Existence of ^3E_g Ground Terms in Tetragonal d^8 Complexes and the Possibility of High-Spin Square-Planar Nickel(II)

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Abstract: A detailed examination of the crystal-field description of tetragonal nickel complexes reveals the possible existence of ^3E_g and $^3A_{2g}$ ground terms as well as the more usual $^3B_{1g}$ ground term. In order to demonstrate the viability of such terms, in addition to the geometric contribution to the tetragonality of the electric field, it is necessary to define an anisotropic mean charge ratio A describing the chemical difference between equatorial and axial ligands. The energy levels are displayed as cross sections of a three-dimensional Tanabe–Sugano distortion space, and the ratio A is used to define the region of physically possible values of Ds and Dt. Both geometric and chemical origins exist within this space. Complexes with ^3E_g ground terms are possible only if A is negative, implying the absence of axial ligands in a high-spin square plane or the presence of a net positive axial charge typically found in halide-bridged polymeric complexes.

The majority of five-coordinate square-pyramidal and six-coordinate tetragonal complexes of nickel(II) display spectroscopic and magnetic behavior[1] consistent with an orbital singlet ground term $^3B_{1g}$.[2] However, a group of complexes exists with anomalous behavior, for which it is impossible to fit the spectroscopic and magnetic data using a $^3B_{1g}$ ground term. Moreover, in many of these compounds, temperature dependence of the magnetic moment has been observed[3] which is inexplicable in terms of magnetically dilute orbital singlets unless an appreciable zero-field splitting is invoked. Attempts to explain this behavior with a spin–spin perturbation in nondilute systems have been made[4] with limited success. In order to investigate these phenomena more deeply, the detailed electronic structure of tetragonal nickel complexes has been reconsidered with the aid of two related formalizing concepts.

The first of these is the construction of a *distortion energy space*. Like the solutions of many central-field theories of molecular structure, the energy levels of the tetragonal nickel ion are functions of four independent experimental parameters Dq, Ds, Dt, and B, or some other equivalent set. To demonstrate the effect of simultaneous variation of all these on the energies of the electronic states would require plots in five-dimensional space. In previous treatments of this and similar systems, the problem has either been avoided or the energies have been plotted in conventional Tanabe–Sugano diagrams in terms of an undefined ligand point charge or dipole moment.[5] This latter scheme involves a continuously changing set of ratios of the four parameters, and the influence of the individual parameters is very difficult to decipher. The effects of the distortion parameters Ds and Dt, however, can be displayed in three dimensions for a fixed value of Dq by plotting Ds/B and Dt/B against E/B for fixed values of Dq and B. In this distortion energy space the origin is the octahedral solution for the energy levels. *Vertical* cross sections parallel to the E/B axis are conventional Tanabe–Sugano diagrams in either Ds/B *or* Dt/B against E/B for fixed values of the other parameters. The *horizontal* cross section at $E/B = 0$ having axes Ds/B and Dt/B is the *energy base* of the distortion space. The surfaces of the various electronic states only intersect this base plane if, for some values of Ds/B and Dt/B at the value of Dq/B fixed for the particular space, they become the ground state. *Thus the energy base displays the regions of the distortion parameters in which certain ground states exist.*

Within this space, it is possible to formally limit the region on the energy base plane in which real compounds can occur by an analysis of the mathematical form of the distortion parameters. The conventional definitions of Ds and Dt attribute, in the crystal-field model, all of the tetragonality to a geometric distortion. In neglecting chemical differences between axial and equatorial ligands, the ranges of allowed signs of the parameters are artificially restricted. The success of the few attempts which have been made to introduce a formal description of ligand chemistry has been very limited in part because of conceptual rather than algebraic difficulties. In this paper, a chemical factor is introduced into the definition of the tetragonal distortion. The ways in which it affects the sign relationships of Ds and Dt and in which it can be used to predict the possible spectra are described in detail. The magnetic aspects of these deliberations will be the subject of a future paper.

These concepts allow consideration of the possibility that the observed spectroscopic and magnetic properties can be explained in terms of an orbitally degenerate ground term in these complexes. In order to demonstrate that degenerate ground terms are viable in six-coordinate D_{4h} complexes of d^2 and d^8 systems, an important assumption which is traditionally used as the basis of the crystal-field calculations[6] must be reexamined. The Hamiltonian is formulated in terms of an octahedral potential *weakly* perturbed by a tetragonal distortion

$$H_{D_{4h}} = V_{O_h} + V_{D_{4h}} \qquad (1)$$

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[1] D. A. Rowley and R. S. Drago, *Inorg. Chem.*, 6, 1092 (1967); 7, 795 (1968).

[2] A. B. P. Lever, *Coord. Chem. Rev.*, 3, 119 (1968).

[3] A. B. P. Lever, *Inorg. Chem.*, 4, 763 (1965).

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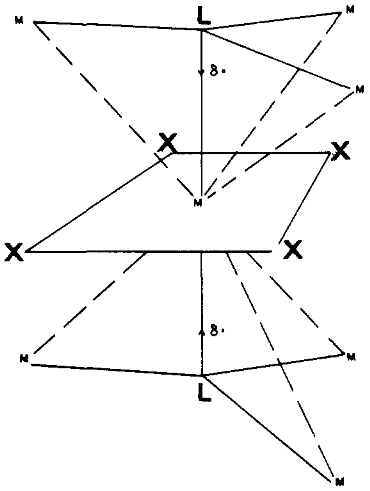

Figure 1. The secondary crystal field due to neighboring metal ions in the tetragonal bridged polymeric complex.

