matrices are listed in Appendix I. Since basis functions transforming according to the irreducible representations of $\Gamma\times\Gamma_S$ have not been constructed, the individual matrices may be attributed to two representations (including spin) at a time, *viz.* Γ_{t1}, Γ_{t2}; Γ_{t3}, Γ_{t4}; two times Γ_{t5a}, Γ_{t5b}.**

(b) *Trigonal Symmetry Case.* In D_{3d} symmetry, the parent octahedral terms are split as indicated by $^5T_{2g} \rightarrow {}^5A_1 + {}^5E$, $^3T_{1g} \rightarrow {}^3A_2 + {}^3E$, and $^3T_{2g} \rightarrow {}^3A_1 + {}^3E$, whereas the $^1A_{1g} \rightarrow {}^1A_1$ and is not split. Again, all resulting states are g on the basis of parity. State functions within the d^4 configuration transforming according to the resulting irreducible representations may be set up on the basis of Eq. (11) producing

$$|^1A_10a_1\rangle = |u_+{}^2u_-{}^2\rangle$$
$$|^5A_12a_1\rangle = -|u_+{}^+u_-{}^+x_+{}^+x_-{}^+\rangle$$
$$|^5E2u_\pm\rangle = -|u_+{}^+u_-{}^+x_\pm{}^+x_0\rangle$$
$$|^3A_21a_2\rangle = \frac{i}{\sqrt{2}}\{|u_+{}^2u_-{}^+x_-{}^+\rangle - |u_-{}^2u_+{}^+x_+{}^+\} \quad (17)$$
$$|^3E(^3T_1)1u_\pm\rangle = \mp\frac{i}{\sqrt{2}}\{|u_-{}^2u_+{}^+x_{\bar{0}}{}^+\rangle - |u_+{}^2u_-{}^+x_{\bar{0}}{}^+\rangle\}$$
$$|^3A_11a_1\rangle = -\frac{1}{\sqrt{2}}\{|u_+{}^2u_-{}^+x_-{}^+\rangle + |u_-{}^2u_+{}^+x_+{}^+\rangle\}$$
$$|^3E(^3T_2)1u_\pm\rangle = \mp\frac{1}{\sqrt{2}}\{|u_-{}^2u_+{}^+x_{\bar{0}}{}^+\rangle + |u_+{}^2u_-{}^+x_{\bar{0}}{}^+\rangle\}$$

Again we list in Eq. (17) only functions characterized by the maximum value of M_S, functions of lower M_S being easily generated by application of S_-. The corresponding energies then result from the matrix elements of V_{trig}, *cf.* Eq. (5), and the interelectronic interaction, Eq. (12)

(*) If the real functions Eq (13) are used, much lower splitting of the overall spin-orbit interaction matrix is produced, *viz.* one 18×18 (Γ_{t1}, Γ_{t2}, Γ_{t3}, Γ_{t4}) and one 16×16 matrix (Γ_{t5a}, Γ_{t5b}).

(**) In what follows we employ the Bethe nomenclature of irreducible representations to denote states including spin-orbit coupling. In particular, Γ_t refers to representations within D_{4h} and Γ^T to those within D_{3d} symmetry.

$$E(^1A_1) = -24Dq - \frac{28}{3}D\tau + 5B + 8C$$

$$E(^3A_2) = -14Dq - D\sigma - \frac{23}{3}D\tau + 5B + 5C$$

$$E(^31E(^3T_1)) = -14Dq + \frac{1}{2}D\sigma - \frac{13}{3}D\tau + 9B + 5C - R_2$$

$$E(^3A_1) = -14Dq - D\sigma - \frac{23}{3}D\tau + 13B + 5C \qquad (18)$$

$$E(^32E(^3T_2)) = -14Dq + \frac{1}{2}D\sigma - \frac{13}{3}D\tau + 9B + 5C + R_2$$

$$E(^5A_1) = -4Dq - 2D\sigma - 6D\tau$$

$$E(^5E) = -4Dq + D\sigma + \frac{2}{3}D\tau$$

where

$$R_2 = \frac{1}{2}\{4(\frac{3}{2}D\sigma + \frac{10}{3}D\tau)^2 + 64B^2\}^{1/2} \qquad (19)$$

The square root Eq. (19) stems from a ligand field interaction between the two ^3E states, *viz.*

	$^3E(^3T_1)u_\pm$	$^3E(^3T_2)u_\pm$
$^3E(^3T_1)u_\pm$	$-14Dq+\frac{1}{2}D\sigma-\frac{13}{3}D\tau+5B+5C$	$\mp\frac{3}{2}D\sigma+\frac{10}{3}D\tau$
$^3E(^3T_2)u_\pm$		$-14Dq+\frac{1}{2}D\sigma-\frac{13}{3}D\tau+13B+5C$

(20)

Spin-orbit interaction may be included, in the same way as shown in section 3a above, by application of $\Sigma_i\zeta l_i \cdot s_i$ to the complex functions corresponding to Eq. (17) including those with $M_S<S$. The total 34×34 matrix then factors into one matrix 12×12 and two identical matrices 11×11 which may be found in Appendix II. The matrices may be labeled by the $\Gamma\times\Gamma_S$ representations Γ_1^T, Γ_2^T; and two times $\Gamma_3^Tu_\mp$.

