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York University, Downsview, Ontario M3J 1P3, Canada

Application of the Normalized Spherical Harmonic (NSH) Hamiltonian and of Ground-State Energy Space Diagrams to the Tetragonal Field

J. C. DONINI, B. R. HOLLEBONE, G. LONDON, A. B. P. LEVER,* and J. C. HEMPEL

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The consequences of applying the normalized spherical harmonic Hamiltonian to molecules of tetragonal symmetry are discussed theoretically and illustrated with data for C_{4v} and D_{4h} complexes of nickel(II), cobalt(II), and chromium(III) obtained from the literature. Related D_{2d} and C_{2v} systems are briefly included. The magnitude of the ratio DT/DQ is shown to be a useful measure of the degree of tetragonal distortion and, in certain circumstances, to indicate, that in a five-coordinate square-pyramidal complex, the metal is out of the molecular plane. The use of ground-state energy space diagrams for both synthetic and theoretical purposes is discussed with particular reference to limits of linear and square-planar bonding and positive ion ligands.

Studies of the electronic spectra of tetragonal complexes have played an important role in the development of ligand field theory and its application to noncubic ligand fields.[1-14] Almost without exception authors have chosen to describe a tetragonally distorted molecule of D_{4h} symmetry in terms of the Hamiltonian

$$\mathcal{H}_{D_{4h}} = Dq\,[Y_4{}^0 + (\sqrt{5/14})(Y_4{}^4 + Y_4{}^{-4})] + DsY_2{}^0 + DtY_4{}^0 \qquad (1)$$

or an equivalent version utilizing Racah-rationalized harmonics. As has, for example, been pointed out by Ballhausen[15] this is incomplete since it omits an off-diagonal fourth-order contribution to Dt. While eq 1 may and has been used to describe the eigenvectors and eigenvalues appropriate to the tetragonal field, the omission of the off-diagonal contribution has hindered the development of a model which can successfully obtain chemical information from the magnitudes of the noncubic parameters.

We have recently proposed[16] that molecules of noncubic symmetry be treated in terms of a Hamiltonian composed of linear combinations of normalized tensor components transforming as representations of one of the cubic groups. Generally this cubic group will be O_h if the molecule of interest belongs to one of the subgroups of O_h. A primary advantage of this approach is the standardization it offers. Thus unless the molecule is highly distorted leading to ambiguity in the appropriate cubic group to choose, the Hamiltonian may be written down succinctly, rapidly, and uniquely, from tabulated lists of tensor components. Moreover the magnitudes of the parameters which may be derived using such a Hamiltonian are independent of the coordinate axis of choice.

This last property arises directly as a consequence of choosing to express the tensor components in terms of normalized spherical harmonics (NSH). In this paper we demonstrate that the use of a NSH Hamiltonian to describe the tetragonal field leads to insights not previously recognized or recognized only imperfectly.

Clearly the appropriate cubic group to use in the case of six-coordinate tetragonally distorted molecules, is O_h. Recognizing that the Hamiltonian must transform as the totally symmetric representation of the group concerned and that this representation in D_{4h} is subduced[7,16,17] by A_{1g} and E_g in O_h, the Hamiltonian may be written in tensor component form as

$$\mathcal{H}_{D_{4h}} = |A_{1g}i|_{O_h} + |E_g\theta|_{O_h} \qquad (2)$$

where the appropriate component labels are included. With the standard choice of coordinate axes[18] the Hamiltonian may be written in terms of Racah-rationalized harmonics as[16]

$$\begin{aligned}\mathcal{H}_{D_{4h}} &= DQ|A_{1g}i|^4{}_{O_h} + DS|E_g\theta|^2{}_{O_h} + DT|E_g\theta|^4{}_{O_h} = \\ &DQ[(\sqrt{7}/\sqrt{12})C_4{}^0 + (\sqrt{5}/\sqrt{24})(C_4{}^4 + C_4{}^{-4})] + \\ &DSC_2{}^0 + DT[(-\sqrt{5}/\sqrt{12})C_4{}^0 + \\ &(\sqrt{7}/\sqrt{24})(C_4{}^4 + C_4{}^{-4})] \qquad (3)\end{aligned}$$