There are no formal requirements for this artificial limitation, since the tetragonal Hamiltonian is a sum of three linearly independent potentials. It does not violate the premises of perturbation theory to allow the tetragonal potentials $V_{D_{4h}}$ to possess much larger values than normally considered reasonable.[6] These potentials are direct perturbations of the central field and are distinct from the octahedral potential. By allowing the ratio of the tetragonal and octahedral potentials $V_{D_{4h}}/V_{O_h}$ to increase, both ^3E_g and $^3A_{2g}$ ground terms become possible. The critical values of this ratio for the appearance of these new ground terms are independent of the crystal-field strength interpreted as the magnitude of the equatorial radial parameter Dq. However, when Dq is large, the values of both Ds and Dt increase to the point of implying the presence of a positive axial charge. This condition is a distinct possibility in polymeric complexes of the type [NiL$_2$Cl$_2$] in which the little structural evidence which is available[7] places the adjacent nickel ions approximately 3.5 Å apart. In D_{4h} symmetry, the neighboring positive ions create a secondary crystal-field perturbation which can be added vectorially to the point charge ligands of the first coordination sphere. If the negative axial ligands are rather diffuse charges at long distances from the central ion it is possible for the effective axial charge to become positive (Figure 1). These features make it obvious that the tetragonality of D_{4h} complexes is not a function of the crystallographic geometry alone, but also of the relative effective nuclear charges of the ligands.

The Calculation of Term Energies

In order to avoid any presumption of the symmetry of the orbital ground term for this calculation and more readily handle changes in it, the medium field is approached from the weak-field approximation. The matrices of configuration interaction are derived using linear combinations of free-ion wave functions.

(i) **The Tetragonal Hamiltonian.** The expansion of the tetragonal perturbation[8] in a central-field approximation for point charge ligands is

$$H_{D_{4h}} = \frac{1}{r_{ij}} = \sum_{n=0}^{6}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\frac{4\Pi}{(2l+1)}\cdot\frac{r_<{}^{l}}{r_>{}^{l+1}}\cdot Y_{l_i}^{m_i}{}^{*}\cdot Y_{l_i}^{m_i} \quad (2)$$

in which r_{ij} is the electron–ligand distance, $r_<$ is the cental ion–electron distance, and $r_>$ is the central ion–ligand separation. If the two values of $r_>$ are defined as R, the central ion–equatorial ligand distance, and S, the central ion–axial ligand distance, then the Hamiltonian can be rearranged to

$$H_{D_{4h}} = \frac{(2\Pi)^{1/2}}{e}\left\{\left(\frac{98}{5}\right)^{1/2} Ds\,Y_2^0 - (98)^{1/2}Dt\,Y_4^0 + (98)^{1/2}Dq\,Y_4^0 + \left(\frac{5}{14}\right)^{1/2}[Y_4^4 + Y_4^{-4}]\right\} \quad (3)$$

The radial parameters are defined[8,9] as

$$\begin{aligned} Dq &= \frac{Ze^2}{6}\cdot\frac{\overline{r_i^4}}{R^5} \\ Dt &= \frac{-2Ze^2}{21}\cdot\overline{r_i^4}\left\{\frac{1}{S^5} - \frac{1}{R^5}\right\} \\ Ds &= \frac{-2Ze^2}{7}\cdot\overline{r_i^2}\left\{\frac{1}{S^3} - \frac{1}{R^3}\right\} \end{aligned} \quad (4)$$

and $\overline{r_i^n} = \langle R(r)|r_i^n|R(r)\rangle$ is the expectation value of power radius. The evaluation of this integral and the consequences of termination at the distance R are discussed in the next section. Z is the effective nuclear charge.

The traditional evaluation of the crystal-field matrix elements proceeds by the substitution of an operator equivalent[6] form of the spherical harmonics. However, in order to facilitate the calculation of magnetic properties, analysis of the crystal field by tensor algebra is more convenient,[10] and the tetragonal Hamiltonian becomes

$$H_{D_{4h}} = \frac{7}{e}\{-DsC_2^0 - 3DtC_4^0 + 3Dq[C_4^0 + (C_4^4 + C_4^{-4})]\} \quad (5)$$

The spherical harmonics have been replaced by Racah's rationalized form which eliminates both the irrational $(\Pi)^{1/2}$ and the degeneracy factor $(2Q + 1)^{1/2}$. The harmonics[10] are

$$C_q^k = [4\Pi/(2Q + 1)]^{1/2}Y_q^k$$

(ii) **The Wave Functions and Matrices of Configuration Interaction.** The crystal-field matrix elements were evaluated using the form of the operator in eq 5 by the application of the Wigner–Eckart theorem. Since the Hamiltonian is a one-electron operator, the two-electron free-ion wave functions were broken into linear combinations of one-electron wave functions by vector-coupling techniques. This treatment is superior to the use of conventional shift operators, since it correctly identifies the phases[11] which are important for the evaluation of spin–orbit coupling. Simultaneously un-

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coupling the wave functions and applying the Wigner–Eckart theorem, the two-electron elements become

$$\langle LM|H_{D_{4h}}|L'M'\rangle = (-1)^{l_1+l_2+M}(2L+1)^{1/2} \times \begin{pmatrix} l_1 & l_2 & L \\ m_1 & m_2 & -M \end{pmatrix} \cdot (-1)^{l_1'-l_2'+M'}(2L'+1)^{1/2} \begin{pmatrix} l_1' & l_2' & L' \\ m_1' & m_2' & -M' \end{pmatrix} \cdot \left[\sum_{qk} \begin{pmatrix} l_1 & q & l_1' \\ -m_1 & k & m_1 \end{pmatrix} \langle l_1||H_{D_{4h}}||l_1'\rangle \cdot \delta_{l_2l_2'} \cdot \delta_{m_2m_2'} + \sum_{qk} \begin{pmatrix} l_2 & q & l_2' \\ -m_2 & k & m_2' \end{pmatrix} \cdot \langle l_2||H_{D_{4h}}||l_2'\rangle \cdot \delta_{l_1l_1'} \cdot \delta_{m_1m_1'}\right] \quad (6)$$

For diagonal matrix elements, the use of this formalism is identical with the operator-equivalent method, but for the off-diagonal elements, the normality conditions are established by the Wigner $3-j$ symbol[12–14] which precede the reduced matrix elements. Thus the normalization constant $(5/14)^{1/2}$ of eq 3 is eliminated in the tensor form of the Hamiltonian in eq 5. The matrix elements are tabulated in Tables I and II.