4. Conditions of Ground State Formation

Obviously, the formation of possible ground states within the problem at hand will be dependent on the parameters Dq, Ds, Dt (or $D\sigma$, $D\tau$), B, and C if, at first, spin-orbit interaction is disregarded. Instead of Ds (or $D\sigma$) it is convenient to introduce a new parameter x such that

$$x = Ds/Dt \text{ in } D_{4h} \text{ symmetry}$$
$$x = D\sigma/D\tau \text{ in } D_{3d} \text{ symmetry}$$

For convenience of presentation we consider below only states resulting from the $^5T_{2g}$, $^3T_{1g}$, and $^1A_{1g}$ terms. It may then be shown that, in D_{4h} symmetry, four different combinations of possible ground states should be distinguished. These four cases are characterized by $Dt>0$ or $Dt<0$ in conjunction with $x>5/3$ or $x<5/3$. The resulting ground states are listed below.

	Dt<0	Dt>0
$x<\frac{5}{3}$	^5E, $^3A_2$, $^1A_1$	$^5B_2$, ^3E, $^1A_1$
$x>\frac{5}{3}$	$^5B_2$, $^3A_2$, $^1A_1$	^5E, ^3E, $^1A_1$

(21)

Employing the energy expressions Eq. (14), conditions for the formation of the various ground states in Eq. (21) may be set up. In general, there are two conditions which have to be met for each single ground state. These conditions are given below. Where one of the equations occurs repeatedly, only the number of the equation is listed where it shows up for the second time. If a change of the unequal sign is involved, this is indicated by a minus sign preceeding the corresponding equation number.

(1) $Dt<0, x<\frac{5}{3}$.

$^1A_1$:
$$Ds+10Dt \leqslant 20Dq-5B-8C \qquad (22)$$
$$0 \leqslant 10Dq-3C \qquad (23)$$

^5E:
$$Ds+10Dt \geqslant 10Dq-5B-5C \qquad (24)$$
−(22)

$^3A_2$: −(23), −(24)

(2) $Dt>0, x<\frac{5}{3}$.

$^1A_1$:
$$-2Ds+15Dt \leqslant 20Dq-5B-8C \qquad (25)$$
$$\frac{35}{4}Dt \leqslant 10Dq-3C \qquad (26)$$

$^5B_2$:
$$-2Ds+\frac{25}{4}Dt \geqslant 10Dq-5B-5C \qquad (27)$$
−(25)

^3E: −(26), −(27)

(3 and 4) $Dt \gtrless 0, x>\frac{5}{3}$.

Dt<0		Dt>0	
$^1A_1$	(25), (23)	$^1A_1$	(22), (26)
$^5B_2$	−(25), (29)	^5E	−(22), (28)
$^3A_2$	−(23), −(29)	^3E	−(26), −(28)

where

$$Ds+\frac{5}{4}Dt \geqslant 10Dq-5B-5C \qquad (28)$$

$$2Ds+15Dt \leqslant 10Dq-5B-5C \qquad (29)$$

If the states originating in the octahedral $^3T_{2g}$ term are taken into account, essentially six different combinations of possible ground states have to be distinguished. These cases may be characterized, in good approximation, as shown below.

	Dt<0	Dt>0
$x > \frac{5}{3}$	$^5B_2$, $^1A_1$, ^32E	^5E, $^1A_1$, $^3B_2$
$\lvert x\rvert < \frac{5}{3}$	^5E, $^1A_1$, $^3A_2$	$^5B_2$, $^1A_1$, ^31E
$x < -\frac{5}{3}$	^5E, $^1A_1$, $^3B_2$	$^5B_2$, $^1A_1$, ^32E

(30)

In addition, for certain specific values of the parameters x and Dt in the transition regions, more complicated ground state combinations may arise. In Eq. (30), the notation ^31E and ^32E refers to the states $^3E(^3T_{1g})$ and $^3E(^3T_{2g})$, respectively. As a consequence of the non-zero ligand field interaction between these two ^3E states, *viz.* Eq. (16), simple conditions for the formation of ground states similar to those given above in absence of the $^3T_{2g}$-based states cannot be set up. However, in a Dt versus Dq plot, the distribution of quintet, singlet, and triplet states is not significantly changed except for the symmetry transformation property of the states involved, *cf.* Eq. (21) and Eq. (30).