where the second- and fourth-order nature of the individual terms is noted. The parameters DQ, DS, and DT are fully capitalized to relate them to the corresponding crystal field parameters yet emphasize their distinction. There is now an explicit off-diagonal contribution to the magnitude of the DT parameter. The parameters of the classically used Hamiltonian and the NSH Hamiltonian are related by

$$\begin{aligned}DS &= -7Ds \\ DT &= (7\sqrt{15}/2)Dt \\ DQ &= (6\sqrt{21})Dq - (7\sqrt{21}/2)Dt\end{aligned} \qquad (4)$$

and the energies of the d^1 representations become

$$\begin{aligned}E(a_{1g}) &= (1/\sqrt{21})DQ - (\sqrt{5}/7\sqrt{3})DT + (2/7)DS \\ E(b_{1g}) &= (1/\sqrt{21})DQ + (\sqrt{5}/7\sqrt{3})DT - (2/7)DS \\ E(b_{2g}) &= -(2/3\sqrt{21})DQ - (4\sqrt{5}/21\sqrt{3})DT - (2/7)DS \\ E(e_g) &= -(2/3\sqrt{21})DQ + (2\sqrt{5}/21\sqrt{3})DT + (1/7)DS\end{aligned} \qquad (5)$$

Note that with this Hamiltonian the tetragonal distortion splits the e_g and t_{2g} levels of the octahedron in a fashion which obeys the center of gravity[19] rule for *both DS* and *DT* in contradistinction to the classical approach.[15] In the limit of octahedral symmetry when DS and DT are zero, the tensor Hamiltonian yields values of DQ which are greater than those of the classically used Hamiltonian by the factor $6(21^{1/2})$.

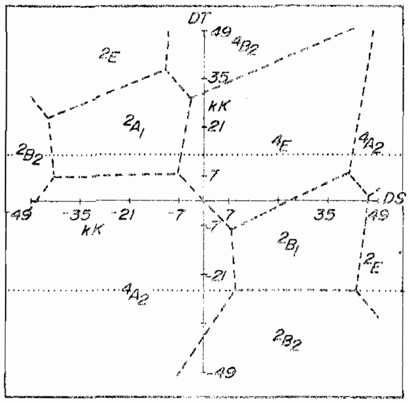

Figure 1. Ground-state energy space diagram for a d^7 species in a tetragonal field; $DQ = 30{,}000$, $B = 700$, and $C = 3000$ cm^{-1}; *DS vs. DT.*

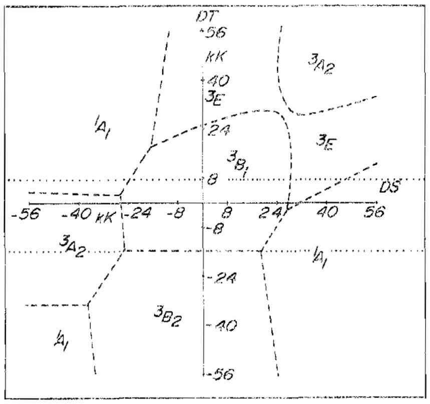

Figure 2. Ground-state energy space diagram for d^8 species in a tetragonal field; $DQ = 18{,}000$, $B = 800$, and $C = 3000$ cm^{-1}; *DS vs. DT.*