Table I. First-Order Crystal-Field Wave Functions

D_{4h}	O_h	Free ion
$\|^3B_{1g}\ \iota\rangle$	$\|^3A_{2g}\ \iota\rangle$	$(^1/_2)^{1/2}\|32\rangle - (^1/_2)^{1/2}\|3{-}2\rangle$
$\|^3B_{2g}\ \iota\rangle$	$\|^3T_{2g}\ 0\rangle$	$(^1/_2)^{1/2}\|32\rangle + (^1/_2)^{1/2}\|3{-}2\rangle$
$\|^3E_g\ (T_2F)\ \theta\rangle$	$\|^3T_{2g}\ 1\rangle$	$(^5/_8)^{1/2}\|31\rangle - (^3/_8)^{1/2}\|3{-}3\rangle$
$\|^3E_g\ (T_2F)\ \epsilon\rangle$	$\|^3T_{2g}\ -1\rangle$	$(^5/_8)^{1/2}\|3{-}1\rangle - (^3/_8)^{1/2}\|33\rangle$
$\|^3A_{2g}\ (F)\ \iota\rangle$	$\|^3T_{1g}\ (F)\ 0\rangle$	$\|30\rangle$
$\|^3E_g\ (T_1F)\ \theta\rangle$	$\|^3T_{1g}\ (F)\ 1\rangle$	$(^3/_8)^{1/2}\|31\rangle + (^5/_8)^{1/2}\|3{-}3\rangle$
$\|^3E_g\ (T_1F)\ \epsilon\rangle$	$\|^3T_{1g}\ (F)\ -1\rangle$	$(^3/_8)^{1/2}\|3 - 1\rangle + (^5/_8)^{1/2}\|33\rangle$
$\|^3A_{2g}\ (P)\ \iota$	$\|^3T_{1g}\ (P)\ 0\rangle$	$\|1\ 0\rangle$
$\|^3E_g\ (T_1P)\ \theta\rangle$	$\|^3T_{1g}\ (P)\ 1\rangle$	$\|1\ 1\rangle$
$\|^3E_g\ (T_1P)\ \epsilon\rangle$	$\|^3T_{1g}\ (P)\ -1\rangle$	$\|1\ -1\rangle$

Table II. Medium-Field Matrix Elements from Weak-Field Model

$\langle ^3B_{1g}|H|^3B_{1g}\rangle = 7Dt - 12Dq$
$\langle ^3B_{2g}|H|^3B_{2g}\rangle = 7Dt - 2Dq$
$\langle ^3A_{2g}\ (F)|H|^3A_{2g}\ (F)\rangle = {}^4/_5Ds - 6Dt + 6Dq$
$\langle ^3A_{2g}\ (P)|H|^3A_{2g}\ (P)\rangle = -{}^{14}/_5Ds + 15B$
$\langle ^3A_{2g}\ (F)|H|^3A_{2g}\ (P)\rangle = -{}^{12}/_5Ds + 4Dt - 4Dq$
$\langle ^3E_g\ (T_2F)|H|^3E_g\ (T_2F)\rangle = -{}^7/_4Dt - 2Dq$
$\langle ^3E_g\ (T_1F)|H|^3E_g\ (T_1F)\rangle = -{}^2/_5Ds - {}^9/_4Dt + 6Dq$
$\langle ^3E_g\ (T_1P)|H|^3E_g\ (T_1P)\rangle = {}^7/_5Ds + 15B$
$\langle ^3E_g\ (T_2F)|H|^3E_g\ (T_1F)\rangle = (^3/_5)^{1/2}Ds + (15)^{1/2}Dt/4$
$\langle ^3E_g\ (T_1F)|H|^3E_g\ (T_1P)\rangle = -{}^6/_5Ds - {}^3/_2Dt + 4Dq$
$\langle ^3E_g\ (T_2F)|H|^3E_g\ (T_1P)\rangle = -2(^3/_5)^{1/2}Ds - (15)^{1/2}Dt/2$

Since the distortion parameters Ds and Dt are found only in the diagonal elements, the first-order weak-field wave functions with components can be identified by descent in symmetry from the octahedral solutions (Table I). With these linear combinations and the matrix elements from eq 6, the full energy level secular determinant is available (Table II). Since manual solution of the submatrices for the $^3A_{2g}$ and the ^3E_g terms is very tedious, the eigenvalues were found here by standard programs for matrix diagonalization over ranges of values of the radial parameters.

(iii) Analysis of Radial Parameters. Since the radial parameters arise from the electronic properties, their relationship to the structure of the complex is usually treated by approximate methods. The ratio

$$K = Ds/Dt \quad (7)$$

can vary considerably both in magnitude and *sign*. The definitions of eq 4 require both Ds and Dt to be positive for elongation and negative for compression of a complex from a crystallographically octahedral configuration. Since the integrated mean radii $\overline{r^n}$ are inherently positive, the only source of change of sign of Ds and Dt arises in the nuclear configuration function. As defined both Ds and Dt are obliged to change signs simultaneously when R is equal to S. However, the experimental fact that K can be negative requires that the condition of Ds negative and Dt positive, [Ds −, Dt +], for example, be allowed. This is only possible if the mean radii $\overline{r^n}$ do not have equal equatorial and axial values. We therefore redefine the nuclear function by

$$F(n) = [(1/R^{n+1}) - (A/S^{n+1})] \quad (8)$$

The new anisotropic mean charge ratio A thus describes the nonspherical mean charge which can arise if the axial and equatorial effective nuclear charges are unequal. This inequality, ignored in most previous treatments,[5,8,14] implies that all of the angular dependence of the crystal-field Hamiltonian has not been factored out by the above precedures. The angular dependence common to all D_{4h} complexes is represented by C_2^0 and C_4^0 in eq 5. However, the angular variation induced by the different equatorial and axial contributions to the effective charge of the central field is represented now by A. This factor essentially allows for nonintegral values of the ligand point charges, and its nature is therefore very complex. It can, however, be factored into two main types of contribution. (a) First, there is the *crystal-field* perturbation which allows for the angular charge dependence from chemically different axial and equatorial ligands. These differences may arise from the shielding of the ligand charges or their diffuseness or because of vectorial addition of the secondary crystal field. Thus the complex may display electronic features characteristic of a tetragonal environment yet have equal crystallographic R and S. (b) The *ligand field* perturbation which allows for varying polarizabilities of the axial and equatorial ligands and the possibility that the effective charge contribution is not centered at the ligand donor atom. This is particularly valid in polyatomic ligands. In general, these effects may not be separable, although the ionic contributions (a) can often be identified. It is clear, however, that the definition of tetragonal distortion relevant to the observation of electronic properties is not dependent on geometry alone.[5,15] The fundamental property is the symmetry of the *electric field gradient* around the central ion which is determined by either or both the geometry and the effective charge contributions of the ligands.