In D_{3d} symmetry, two combinations of possible ground states have to be distinguished if, at first, again states originating in the octahedral terms $^5T_{2g}$, $^1A_{1g}$, and $^3T_{1g}$ only are considered. These combinations may be characterized by $x \gtrless -20/9$ as shown below.

$x > -\frac{20}{9}$	$x < -\frac{20}{9}$
^5E, ^3E, $^1A_1$	$^5A_1$, $^3A_2$, $^1A_1$

(31)

The notation in the following conditions is the same as above.

(1) $x > -\frac{20}{9}$.

$^1A_1$:
$$-\frac{1}{2}D\sigma - 5D\tau \leqslant 10Dq - 3C \qquad (32)$$
$$-\frac{1}{2}D\sigma - 5D\tau \leqslant 10Dq - \frac{1}{2}(5B + 8C) \qquad (33)$$

^5E:
$$-\frac{1}{2}D\sigma - 5D\tau \geqslant 10Dq - 5B - 5C \qquad (34)$$
$$-(33)$$

^3E:
$$-(34)$$
$$-(32)$$

(2) $x < -\frac{20}{9}$.

$^1A_1$:
$$D\sigma - \frac{5}{3}D\tau \leqslant 10Dq - 3C \qquad (35)$$
$$D\sigma - \frac{5}{3}D\tau \leqslant 10Dq - \frac{1}{2}(5B + 8C) \qquad (36)$$

$^5A_1$:
$$D\sigma - \frac{5}{3}D\tau \geqslant 10Dq - 5B - 5C \qquad (37)$$
$$-(36)$$

$^3A_2$:
$$-(35)$$
$$-(37)$$

However, the situation in D_{3d} symmetry is considerably more involved than if the symmetry is D_{4h}. Thus, in case (1), it is easily visualized that Eq. (33) is sufficient to specify a $^1A_1$ ground state and, similarly, Eq. –(33) to establish a ^5E ground state. In addition, the conditions Eq. –(34) and Eq. –(32) for a ^3E ground state (valid in absence of $^3T_{2g}$ interaction) cannot be met at the same time. Likewise, in case (2), Eq. (36) and Eq. –(36) are sufficient to characterize the ground states $^1A_1$ and $^5A_1$, respectively. Again, the conditions Eq. –(35) and Eq. –(37) for a $^3A_2$ ground state cannot be satisfied simultaneously. It follows that, in D_{3d} symmetry, spin triplet ground states are not formed if only the terms arising from $^5T_{2g}$, $^1A_{1g}$, and $^3T_{1g}$ are taken into account.

Similar to D_{4h} symmetry, the inclusion of the states resulting from the $^3T_{2g}$ term complicates and modifies the conditions listed above. However, Eq. (31) remains approximately valid if the $^3A_2$ term under $x < -20/9$ is replaced by a ^3E state and if always $^3E = {}^31E$. The most important change thus introduced is that now a $^3E(^3T_{1g})$ ground state may be stabilized, whereas, as before, the $^3A_2$ state (and the $^3A_1$ resulting from $^3T_{2g}$ as well) cannot become ground state.

No closed expressions concerning formation of ground states can be given if spin-orbit interaction is included.

5. Results: Parameter Dependence of Ground State Regions

(a) *Without Spin-Orbit Coupling.* Disregarding the $^3T_{2g}$ term, the conditions for ground state formation in section 4 have been written in form of a linear equation, *viz.*

$$f(Ds(x) + Dt) = aDq + bB + cC \qquad (38)$$

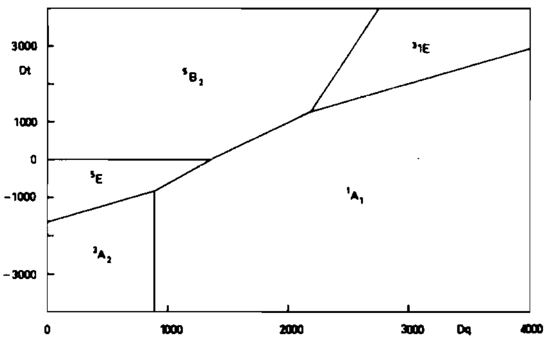

Figure 2. Ground state regions for the d^6 configuration in D_{4h} symmetry without spin-orbit coupling as function of the tetragonal and cubic field strengths Dt and Dq, respectively (B = 730 cm^{-1}, C = 4B, x = 1.0).

In Eq. (38), Dq may be considered as the independent variable with bB+cC as the intercept on the ordinate. Consequently, if f(Ds(x)+Dt) is plotted *vs.* Dq, existence regions of the various ground states are obtained for fixed values of B and C.

If, on the other hand, the $^3T_{2g}$ term is included, numerical solutions of the resulting equations are required. The results are illustrated in Figure 2 for D_{4h} symmetry and for $\varkappa = 1.0$ where B = 730 cm^{-1} and C = 4B has been assumed.