Two additional parameters derived from the spectra of tetragonal molecules such as *trans*-ML_4Z_2 are Dq_L and Dq_Z, the magnitudes of the crystal field parameter in the hypothetical octahedral ML_6 and MZ_6, respectively.[14,20] In the NSH Hamiltonian these quantities are related to those preceding through

$$\begin{aligned} DQ &= (1/6)(4DQ_L + 2DQ_Z) \\ DT &= (1/3)(\sqrt{5}/\sqrt{7})(DQ_L - DQ_Z) = \\ &\quad (1/2)(\sqrt{5}/\sqrt{7})(DQ - DQ_Z) = (\sqrt{5}/\sqrt{7})(DQ_L - DQ) \end{aligned} \qquad (6)$$

It is clear that *DQ*, the modifier of the totally symmetric fourth-order tensor component, is a measure of the average ligand field experienced by the metal ion, unlike the classical *Dq* which is a measure of the in-plane ligand field.

The energy of the ${}^3B_{2g} \leftarrow {}^3B_{1g}$ transition, formerly $10Dq$, is now seen to be for the d^8 system

$$E({}^3B_{2g} \leftarrow {}^3B_{1g}) = (\sqrt{25}/\sqrt{189})DQ + (\sqrt{5}/\sqrt{27})DT \qquad (7)$$

revealing that the energy of this band is indeed a function of the axial distortion.[9,11,14] Moreover it is now possible for the ${}^3B_{2g}$ state to become the ground state, for appropriate values of *DQ* and *DT*. Previously this possibility was not considered since this state lay $10Dq$ above ${}^3B_{1g}$ and *Dq* is regarded, generally, to be positive (*vide infra*).

For completion we note the relationship between McClure's parameters[21] and the NSH parameters, *viz.*

$$\begin{aligned} d\sigma &= (1/28)(6DS - (\sqrt{15})DT) \\ d\pi &= (1/14)(3DS + 2(\sqrt{5}/\sqrt{3})DT) \end{aligned} \qquad (8)$$

Ground-State Energy Space Diagrams

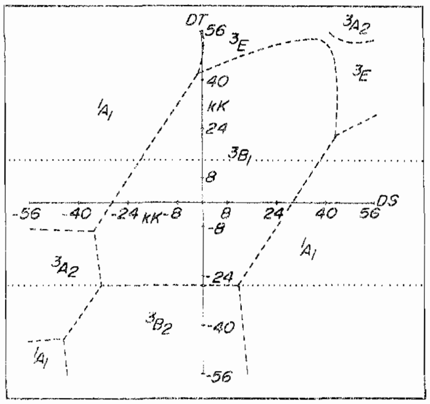

Figure 3. Ground-state energy space diagram for a d^8 species in a tetragonal field; $DQ = 31{,}800$, $B = 800$, and $C = 3000$ cm^{-1}; *DS vs. DT.*

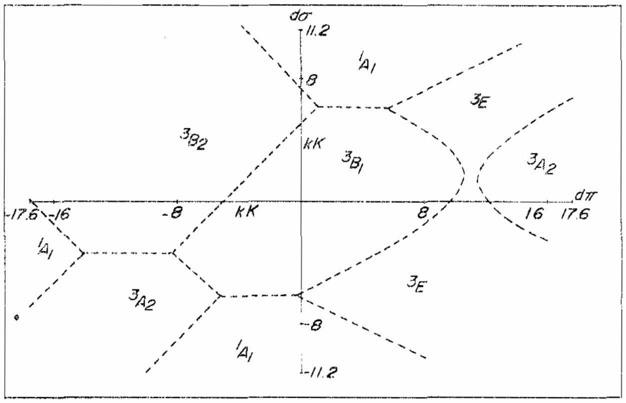

Figure 4. Ground-state energy space diagram for a d^8 species in a tetragonal field; $DQ = 18{,}000$, $B = 800$, and $C = 3000$ cm^{-1}; dσ *vs.* dπ.