It is useful to evaluate A for limiting conditions of signs of Ds and Dt using normal crystallographic bond lengths and the crystal-field assumption that the effec-

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[12] M. Rotenberg, R. Bivens, N. Metropolis, and J. K. Weston, "The $3-j$ and $6-j$ Symbols," Technology Press, Boston, Mass.

[13] D. M. Brink and G. R. Satchler, "Angular Momentum," Clarendon Press, Oxford, 1968.

[14] R. S. Coswell and L. C. Maximon, National Bureau of Standards Technical Note 409, U. S. Government Printing Office, Washington, D. C., 1967.

[15] A. B. P. Lever, *Proc. Int. Conf. Coord. Chem., 1964*, 8, 123 (1964).

tive ligand charges are centered on the donor atom nuclei.

From eq 8, the sign of the nuclear function and hence the distortion parameter $D(n)$ is determined by the inequality

$$\begin{gathered}[(1/R^{n+1}) - (A/S^{n+1})] \lessgtr 0 \\ A \lessgtr S^{n+1}/R^{n+1}\end{gathered} \tag{9}$$

The various possibilities are shown in Table III. If representative bond lengths, *e.g.*, $R = 2.0$ Å, $S = 2.5$ Å, are inserted, the parameter can be evaluated. The two possibilities [Ds +, Dt −] and [Ds −, Dt +] are clearly mutually exclusive. The condition [Ds +, Dt −] *cannot* occur if $S > R$ nor can [Ds −, Dt +] occur if $R < S$. Moreover, the ranges of the parameter A are mutually exclusive. If A falls between 2 and 3 (approximately), then [Ds −, Dt +] is the only allowed condition. It is also important to observe that the range in which the signs of Ds and Dt differ falls in the middle of the range of A values and that this range *vanishes* when $R = S$. Therefore, if the tetragonality of the Hamiltonian is due only to the chemical differences of the axial and equatorial ligands and not to differences in bond lengths, then the two parameters *must* be both negative or both positive.

Table III. Limiting Values of A for an Elongated Complex

Sign of parameter			
Ds	Dt	Inequality	Range of A^a
+	+	$S^5/R^5 > S^3/R^3 > A$	2 to − ∞
+	−	$S^5/R^5 < A < S^3/R^3$	Impossible
−	+	$S^5/R^5 > A > S^3/R^3$	3–2
−	−	$A > S^5/R^5 > S^3/R^3$	>3

[a] $R = 2.0$ Å, $S = 2.5$ A.

It is possible to further clarify the meaning of A. The effective charge and integrated mean radius described in eq 4 represent the average of all individual ligand perturbations. If instead these effects are factored to attribute effective charges and mean radii to both equatorial and axial classes of ligands, then eq 4 may be rewritten

$$D(n) = \frac{1}{(n-1)}\cdot\frac{2e^2}{7}\left(\frac{Z_E\overline{r_E{}^n}}{R^{n+1}} - \frac{Z_A\overline{r_A{}^n}}{S^{n+1}}\right) = \frac{2e^2}{7(n-1)}Z_E\overline{r_E{}^n}\left(\frac{1}{R^{n+1}} - \frac{A}{S^{n+1}}\right) \tag{10}$$

where Z_A and Z_E are the effective axial and equatorial nuclear charges and in which

$$A = Z_A\overline{r_A{}^n}/Z_E\overline{r_E{}^n}$$

is the ratio of the products of effective charges and the integrated mean radii for the axial and equatorial ligands, respectively. However, the mean radii are themselves functions of the effective charges as well as of the metal–ligand distances. Before the effect of A on the magnitudes of the distortion parameters $D(n)$ can be predicted, therefore, the analytical dependence of the integrated mean radii on the effective charge needs to be defined. Using normalized hydrogenic wave functions, $\overline{r^n}$ is evaluated with an analytical integration which for 3d orbitals is[16]

$$\overline{r^n} = \left(\frac{4Z^3}{81(30)^{1/2}a_0{}^3}\right)^2 e^{-10Zr/3a_0} \times \left.\sum_{j=0}^{n+6}\frac{(-1)^j(n+6)!\,r^{n+6-j}}{(n+6-j)!\left(\dfrac{8Z}{3a_0}\right)j+1}\right]_0^R \tag{11}$$

The integration is evaluated for the in-plane metal–ligand bond distance R.

The maxima of both $\overline{r^2}$ and $\overline{r^4}$ for a given value of effective central charge Z coincide within computational error as has recently been observed.[17] Because of this, the polynomial sum can be replaced by a logarithmic function and the integral simplified to

$$\overline{r^n} = \gamma_n R^n e^{-1.90ZR}\ln(1.90ZR) \tag{12}$$

in which $\gamma_4 = 0.12806$ and $\gamma_2 = 0.05286$.

This simple model is inadequate for the calculation of Dq.[18] It fails to recognize the overlap of metal d orbitals with those from the ligand and hence the covalency terms which account for the greatest part of the magnitude of Dq. The calculations which have had some success have all been based on an LCAO approximation.[18–20] However, both eq 11 and 12 are essentially evaluations of $\overline{r^n}$ using one wave function of a complete basis set of single-center Slater-type orbitals. Therefore while the magnitude of the observed perturbation is very much greater, the calculated shape of $\overline{r^n}$ is probably similar to its true distribution.