(b) *The Effect of Spin-Orbit Coupling.* If spin-orbit interaction is taken into account, there may be non-zero contributions of various spin multiplicities to each state in question. In addition to spin singlet, triplet, and quintet ground states, substantially spin-mixed ground states are thus expected. We therefore arbitrarily define a pure spin ground state as one having less than 2% admixture of any other spin multiplicity (blank areas in Figures 3, 4, 5, 6, and 7) and all other ground states as spin-mixed (shaded areas in Figures 3, 4, 5, 6, and 7). In all calculations comprising spin-orbit coupling, the states $^5T_{2g}$, $^1A_{1g}$, $^3T_{1g}$, *and* $^3T_{2g}$ have been included.

Figures 3, 4, and 5 show the results for D_{4h} symmetry with $\varkappa = 1.0$, $\varkappa = 3.0$, and $\varkappa = -3.0$, respectively. Similarly, the results for D_{3d} symmetry with $\varkappa = 1.0$ and $\varkappa = 3.0$ are displayed in Figures 6 and 7, respectively.

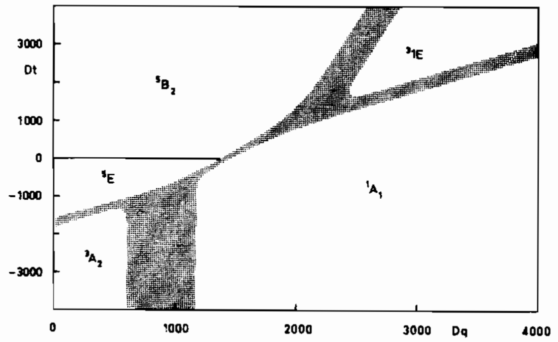

Figure 3. Ground state regions for the d^6 configuration in D_{4h} symmetry with spin-orbit coupling (B = 730 cm^{-1}, C = 4B, ζ = 420 cm^{-1}) assuming $\varkappa = 1.0$.

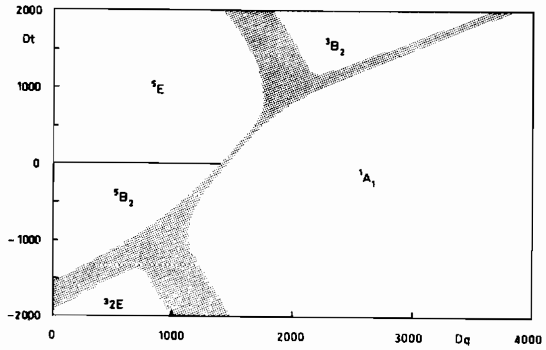

Figure 4. Ground state regions for the d^6 configuration in D_{4h} symmetry with spin-orbit coupling (B = 730 cm^{-1}, C = 4B, ζ = 420 cm^{-1}) assuming $\varkappa = 3.0$.

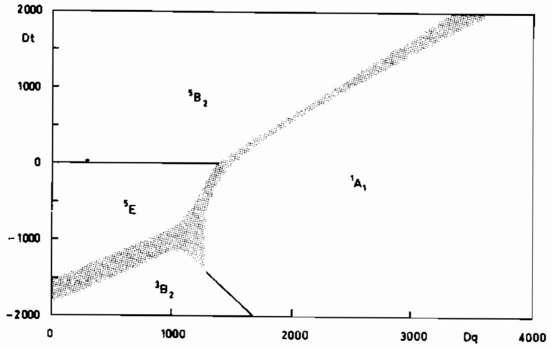

Figure 5. Ground state regions for the d^6 configuration in D_{4h} symmetry with spin-orbit coupling (B = 730 cm^{-1}, C = 4B, ζ = 420 cm^{-1}) assuming $\varkappa = -3.0$.

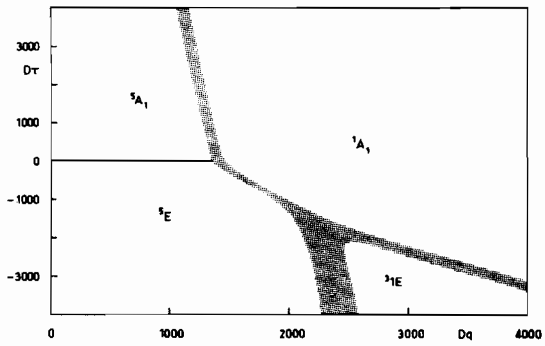

Figure 6. Ground state regions for the d^6 configuration in D_{3d} symmetry with spin-orbit coupling (B = 730 cm^{-1}, C = 4B, ζ = 420 cm^{-1}) assuming $\varkappa = 1.0$.