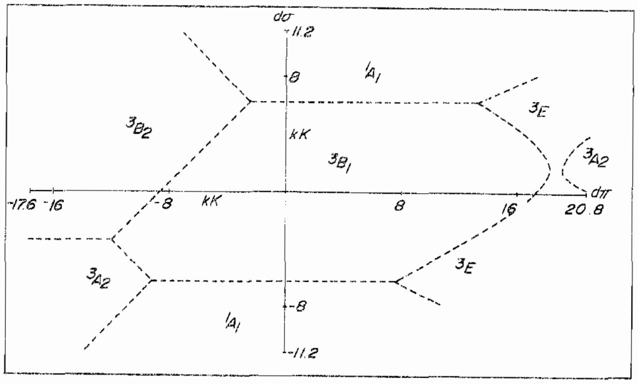

Figure 5. Ground-state energy space diagram for a d^8 species in a tetragonal field; $DQ = 31{,}800$, $B = 800$, and $C = 3000$ cm^{-1}; dσ *vs.* dπ.

Such diagrams portray at a glance the ground states theoretically accessible for a given configuration in a tetragonal (or other) environment.[7,22] They are a cross section of the multiparameter space, at $E = 0$. Any excited state which can, for some combination of the variables, become the ground state, must intersect this cross section. Since the tetragonal system, inclusive of all possible spin states, is characterized by five variables (*DQ*, *DS*, *DT*, *B*, and *C*), it is necessary to hold certain of these constant. In common with other authors we assume a fixed value of the *C*/*B* ratio (3.75) and also maintain *DQ*, the average field, constant at a value appropriate to the complexes under discussion. Figures 1–3 illustrate such diagrams for d^3, d^7, and d^8 tetragonal complexes in terms of *DS vs. Dt.* Figures 4 and 5 illustrate such diagrams constructed in terms of the McClure parameters for d^8 species of low and high *DQ* values, respectively, and Figure 6 is likewise for a d^7 species.

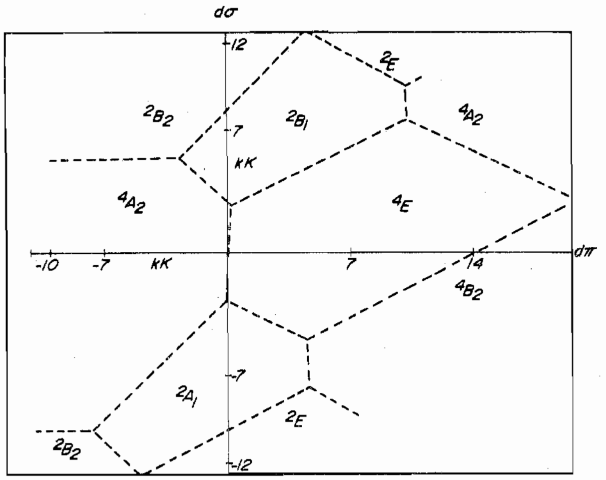

Figure 6. Ground-state energy space diagram for a d^7 species in a tetragonal field; $DQ = 30{,}000$, $B = 700$, and $C = 3000\ \text{cm}^{-1}$; dσ *vs.* dπ.

Before discussing briefly the means by which such diagrams may be used for chemical design, it is relevant to ask whether all regions of the diagrams are accessible for real molecules. We have discussed this question in the past[7] in terms of a parameter A, being a measure of the chemical rather than the geometric distortion; *i.e.*, it is a measure of the difference in chemical bonding between the ligands L and Z in a complex *trans*-ML_4Z_2. However further development of this parameter requires structural information which is not yet available. An alternative approach is suggested here.

The tetragonal distortion of an octahedron, be it chemical or geometric can occur in two different fashions. The axial field may become less than the equatorial field and may approach zero, in which case the four-coordinate square-planar, ML_4, limit is achieved. Alternatively the axial field may be stronger than the equatorial, and in the limit of infinite axial field, or zero equatorial field, the linear MZ_2 limit is achieved.