Using this assumption, then from eq 10 and 12

$$A = \frac{Z_AS^ne^{-1.90Z_AS}\ln Z_AS}{Z_ER^ne^{-1.90Z_ER}\ln Z_ER} \tag{13}$$

for constant R. For small differences between Z_A and Z_E, the magnitude of A depends essentially on the ratio of the axial and equatorial integrated mean radii. The plot of $\overline{r^n}$, eq 12, Figure 2, demonstrates for normally anticipated values of the effective charge, 0.6–1.2, that this function is highly dependent on Z. In this region, a difference of 0.1 in effective charge between axial and equatorial ligands implies a factor of two between the magnitudes of $\overline{r_A{}^n}$ and $\overline{r_E{}^n}$. This behavior must be reflected by the ratio A and hence by the magnitudes of the distortion parameters themselves. Thus, by the *formal* recognition of an effective charge difference between classes of ligands, very much larger values of the distortion parameters may be predicted than would be anticipated from a purely geometric distortion mechanism.

The strongly negative value of the $\overline{r^n}$ for Z less than 0.25 is bad behavior caused by the truncation of the integral at $r = R$ (eq 11). The lowest value of Z for which the model is valid is certainly higher than 0.5. For the more covalent situations a central field theory explicitly involving metal–ligand overlap[21] is required.

Changing the sign of the ligands to positive implies only that the effective central charge is increased rather

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(20) D. R. Davies and G. A. Webb, *Coord. Chem. Rev.*, **6**, 95 (1971).

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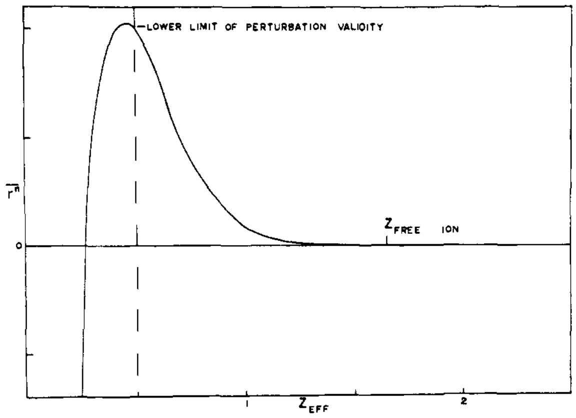

Figure 2. The behavior of the mean power radii with effective central charge. The metal–ligand distance is 2.0 Å.

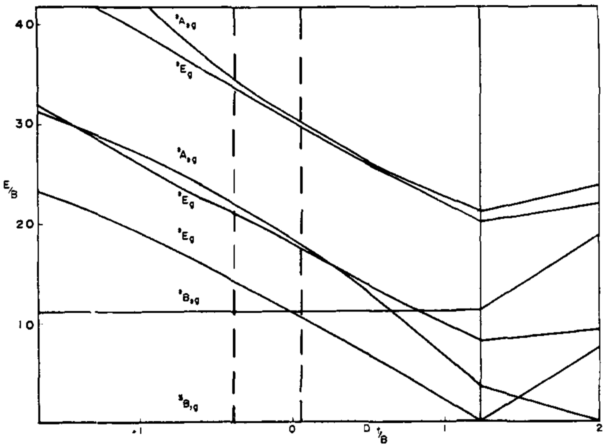

Figure 3. Transition energy diagram for $Ds/B = -0.045$. The range of expected spectra for physically reasonable complexes with $R = 2.0$ Å lies between the vertical dashed lines. Only positive values of Dt/B are predicted, and all complexes have a $^3B_{1g}$ ground term ($Dq = 1000\ \text{cm}^{-1}$, $B = 900\ \text{cm}^{-1}$).

than decreased from its free-ion value. Thus, a complex with positive ligands on the axis, for example, would appear in eq 10 to have a very small value of A. However, it is possible that the presence of the positive charge could stabilize a different ionic ground term; this would place a strong negative contribution close to the nucleus and from eq 12 implies a large increase in magnitude of both $\overline{r^2}$ and $\overline{r^4}$. Moreover, since this increase is achieved with a *positive* ligand, the parameter A would become *negative* in sign. As shown in Figure 1, the effective charge of the axial ligand changes sign in a polymeric environment in which the negative axial ligand is surrounded by a strong positive field. The secondary ligand field is not generally octahedral and can exert its own influence on the splitting of the central ion levels, further distorting the complex. The effect of both this perturbation and the change of ground term is measured in the sign and magnitude of A.

(iv) The Tanabe–Sugano Distortion Space. The electronic spectra of tetragonally distorted d^8 complexes can now be predicted for all values of Ds and Dt. It is convenient to construct a transition energy distortion space by analogy with conventional crystal-field Tanabe–Sugano diagrams[8] from the energy level space described above. The energy surfaces within this space are found using the matrices derived from Table II, and

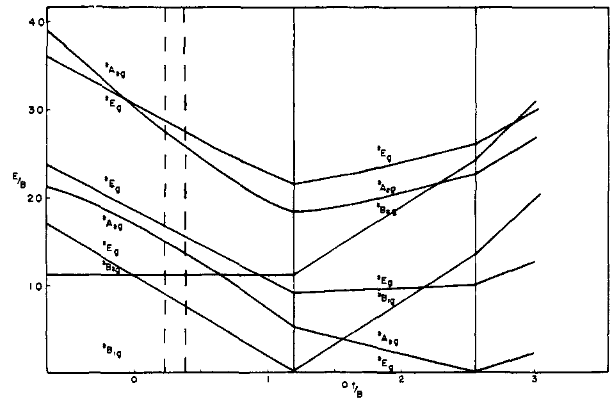

Figure 4. Transition energy diagram for $Ds/B = 0.67$. The range of expected spectra is limited to positive Dt/B and a $^3B_{1g}$ ground term ($Dq = 1000\ \text{cm}^{-1}$, $B = 900\ \text{cm}^{-1}$).