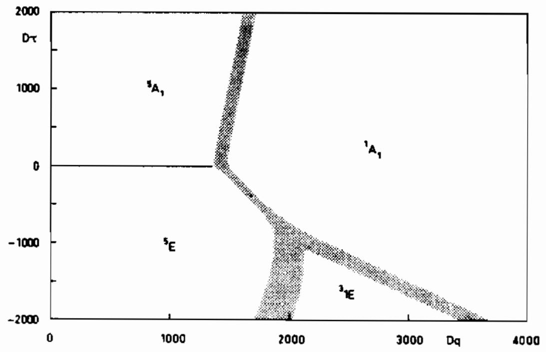

Figure 7. Ground state regions for the d^6 configuration in D_{3d} symmetry with spin-orbit coupling (B = 730 cm^{-1}, C = 4B, ζ = 420 cm^{-1}) assuming $\varkappa = 3.0$.

6. Discussion

The results for D_{4h} symmetry demonstrate that, if $\varkappa = 1.0$ (*cf.* Figure 2), a $^3A_2$ ground state indeed appears at low values of Dq, *i.e.* specifically, if Dq $\leqslant$ 876 cm^{-1} and Dt $\leqslant$ –863 cm^{-1} where Dt is dependent on Dq, *viz.* section 4. On the other hand, a ^31E ground state is formed at high values of Dq, *i.e.* if Dq $\geqslant$2200 cm^{-1} and Dt $\geqslant$1300 cm^{-1} where, in this case, Dq and Dt are dependent on each other. If spin-orbit interaction is included, the ground state regions arise approximately for the same parameter values as without spin-orbit coupling. However, the clear boundaries between these regions are now replaced by spin-mixed areas (*viz.* Figure 3), some of these extending over a considerable range of values of one or two specific parameters. Thus, if $x = 1.0$, the $^3A_2$-$^1A_1$ spin-mixed area covers a range from Dq = 600 cm^{-1} to Dq = 1170 cm^{-1} and the ^3E-$^5B_2$ area extends over about 300 cm^{-1} in Dq.

With x increasing, *i.e.* $1<x<5/3$, the $^3A_2$ changes little, the ^31E slowly moving to lower Dq. If $x = 5/3$, the possible ground states change as demonstrated in section 4 above. Thus, if $x = 3.0$ (*cf.* Figure 4), a ^32E ground state is now encountered with low values of Dq and Dt<0, whereas if Dt>0 in conjunction with high values of Dq, a $^3B_2$ ground state may form. With still larger x, the ^32E and the $^3B_2$ are shifted to higher and to lower Dq, respectively. At $x \sim 10.0$, the two triplet regions are distributed almost symmetrically to the singlet-quintet crossover. Let us consider a decrease of x below 1.0, *i.e.* $1>x>0$. In this case, the ^31E moves slowly to higher Dq, the $^3A_2$ changing little. The behavior at $0>x>-5/3$ is similar to that at $5/3>x>0$, except that below $x<-1/2$ the ^31E is shifted out of the region considered. At $x = -5/3$, the $^3B_2$ arises at low values of Dq and Dt<0 and moves to higher Dq if $x < -5/3$ (*cf.* Figure 5). Finally, at $x < -3.0$, the ^32E appears at Dt>0 and high Dq slowly shifting to lower Dq as x becomes more negative.

In D_{3d} symmetry, the relation between the results obtained with spin-orbit coupling having not and having been taken into account is similar to that in D_{4h} symmetry discussed above. If $x = 1.0$ (*cf.* Figure 6), a ^31E ground state is formed if Dq $\geqslant$ 2500 cm^{-1} and D$\tau \leqslant -2000$ cm^{-1}, Dq and Dτ being mutually dependent to a certain extent. Again a ^3E-^5E spin-mixed region of about 300 cm^{-1} in Dq is found. With increasing x, the ^31E region is shifted to lower Dq (*viz.* Figure 7) ariving with $x \sim 10.0$ at the singlet-quintet crossover. If negative values of x are considered, the ^31E disappears below $x = -1.0$, and below $x = -20/9$ a new region of ^31E is encountered at D$\tau > 0$ and small Dq. This ^31E slowly shifts to larger Dq as x decreases further.

It should be observed that there is, in general, a considerable mixing involved between the $^3E(^3T_{1g}) = {}^31E$ and $^3E(^3T_{2g}) = {}^32E$ states, the actual amount of the admixture being dependent on Dt or Dτ in D_{4h} and D_{3d} symmetry, respectively. For the lowest values of Dq and Dt or Dτ applicable, the contribution of the ^32E to the ^31E is specifically 13% in D_{4h} and 33% in D_{3d} symmetry if $x = 1.0$. On the other hand, the ^31E contributes about 40% to the ^32E in D_{4h} symmetry if $x = 3.0$.