(i) Square-Planar Limit. At this limit DQ_Z is zero. Insertion of this value into eq 5 leads to

$$\begin{aligned} DT &= (1/2)(\sqrt{5}/\sqrt{7})DQ \\ DT/DQ &= (1/2)(\sqrt{5}/\sqrt{7}) \cong 0.4226 \end{aligned} \tag{9}$$

There is therefore an upper limit for the DT/DQ ratio when the molecule becomes square planar. This limit should not be exceeded except in certain special cases which will be considered below. This limit is shown, for a typical value of B, as a dotted line in Figures 1–3 at positive DT. The implication of this limit is that all complexes for which the axial field strength is less than the equatorial field strength (including five-coordinate C_{4v} ML_5 derivatives in which the metal lies in the equatorial plane) lie within the area bounded by $DT/B = 0$ and the dotted limit line.

(ii) Linear Limit. At this limit, DQ_L is zero. Insertion of this value in (5) yields

$$\begin{aligned} DT &= -(\sqrt{5}/\sqrt{7})DQ \\ DT/DQ &= -(\sqrt{5}/\sqrt{7}) \cong -0.8452 \end{aligned} \tag{10}$$

This limit is indicated as a dotted line at negative DT. With the exception of the special cases alluded to below, all real complexes should lie within the area bounded by the square-planar and linear limits.

The special cases arise if either DQ_L or DQ_Z can become negative. Thus for example the $^3B_{2g}$ ground state in Figure 2 lines outside the accessible region defined by these limits but becomes accessible if negative DQ_L values are admitted. Given that DQ_L is related to the orbital angular overlap model parameters through[7,23]

$$DQ_L = (3\sqrt{21}/5)(3e'_{\sigma L} - 4e'_{\pi L}) \tag{11}$$

negative DQ_L values may be achieved in two ways, by the use either of positively charged ligands ($e'_{\sigma L}$ negative) or of ligands whose π-donor capacity exceeds 75% of their σ-donor capacity. Similarly the square-planar limit may be exceeded if DQ_Z becomes negative.

From a chemical intuition point of view, Figures 4 and 5 utilizing the McClure parameters are perhaps of more value though it is more diffcult to assign limits of chemical accessibility. Granted the chemical significance of the McClure parameters, then ligands of known but differing σ- and π-bonding capabilities may be bound to a metal to generate molecules having desired ground states. For example, using Figures 4 and 5, a ^3E_g ground term should become accessible for Ni(II) if NiL_4Z_2 is designed in which the ligands L and Z have similar σ capability and, either, the axial ligand is a very much better π donor than the equatorial ligand or the axial ligand has little or no π capability, but the equatorial ligands have strongly π-bond acceptor orbitals *perpendicular* to the molecular plane[7] (but not in the molecular plane). These situations will generate a small value of dσ and a large and positive value of dπ. Alternatively a ^3E_g ground term should be achieved if the ligands have similar or little π-bonding capability but L is a much weaker σ donor than Z (dπ small, and dσ large and negative). Comparison of Figures 4 and 5 suggests that for such a ground state DQ should be as small as possible. This is exemplified by consideration of Figures 2 and 3, where it is seen that the ^3E_g ground state lies outside the accessible region for higher DQ.

As far as the $^3B_{2g}$ ground term is concerned, this may be achieved *via* a large positive dσ together with a small or negative dπ or by means of a large negative dπ. The former could be achieved by means of positively charged in-plane ligands, while the latter requires the in-plane ligands to be strong π donors (or the axial ligands strong π acceptors; see further discussion in ref 7).

No complexes in either of these ground states have been characterized with Ni(II). Two points are however worth noting. First, many binuclear and polynuclear nickel(II) complexes are known in which one Ni^{2+} ion resides close to another. When dealing with the magnetic properties of such systems, interest has usually focused upon the spin of the ground state with little or no attention paid to the orbital nature of the ground state. It is not unreasonable to believe that in such systems one nickel(II) ion would behave as a positively charged ligand toward another insofar as the energy levels of the system are concerned. One may therefore expect to find unusual orbital ground states in such systems.