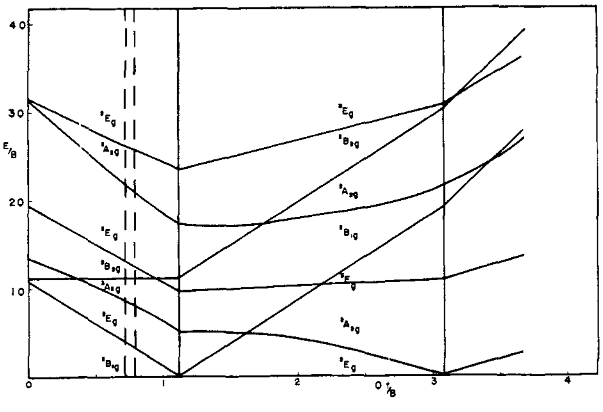

Figure 5. Transition energy diagram for $Ds/B = 1.83$. The range of expected spectra is very narrow near the chemical origin. A is negative, but the complex still has a $^3B_{1g}$ ground term ($Dq = 1000\ \text{cm}^{-1}$, $B = 900\ \text{cm}^{-1}$).

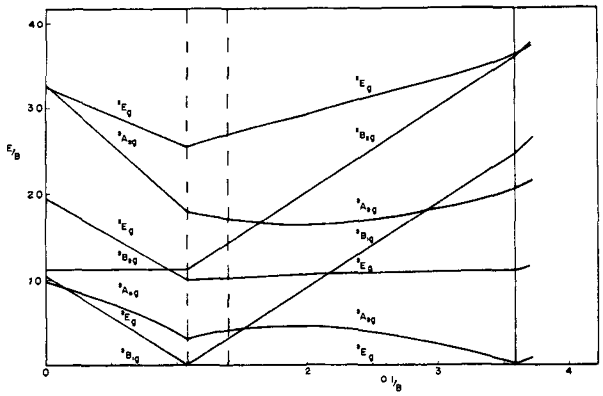

Figure 6. Transition energy diagram for $Ds/B = 2.90$. All of the expected spectra have Dt/B positive, A negative, and a ^3E_g ground term ($Dq = 1000\ \text{cm}^{-1}$, $B = 900\ \text{cm}^{-1}$).

the spectrum of any individual complex is represented by a line parallel to the E/B axis.

It is convenient to examine some cross sections taken parallel to the E/B axis holding one distortion parameter constant. Typical cross sections are shown in Figures 3–6. These are constructed for constant Ds, as they were found to be the most informative. They are also necessarily constructed with constant Dq. Change of Dq will simply expand or contract the diagrams ac-

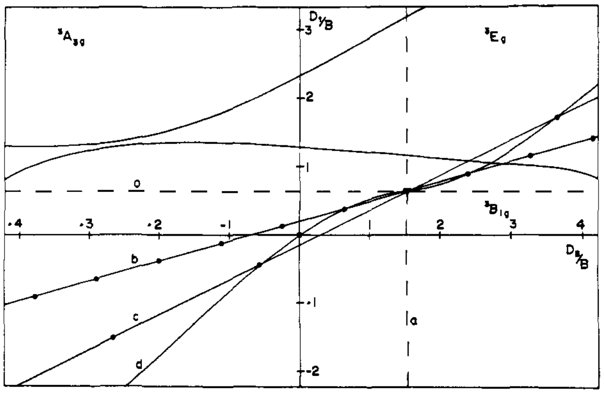

Figure 7. The energy base of the transition energy distortion space. The geometric origin (■) representing the octahedron is at $Ds/B = Dt/B = 0$. The chemical origin (▼) at which $A = 0$ occurs at $Ds/B = 1.52$, $Dt/B = 0.63$ (see text) for a parametric ratio of 2.4. Lines a define the axes of the chemical base plane, and all physically possible complexes must occur in the first or third quadrant. Lines b and c are isogeometric lines for $R = 2.0$ Å, $S = 1.8$ and 2.4 Å, respectively, defining the conic section of physically most probable compounds. The points on these lines are integer values of A increasing with decreasing Ds/B and Dt/B. Curve d is the isochemical curve for $A = \pm 1$ ($Dq = 1000\ \text{cm}^{-1}$, $B = 900\ \text{cm}^{-1}$).

cording to an increase or decrease in Dq, respectively. The value of Dq chosen is appropriate to tetragonal nickel complexes with nitrogenous ligands.

Some important features are immediately apparent. With increasing positive Dt/B, all levels except $^3B_{2g}$, which is separated from $^3B_{1g}$ by $10Dq$, decrease rapidly in energy. At the same time, the interterm separations remain relatively unchanged except for their relationship to the $^3B_{2g}$ level, and the whole spectrum simply appears to be shifted to lower energies. At a point $Dt/\text{B} \simeq +{}^4/_3$, which is almost independent of Ds, the ^3E_g ground term occurs. At this point all the transition energies with the exception of that to $^3A_{2g}$ begin to increase so that the most compressed spectrum appears at the point of change of orbital ground term. A characteristic feature of the ^3E_g ground-term spectroscopic region is that the $^3B_{1g}$ and $^3A_{2g}$ levels must cross. This usually occurs at very low transition energies, $E/B \simeq 3$, and is relatively independent of both Ds and Dt. Therefore, the spectra of ^3E_g ground-term complexes would normally display only four or occasionally five transitions in accessible energy regions. For positive values of Dt/B, there is little possibility of any bands occurring above $E/B \simeq 25$, but in most cases two transitions would occur with energies less than $E/B \simeq 7$.

A key problem in the analysis of tetragonal spectra is the correct identification of the transitions involved. In the absence of unequivocal techniques such as polarized single-crystal spectra or MCD studies, attempts are made to solve the energy matrices with various permutations of the input observed energies.[2] In favorable cases, one particular assignment will solve the matrices, yielding chemically acceptable values of the radial parameters,[22] but this does not always occur. The possibility that complexes whose spectra have in the past been satisfactorily assigned in terms of a $^3B_{1g}$ ground term really possess a ^3E_g ground term is very real. A cursory examination of Figures 3–6 reveals various regions of the distortion space involving various ground terms where spectra of similar appearance at least in terms of transition energies may be expected.

As will be discussed below, the entire space is not relevant to real complexes, so many, but not all, of these coincidences can be ignored.