The effect of including a limited number of additional states originating in the next higher excited states of O_h symmetry has been considered, especially with respect to $^1T_{1g}(t_{2g}{}^5e_g)$ and $^5E_g(t_{2g}{}^3e_g{}^3)$. These states are split in a field of D_{4h} symmetry according to $^1T_1 \rightarrow {}^1A_2 + {}^1E$ and $^5E \rightarrow {}^5A_1 + {}^5B_1$. However, it is found that the $^1T_{1g}$ is always by 2C higher in energy than the $^3T_{1g}$ and the $^5B_1(^5E_g)$ is by 10 Dq higher than the $^5B_2(^5T_{2g})$. Consequently both the $^1T_{1g}$ or states originating therefrom and the $^5B_1(^5E_g)$ are unlikely to become ground state. The only additional state to be considered, in this approximation, is $^5A_1(^5E_g)$. Indeed, it may be demonstrated that for higher values of Dt > 0 a $^5A_1$ ground state replaces the $^5B_2$ ground state in the diagrams Figures 3 and 4. Since, in this paper, we are interested in spin triplet rather than in spin quintet ground states, the $^5A_1$ state will not be considered further.

Within a field of D_{3d} symmetry, the splitting is according to $^1T_1 \rightarrow {}^1A_2 + {}^1E$, whereas the ^5E is not split. There arises now a non-zero interaction between $^5E(^5E_g)$ and $^5E(^5T_{2g})$ by way of the off-diagonal matrix element $+\sqrt{2/3}(3D\sigma\text{-}5D\tau)$, although the results (*cf.* Figures 6 and 7) are not affected to any significant extent.

7. Experimental Evidence for Triplet Ground States

The first compound of iron(II) in which a spin triplet ground state was suggested is, to the authors' knowledge, ferrous phthalocyanine, Fe(pc).[8] On the basis of magnetic measurements between 292.5 and 1.25°K[9] and the study of magnetic anisotropy,[10] the ground state is assumed to be $^3B_2$ with a zero-field splitting D = 64 cm^{-1}. From section 4 it then follows that $x > 5/3$ and Dt > 0. Recently, a $^3B_2$ ground state has likewise been suggested in the planar bis(biuretato)cobalt(III) complexes from magnetic and optical spectral studies.[11] In addition, spin triplet ground states were tentatively assigned to a series of bis(1,10-phenanthroline)iron(II) complexes and several related bis(diimine)iron(II) compounds.[12,13] In this case it was demonstrated by extending magnetic measurements and Mössbauer effect studies to 1.2 and 4.2°K, respectively, that the ground state is $^3A_2$.[14]. Again the $^3A_2$ is slightly split by 2.0 to 3.0 cm^{-1} and is considerably spin-mixed in addition.[15] It may then be concluded that here, $x < 5/3$ and Dt < 0 is required. There are various other occasions where triplet ground states have been observed in iron(II). One of the most conspicuous encounters of this sort is the formation of an S = 1 ground state on reduction from iron(III) to iron(II) under high pressure. This has been observed recently in biological compounds like hemin, hematin, and imidazole protohemichrome.[16] As it stands, there has been no report on a ^3E ground state in iron(II), although, as shown above, this state should likewise be stable. Finally, there are numerous inorganic compounds and biological materials containing iron(II) reported in literature where the value of the effective magnetic moment suggests that triplet ground states might be involved. In a forthcoming publication,[17] the known physical properties of the compounds listed above will be compared in detail with calculated values and predictions concerning unknown data will be made.

(8) A.B.P. Lever, *J. Chem. Soc.*, 1821 (1965).
(9) B.W. Dale, R.J.P. Williams, C.E. Johnson, and T.L. Thorp, *J. Chem. Phys*, *49*, 3441 (1968).
(10) C.G. Barraclough, R.L. Martin, S. Mitra, and R.C. Sherwood, *J. Chem. Phys.*, *53*, 1643 (1970).
(11) J.J. Bour, P.T. Beurskens, J.J. Steggerda, *Chem. Commun.*, 221 (1972).
(12) E. König, K. Madeja, *J. Am. Chem. Soc.*, *88*, 4528 (1966).
(13) E. König, K. Madeja, *Inorg. Chem.*, *7*, 1848 (1968).
(14) E. König, B. Kanellakopulos, *Chem. Phys. Lett.*, *12*, 485 (1972).
(15) E. König, G. Ritter, B. Kanellakopulos, *J. Chem. Phys.*, *58*, 3001 (1973).
(16) D.C. Grenoble, C.W. Frank, C.B., Bargeron, H.G. Drickamer, *J. Chem. Phys.*, *55*, 1633 (1971).
(17) E. König, R. Schnakig, to be published.

Appendix I. Complete ligand field, interelectronic repulsion, and spin-orbit coupling matrices in D_{4h} symmetry including the cubic parent terms $^5T_{2g}(t_{2g}^4e_g^2)$, $^1A_{1g}(t_{2g}^6)$, $^3T_{1g}(t_{2g}^5e_g)$, and $^3T_{2g}(t_{2g}^5e_g)$.

Matrix A. $\Gamma_{t1},\Gamma_{t2}(=A_1,A_2)$.