Second, it is worth noting that given a fit of the excited states of a d^8 complex with a $^3B_{1g}$ ground term, *exactly the same fit*, but with interchange of the B_1 and B_2 labels, can be achieved for a complex with the $^3B_{2g}$ ground term. The relationships between the parameters necessary to generate these fits are

$$\begin{aligned} DQ(B_2) &= (1/6)DQ(B_1) - (\sqrt{35}/6)DT(B_1) \\ DT(B_2) &= -(\sqrt{35}/6)DQ(B_1) - (1/6)DT(B_1) \\ DS(B_2) &= DS(B_1) \end{aligned} \tag{12}$$

As would be anticipated spin singlet states arise if dσ becomes large (positive or negative). The observation that some spin singlet states lie within the accessible region for six-coordinate complexes emphasizes that *six-coordinate* tetragonally distorted nickel complexes can be diamagnetic, a contentious issue in the past (*e.g.*, $Ni(diarsine)_2I_2$[24]). Although there is a marked change in metal–ligand bond length when spin pairing occurs, the ground-state diagram implies that the series of high- and low-spin tetragonal complexes should be considered continuous rather than discontinuous. Complexes intermediate between the two spin states exist and exhibit magnetic properties consequent on the spin-state equilibrium. Their metal–ligand bond lengths are presumably intermediate between the two extremes. One example is discussed in the experimental correlation section.

Figure 1 illustrates a ground-state energy space diagram for a tetragonal d^7 complex, such as tetragonal cobalt(II). In this case an orbital triplet lies lowest in octahedral symmetry, thereby giving rise to a much greater number of possible ground states. Use of the diagram to predict the kind of molecule necessary to generate a given ground state parallels that used above and will not be further enlarged. Of particular interest is Figure 6 showing the same system as Figure 1 but in terms of the McClure parameters. Here we see a very simple distinction between the ^4E_g and $^4A_{2g}$ ground terms. One would certainly expect such a simple situation, to first order, since the sense of the splitting of the t_{2g} (in O_h) orbitals is determined by the relative π-bonding capabilities of the in-plane and axial ligands.[14] That this simple situation is not obviated by configurational interaction must be due to the fact that there are no sufficiently low-lying ^4E_g or $^4A_{2g}$ excited states. As a consequence in ML_4Z_2 complexes where L and Z have markedly different π propensities, the ground state should be readily predictable, at least in the limits of low distortion. The $^4B_{2g}$ ground state should become accessible when the axial ligand is a much stronger π donor than the equatorial ligand or when the latter is a π acceptor.

Complexes of Related Coordination Numbers and Point Groups

(i) Four-Coordinate Square Plane. D_{4h} point group symmetry results in the d orbitals spanning a_{1g}, e_g, b_{1g} and b_{2g}. Therefore *three* parameters are apparently required to describe the energy separations therein. The relationship in (9) infers that only two parameters (*DS* and *DQ* (or *DT*)) are required, however, in the limit of strict square-planar coordination. While this has certainly been recognized in the past, *e.g.*,[25] little advantage has been taken of this simplicity. This may justifiably be due to the fact that most of the characterized square-planar first-row transition metal complexes are those of low-spin d^8 nickel(II) and that such complexes generally exhibit a single broad band in the d–d region. In most such complexes four of the five d levels are believed to lie close together and even single crystal polarized studies, of which there have been many, do not yield much definitive information. There appear to have been no attempts, therefore, to analyze such spectra in terms of crystal field radial integrals, although molecular orbital approaches have been used, *e.g.*[26] Unfortunately the requirements for the two-parameter model to be valid are very stringent and are probably rarely met. Not only must there be no electron density within interaction distance along the *z* axis, but the in-plane ligands must not possess any π-bonding orbitals perpendicular to the molecular plane (p_z or d_{xz}, d_{yz}). Any such π bonding between the ligand and the metal generates an interaction which is equivalent to having π-electron density along the *z* axis. Reversing the argument, measurement of the *DT*/*DQ* ratio, in the absence of ligands along the *z* axis, may provide information about out-of-plane π bonding.