Nevertheless, it is very desirable in these tetragonal systems to use alternative methods to identify the ground term before attempts are made to solve the spectra. The magnetic properties of $^3B_{1g}$ and ^3E_g ground terms are distinctly different. The magnetic moment of a $^3B_{1g}$ ground term is essentially independent of temperature (except in the presence of a large zero-field splitting) but includes a substantial second-order orbital contribution and an important temperature-independent paramagnetism term. The magnetic moment of a ^3E_g ground term,[22] by contrast, is temperature dependent and highly anisotropic. There is a first-order orbital contribution to the moment and except for zero-field splittings, the ground term is magnetically isolated and there are no contributions from either second-order distortion of the g tensor or temperature-independent paramagnetism.

The ^3E_g ground term, unlike the $^3B_{1g}$, displays temperature-dependent C terms in the MCD spectra, and this technique can aid in the identification of excited levels.[23]

Physical Significance of Radial Parameters

The Tanabe–Sugano distortion space derived in the preceding section illustrates the wide range of spectra predicted from a straightforward application of the crystal-field Hamiltonian. Most of these solutions are not observed experimentally in real complexes,[2] however, and a discriminatory theory defining the limits of physically achievable complexes would be very useful.

The angular part of the Hamiltonian can only be used to define the ranges of the distortion parameters in which the various possible ground terms occur, as is shown on the energy base of the distortion space (Figure 7) (*vide supra*).

Using the radial Hamiltonian, it is possible to predict semiquantitatively the regions in which physically possible complexes are expected. By setting the anisotropic mean charge ratio equal to zero, a chemical origin of the space is obtained which is quite distinct from the geometric origin in which the bond lengths are equal. From eq 10 and 12, the two radial parameters can be written as

$$Ds = \frac{2}{7}Z_Ee^2\gamma_2R^2 \times \ln\,(1.90Z_ER)e^{-1.90Z_ER}\left(\frac{1}{R^3} - \frac{A}{S^3}\right)$$

$$Dt = \frac{2}{21}Z_Ee^2\gamma_4R^4 \times \ln\,(1.90Z_ER)e^{-1.90Z_ER}\left(\frac{1}{R^5} - \frac{A}{S^5}\right) \tag{14}$$

When A vanishes, these become

$$Ds = \gamma_2\,\text{f}(Z_ER)$$

$$Dt = \frac{\gamma_4}{3}\text{f}(Z_ER) \tag{15}$$

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[22] J. C. Donini, B. R. Hollebone, and A. B. P. Lever, manuscript in preparation.

[23] B. R. Hollebone, S. F. Mason, and A. J. Thomson, *Symp. Faraday Soc.*, No. 3, 146 (1969).

in which

$$f(Z_ER) = \frac{2Z_Ee^2 \ln (1.90Z_ER)e^{-1.90Z_ER}}{7R}$$

At the chemical origin, using eq 9, Dt becomes $^4/_7Dq_{xy}$.[24] A similar definition of the second-order radial parameter is possible, *i.e.*

$$Ds = \frac{8}{7}Dp_{xy}$$

in which

$$Dp = \frac{1}{4}Z_Ee^2\frac{\overline{r^2}}{R^3} \tag{16}$$

The new second-order parameter Dp, defined from the second-order one-electron crystal-field matrix elements by analogy with Dq,[8] is not observed in octahedral systems, not because it has no intrinsic magnitude, but because the angular part of the Hamiltonian vanishes. In principle, however, it could be measured directly in a high-spin square-planar complex in which the axial field is zero. At any other point in the energy space

$$\begin{aligned} Ds &= \frac{8}{7}(Dp_{xy} - Dp_z) \\ Dt &= \frac{4}{7}(Dq_{xy} - Dq_z) \end{aligned} \tag{17}$$

The position of the chemical origin depends on the evaluation of the parameter ratio γ_2/γ_4. (This ratio is equivalent to previous formulations but not identical because of the factorization in eq 14.) Opinions of the value of this ratio have varied greatly, but some recent spectroscopic[24] and kinetic[25] data indicate that it is less than unity. Theoretically, in spite of the aforementioned inadequacy of the central field calculations of the magnitude of $\overline{r^n}$, it is clear from eq 11 that a hydrogen-like basis set yields $\overline{r^2} < \overline{r^4}$. Using a value of 0.80 for this ratio[22] and thus a ratio of Ds to Dt of 2.4, the chemical origin can be placed on the energy base of the distortion space as shown in Figure 7. Isogeometric lines in which R and S are held constant and A is varied can then be plotted using eq 14. Any complex with this geometry and parametric ratio must fall as a point on this line, and, with experimental knowledge of Ds and Dt, the chemical parameter A can be determined. Conversely, isochemical curves crossing the isogeometric plots can be drawn, as shown for $A = \pm 1$ in Figure 7, so that geometries can be predicted from the chemical information. All the isogeometric lines have positive slope. As the slope approaches zero and the line parallels the Ds axis, it also contracts to an infinitely short line, as can be seen from the isochemical curve. Approaching this limit, the axial ligand is being removed and the chemical factor A, which becomes increasingly less important, is irrelevant in the limit. All isogeometric lines with slopes less than the parametric ratio represent elongated systems, as was predicted in Table III. The line which would pass through the two origins does not exist because at the octahedral configuration the angular Hamiltonian vanishes. Lines with slopes greater than the parametric ratio represent compressed systems. As the slope is further increased, the chemical factor is increasingly more important and becomes the dominant factor as the ligand coalesces with the central ion in the limit of infinite slope parallel to the Dt axis. Obviously, no complexes can fall outside this region and most chemically observed systems would be expected to fall within a narrow conic section represented by ratios of S/R between approximately 1.4 (elongated) and 0.8 (compressed), as shown in Figure 7.