^5E -11	^5E 1-1	$^5B_2$ 2b_2	$^5B_2$ -2b_2	^{3}1E -11	^{3}1E 1-1	$^3A_2$ 0a_2	^{3}2E 1-1	^{3}2E -11	$^1A_1$ 0a_1
1/4ζ −4Dq −Ds+4Dt			1/4√2 ζ	−1/2√3 ζ		1/2√3 ζ		1/2 ζ	
	1/4ζ −4Dq −Ds+4Dt	1/4√2 ζ			1/2√3 ζ	−1/2√3 ζ	−1/2 ζ		
		−4Dq +2Ds−Dt			1/2√6 ζ		1/2√2 ζ		
			−4Dq +2Ds−Dt	−1/2√6 ζ				−1/2√2 ζ	
				1/4ζ −14Dq+21/4Dt +5B+5C		−1/4 ζ		−1/4√3 ζ +√3(Ds+5/4Dt)	−√2 ζ
					1/4ζ −14Dq+21/4Dt +5B+5C	−1/4 ζ	−1/4√3 ζ +√3(Ds+5/4Dt)		−√2 ζ
						−14Dq+14Dt +5B+5C	−1/4√3 ζ	−1/4√3 ζ	√2 ζ
							−1/4ζ−14Dq +2Ds+31/4Dt +13B+5C		
								−1/4ζ−14Dq +2Ds+31/4Dt +13B+5C	
									−24Dq+14Dt +5B+8C

Matrix B. $\Gamma_{t3},\Gamma_{t4}(=B_1,B_2)$.

^5E -1-1	^5E 11	$^5B_2$ 0b_2	^{3}1E -1-1	^{3}1E 11	^{3}2E -1-1	$^3B_2$ 0b_2	^{3}2E 11
−1/4ζ −4Dq −Ds+4Dt		1/4√3 ζ	1/2√3 ζ		−1/2 ζ	−1/2 ζ	
	−1/4ζ −4Dq −Ds+4Dt	1/4√3 ζ		−1/2√3 ζ		1/2 ζ	1/2 ζ
		−4Dq +2Ds−Dt	1/2 ζ	−1/2 ζ	1/6√3 ζ		−1/6√3 ζ
			−1/4ζ −14Dq+21/4Dt +5B+5C		1/4√3 ζ +√3(Ds+5/4Dt)	1/4√3 ζ	
				−1/4ζ −14Dq+21/4Dt +5B+5C		1/4√3 ζ	1/4√3 ζ +√3(Ds+5/4Dt)
					1/4ζ−14Dq +2Ds+31/4Dt +13B+5C	−1/4 ζ	
						−14Dq −4Ds+9Dt +13B+5C	−1/4 ζ
							1/4ζ−14Dq +2Ds+31/4Dt +13B+5C

Matrix C. $\Gamma_{15a},\Gamma_{15b}(=E\mp1)$.

$^5E0\pm1$	$^5E\mp2\mp1$	$^5E\pm2\pm1$	$^5B_2\mp1b_2$	$^31E0\pm1$	$^3A_2\pm1a_2$	$^3B_2\mp1b_2$	$^32E0\pm1$
$-4Dq$ $-Ds+4Dt$			$1/4\sqrt{3}\zeta$	$\mp\zeta$	$\pm1/2\zeta$	$\pm1/6\sqrt{3}\zeta$	$\pm1/3\sqrt{3}\zeta$
	$-1/2\zeta-4Dq$ $-Ds+4Dt$		$1/4\sqrt{2}\zeta$			$\pm1/2\sqrt{2}\zeta$	
		$1/2\zeta-4Dq$ $-Ds+4Dt$			$\mp1/2\sqrt{6}\zeta$		
			$-4Dq$ $+2Ds-Dt$	$\mp1/2\sqrt{3}\zeta$			$\mp1/2\zeta$
				$-14Dq+21/4Dt$ $+5B+8C$	$-1/4\zeta$	$1/4\sqrt{3}\zeta$	$\sqrt{3}(Ds+5/4Dt)$
					$-14Dq+14Dt$ $+5B+5C$		$-1/4\sqrt{3}\zeta$
						$-14Dq$ $-4Ds+9Dt$ $+13B+5C$	$-1/4\zeta$
							$-14Dq$ $+2Ds+31/4Dt$ $+13B+5C$

Appendix II. Complete ligand field, interelectronic repulsion, and spin-orbit coupling matrices in D_{3d} symmetry including the cubic parent terms $^5T_{2g}(t_{2g}^4e_g^2)$, $^1A_{1g}(t_{2g}^6)$, $^3T_{1g}(t_{2g}^5e_g)$, and $^3T_{2g}(t_{2g}^5e_g)$.

Matrix A. $\Gamma^T_1,\Gamma^T_2(\doteq A_1,A_2)$.