(ii) Five-Coordinate Square Pyramid. The representations subduced by the octahedral point group in C_{4v} are identical to those of D_{4h}, except that since the former group lacks a center of symmetry, it does not distinguish odd and even representations. As a consequence, the tensor Hamiltonian for the C_{4v} group is identical with that for D_{4h} (as given in (2)) except in the special case where configurational interaction between bases of different inversion parity are concerned. Thus the previous description for the D_{4h} complexes applies equally to square-pyramidal C_{4v} complexes. This is analogous to the crystal field argument that the energy levels in a tetragonal complex are determined by the total potential along the *z* axis, regardless of whether this potential is equally or unequally distributed above and below the molecular plane.

There is however one difference. The chemically accessible regions of the ground-state spaces (Figures 1–3), bounded by the dotted lines, are valid for equatorial or axial fields varying from zero to infinite strength. Only by allowing a negative DQ_L or DQ_Z can a real complex fall outside this region. In the C_{4v} case this is equally true if the metal lies in the molecular plane. However comparison of the tensor Hamiltonian with that derived through a crystal field analysis reveals that if the metal lies outside the molecular plane, above or below, ratios of *DT*/*DQ* may fall outside the accessible regions even when both equatorial and axial fields are positive. Although few data are available to test this prediction at the present time (see below), it is intriguing to speculate that this observation might provide a novel way of locating the position of the metal in five-coordinate porphyrin derivatives. Note that eq 5 may still be used to determine values of DQ_L and DQ_Z. The former retains its previous significance. The latter has the significance of the field experienced by the metal ion, along the *z* axis. It is not equal to the field strength of the axial ligand since the absence of a ligand in the sixth position is averaged therein. *If* the metal lies in the *xy* plane and *if* the field strength in the sixth position is exactly zero, then DQ_Z has a magnitude of half the field strength of the axial ligand.

(iii) *cis*- and *trans*-MY_2X_2 Complexes. Although these are not tetragonal, we complete our discussion of four-coordinate planar complexes with brief reference to these species. The cis complexes have C_{2v} symmetry (C_{2v}(III) in the previous nomenclature[16]). Assuming 90° angles, Hamiltonian (2) is also appropriate for these species.[16] This observation provides the group theoretical rationalization for considering such derivatives "pseudotetragonal".[15] Of course the relationships between *DT* and DQ_X and DQ_Y, for example, will differ from the D_{4h} case; nevertheless the ground-state energy space diagrams (Figures 1–3) may be utilized for such species. *trans*-MY_2X_2 compounds of D_{2h} symmetry (D_{2h}(II)[16]) are more complex requiring, for intraconfigurational matrix elements, the Hamiltonian

$$\mathcal{H}_{D_{2h}} = |A_{1g}i|_{O_h} + |E_g\theta|_{O_h} + |E_g\epsilon|_{O_h} \qquad (13)$$

where $|E_g\epsilon|O_h$ introduces the additional terms

$$DU[(1/\sqrt{2})(C_2^{\,2} + C_2^{\,-2})] + DV[(1/\sqrt{2})(C_4^{\,2} + C_4^{\,-2})] \qquad (14)$$

which will result in the loss of degeneracy of all five d orbitals. Expression 9 is valid when all angles are 90° leading to a four empirical parameter system (*DQ*, *DS*, *DU*, and *DV*).