Applying this model, the maximum values of Dt and Ds with positive values of A are $^4/_7Dq_{xy}$ and $^8/_7Dp_{xy}$, respectively. However, it is clear from the distortion space diagrams that a ^3E_g ground term cannot be achieved with such values of the radial parameters. Therefore, for a ^3E_g ground term to exist, A must be negative. In a physical sense, the system must become more distorted than is achievable with the complete removal of a negative ligand or its neutralization. The electronic configuration of the ground state must change, and in a strong-field sense this can be written as the transition

$$^3E_g(d_{z^2})^2(d_{xz,yz})^3 \leftarrow {}^3B_{1g}(d_{z^2})(d_{xz,yz})^4 \tag{18}$$

The other hole remains in $(d_{x^2-y^2})$. The ^3E_g ground state is stabilized by the absence of any negative ligand or more strongly by the presence of a positive ligand on the axis. The electron either remains nonbonding or becomes more binding in nature in the ^3E_g ground state compared to its nature for the $^3B_{1g}$ ground state. This movement of charge due to the presence of a positive ligand places *more negative charge* on the axis than was present for the $^3B_{1g}$ ground term because the maximum probability of the electron is closer to the central charge than any negative ligand could be. Thus, the effective central nuclear charge is reduced, and from Figure 2 it can be seen that $\overline{r^n}$ and hence Ds and Dt should increase. The new axial electron becomes increasingly localized with the approach of a positive ligand and thus the A factor describing the effect of such a ligand must have a negative value. With such values of A, achieved with geometries such as described in Figure 1, compounds would be expected in the first quadrant of the energy base *beyond* the chemical origin. The same limiting conditions described above for $^3B_{1g}$ ground terms are applicable, and the region of chemically achievable complexes is again restricted to a narrow conic section (Figure 7).

These conclusions greatly simplify the problem of spectroscopic analysis of complexes with ^3E_g ground states. With reasonable values of the parametric ratio obtained from $^3B_{1g}$ ground-state systems, most ^3E_g ground-term complexes will fall in the low Dt part of the ^3E_g region. Thus, the order of excited energy levels can be defined from the Tanabe–Sugano diagrams as $^3B_{1g} < {}^3A_{2g}$ (F) $< {}^3E_g$ ($^3T_{1g}$ (F)) $< {}^3B_{2g} < {}^3A_{2g}$ (F) $<$ ^3E_g (T_{1g} (P)) (Figure 6). Furthermore, it is probably impossible to ever achieve a complex with a $^3A_{2g}$ ground term because the conic section of highest probability never approaches this region of the distortion space.

The Chemistry of Complexes with a ^3E_g Ground Term

From these considerations, the chemistry of complexes with a ^3E_g ground term is closely defined. No isolated complex with six negative ligands can possess

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a ^3E_g ground term. Such a term can be stabilized by positive axial ligands, which emphasizes the importance of further studies in this largely neglected area of ligand chemistry. Aside from the previously discussed case of positive effective axial charges in polymeric complexes, no other systems appear to have been studied in which positive ligands are unequivocally placed in the first coordination sphere. An obvious candidate for this kind of chemistry would be an amine-bridged ligand in which an axial nitrogen fixed in relation to the plane has been quaternized.

It may be possible for high-spin square-planar nickel to exist with a ^3E_g ground term. However, this depends on the π-donor ability of the equatorial ligands. For a purely ionic or σ-bound complex, high-spin square-planar complexes could exist only at the chemical origin, since S is infinite and the value of A is irrelevant. Such complexes could only have a $^3B_{1g}$ ground term. If, however, the equatorial ligands were strong π donors, the interelectron repulsion in the d_{xz}, d_{yz} orbitals would be increased[26] to the point where the rearrangement to the ^3E_g ground term would occur. In the present formalism, this implies a finite *apparent* value of S. That is, the z component of the equatorial π-donor orbitals is equivalent to the presence of an axial positive charge and A again will have a substantial negative magnitude. It appears to be relevant that recently reported nickel complexes purporting to be high-spin square planar[27] were prepared with π-donating equatorial ligands and display high magnetic moments which would most easily be described with a ^3E_g ground term. The salicylate ligands employed also create a very small Dq_{xy} splitting which further promotes the stabilization of this ground term.

Throughout this treatment, it has been assumed that the spin singlet terms can be ignored. It is obvious from the calculations on these levels that for large values of Dq the $^1A_{1g}$ level soon becomes the ground term as Ds and Dt increase. No high-spin complexes of tetragonal nickel have been observed with Dq values greater than about 13 kK.[28] For this reason, as well as the fact that the position of the chemical origin depends on the value of Dq, high-spin tetragonal complexes with ^3E_g ground terms are expected only with relatively low values of this parameter. The influence of the spin singlets cannot be predicted with greater precision because of the very large discontinuity in Dq when spin pairing occurs. The change in values of $10Dq$ is 3–4 kK[28] because of shortening of the equatorial bond distance and the consequent shift in the chemical origin means that this rearrangement cannot be displayed in a three dimensional diagram.

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Isocyanide–Nickel(0) and –Palladium(0) Complexes Involving Unsaturated Ligands

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Abstract: The complexes $ML(\textit{tert}\text{-BuNC})_3$, $ML(\textit{tert}\text{-BuNC})_2$, and $ML_2(\textit{tert}\text{-BuNC})_2$ (L = tetracyanoethylene, fumaronitrile, maleic anhydride, dimethyl maleate, azobenzene, dimethyl acetylenedicarboxylate, and diphenylacetylene) have been prepared; all three complex types were prepared for M = Ni, but for M = Pd only complexes of formula $ML(\textit{tert}\text{-BuNC})_2$ were isolated. Ir and ^1H nmr data have been used to suggest structures for the complexes in solution. For many of the complexes $ML(\textit{tert}\text{-BuNC})_2$, the ir NC stretching frequencies (a and b modes) increase linearly with an increase in the electronegativity of L. A plot of the stretch–stretch interaction $[\Delta\nu(\text{a}-\text{b})]$ against the electron affinity of L appears to provide an even better measure of metal–ligand back-bonding.

A few transition metal complexes have been proven to be versatile for the preparation of a wide variety of compounds containing an olefin, acetylene, or related π acid. Among such complexes are Vaska's complexes of iridium(I)[1-3] and the tertiary phosphine complexes of platinum(0).[4] Study of the ir CO stretching frequencies for complexes incorporating unsaturated molecules linked to Vaska's compounds has provided important information on the bonding of the unsaturated ligand to the metal. An approximate linear relation between ν_{CO} and the electron affinity of the unsaturated ligand has been observed and discussed[5,6] on the basis of the Dewar–Chatt–Duncanson (DCD) model of bonding.[7a,b] Such an argument is relevant only if the complexes are isostructural, since

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