$^5E1u+$	$^5E-2u+$	$^5A_10a_1$	$^5E2u-$	$^5E-1u-$	$^31E1u+$	$^31E-1u-$	$^3A_20a_2$	$^32E1u+$	$^32E-1u-$	$^3A_10a_1$	$^1A_10a_1$
$-1/4\zeta-4Dq$ $+D\sigma+2/3D\tau$		$1/4\sqrt{3}\zeta$			$-1/2\zeta$		$-1/2\zeta$	$1/2\zeta$		$-1/2\zeta$	
	$1/2\zeta-4Dq$ $+D\sigma+2/3D\tau$					$\sqrt{2}\zeta$					
		$-4Dq$ $-2D\sigma-6D\tau$		$1/4\sqrt{3}\zeta$	$-1/6\sqrt{3}\zeta$	$-1/6\sqrt{3}\zeta$	$-2/3\sqrt{3}\zeta$	$-1/6\sqrt{3}\zeta$	$1/6\sqrt{3}\zeta$		
			$1/2\zeta-4Dq$ $+D\sigma+4/3D\tau$		$-\sqrt{2}\zeta$						
$-24Dq$ $-28/3D\tau$ $+5B+8C$				$-1/4\zeta-4Dq$ $+D\sigma+2/3D\tau$		$-1/2\zeta$	$-1/2\zeta$		$-1/2\zeta$	$1/2\zeta$	
	$-14Dq$ $-D\sigma-23/3D\tau$ $+13B+5C$				$1/4\zeta-14Dq$ $+1/2D\sigma-13/3D\tau$ $+5B+5C$		$1/4\zeta$	$1/4\zeta$ $+3/2D\sigma-10/3D\tau$		$-1/4\zeta$	$-\sqrt{2}\zeta$
	$1/4\zeta$	$1/4\zeta-14Dq$ $+1/2D\sigma-13/3D\tau$ $+13B+5C$				$1/4\zeta-14Dq$ $+1/2D\sigma-13/3D\tau$ $+5B+5C$	$1/4\zeta$		$-1/4\zeta$ $+3/2D\sigma+10/3D\tau$	$1/4\zeta$	$-\sqrt{2}\zeta$
	$1/4\zeta$		$1/4\zeta-14Dq$ $+1/2D\sigma-13/3D\tau$ $+13B+5C$				$-14Dq$ $-D\sigma-23/3D\tau$ $+5B+5C$	$-1/4\zeta$	$1/4\zeta$		$-\sqrt{2}\zeta$
$^1A_10a_1$	$^3A_10a_1$	$^32E-1u-$	$^32E1u+$								

Matrix B. $\Gamma^{\prime\prime}{}_3 u\pm(=Eu\pm)$.

$^5E\pm2u_\pm$	$^3E\mp1u_\pm$	$^5E0u_\mp$	$^5A_1\pm1a$	$^5A_1\mp2a_1$	$^31E\mp1u_\pm$	$^31E0u_\mp$	$^3A_2\pm1a_2$	$^32E\mp1u_\pm$	$^32E0u_\mp$	$^3A_12a_1$
$-1/2\zeta-4Dq+D\sigma+1/2D\tau$			$1/4\sqrt{2}\zeta$				$-1/2\sqrt{2}\zeta$			$\mp1/2\sqrt{2}\zeta$
	$1/4\zeta-4Dq+D\sigma-2/3D\tau$			$1/4\sqrt{2}\zeta$	$-1/2\zeta$	$\pm\zeta$		$\pm1/2\zeta$		
		$-4Dq+D\sigma+2/3D\tau$	$1/4\sqrt{3}\zeta$		$\mp1/3\sqrt{3}\zeta$	$-1/3\sqrt{3}\zeta$	$-1/6\sqrt{3}\zeta$		$\mp1/3\sqrt{3}\zeta$	$\pm1/6\sqrt{3}\zeta$
			$-4Dq-2D\sigma-6D\tau$			$-1/2\zeta$	$-\zeta$		$\pm1/2$	
				$-4Dq-2D\sigma-6D\tau$	$-1/2\sqrt{2}\zeta$			$\mp1/2\sqrt{2}\zeta$		
					$-1/4\zeta-14Dq+1/2D\sigma-13/3D\tau+5B+5C$			$\mp1/4\zeta\mp3/2D\sigma\mp10/3D\tau$	$-1/2\zeta$	
						$-14Dq+1/2D\sigma-13/3D\tau+5B+5C$	$1/4\zeta$	$-1/2\zeta$	$\pm3/2D\sigma\pm10/3D\tau$	$\pm1/4\zeta$
							$-14Dq-D\sigma-23/3D\tau+5B+5C$		$\pm1/4\zeta$	$\mp1/2\zeta$
								$-1/4\zeta-14Dq+1/2D\sigma-13/3D\tau+13B+5C$		
									$-14Dq+1/2D\sigma-13/3D\tau+13B+5C$	$1/4\zeta$
										$-14Dq-D\sigma-23/3D\tau+13B+5C$

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