(iv) Tetragonally Distorted Tetrahedra. Two general areas of interest with respect to tetragonal distortion are (i) the existence of many copper(II) complexes which may be described alternately as flattened (tetragonally distorted) tetrahedra or tetrahedrally distorted square planar[27] and (ii) the electronic spectra of square-planar platinum(II) complexes where the interpretation relies on the existence of excited states whose equilibrium stereochemistry is tetrahedral.[28] We show briefly here how the NSH Hamiltonian may conveniently be utilized in problems of this type. Both the D_{4h} and T_d Hamiltonians are treated as special cases of the Hamiltonian for the D_{2d} group since this is a subgroup of both D_{4h} and T_d. We require a Hamiltonian formulated in such a way that it may be used for all three groups, D_{4h}, D_{2d}, and T_d, without change. The appropriate D_{2d} Hamiltonian, expressed in octahedral group representations, may be written as

$$\mathcal{H}_{D_{2d}} = |A_{1g}i|_{O_h} + |E_g\theta|_{O_h} \qquad (15)$$

Table I. Parameter Values for Some Selected Tetragonal Complexes of Chromium(III), Cobalt(II), and Nickel(II)

Complex[c]	DS	DQ	DT	B	DQ_L	DQ_Z	dσ	dπ	DT/DQ	CN[a]	St[b]	Ref
$Ni(py)_4Cl_2$	−3,359	27,713	3,836	820	32,252	18,635	−1250	−12	0.14	6	N_4Cl_2	9
$Ni(py)_4Br_2$	−4,444	26,551	4,284	810	31,620	16,415	−1544	−162	0.16	6	N_4Br_2	9
$Ni(py)_4I_2$	−5,732	26,224	5,327	742	32,527	13,617	−1964	−245	0.20	6	N_4I_2	1
$Ni(py)_4(ClO_4)_2$	−6,287	27,330	6,925	877	35,524	10,942	−2305	−70	0.25	6	N_4O_2	9
$Ni(py)_4(BF_4)_2$	−8,577	27,266	7,281	896	35,881	10,036	−2845	−495	0.27	6	N_4F_2	9
$Ni(py)_2Cl_2$	4,127	22,464	−4,415	846	17,240	32,912	1495	70	−0.20	6	Cl_4N_2	9
$Ni(py)_2Br_2$	4,463	21,941	−4,508	807	32,609	16,607	1580	125	−0.21	6	Br_4N_2	9
$Ni(tempa)Cl_2$	−7,417	30,135	7,994	830	39,594	11,218	−2695	−115	0.26	6	N_4Cl_2	9
$Ni(CR)Cl_2$	−9,618	37,206	12,173	775	51,609	8,400	−3745	184	0.33	6	N_4Cl_2	29
$Ni(CTH)Br_2$	−10,080	29,251	9,950	793	41,023	5,705	−3536	−326	0.34	6	N_4Br_2	29
$Ni(2MeIm)_4Cl^+$	−10,283	22,616	7,610	881	31,620	4,607	−3256	−800	0.34	5	N_4Cl	4
$Ni(dtp)_2PPh_3$	−7,090	29,970	6,042	376	37,119	15,672	−2355	−405	0.20	5	S_4P	31
$Ni(RAsO)_4NO_3^+$	−8,799	17,081	6,802	850	25,129	984	−2826	−631	0.40	5	O_4O'	34
$Co(RAsO)_4NO_3^+$	−5,811	15,265	7,061	850	23,619	−1,443	−2222	57	0.46	5	O_4O'	34
$Cr(en)_2(OH)_2^+$	8,288	52,365	2,033	789	54,770	47,554	1495	2151	0.04	6	N_4O_2	13
$Cr(en)_2(H_2O)_2^+$	2,764	56,682	4,311	744	61,783	46,480	−22	1368	0.08	6	N_4O_2	13
$Cr(en)_2F_2^+$	5,187	53,875	4,894	692	59,665	42,294	435	2014	0.09	6	N_4F_2	13
$Cr(en)_2Cl_2^+$	−1,749	52,310	6,913	670	60,490	35,951	−1330	900	0.13	6	N_4Cl_2	13
$Cr(en)_2Br_2^+$	−2,449	52,631	8,269	560	62,415	33,063	−1668	1000	0.16	6	N_4Br_2	13
$Cr(das)_2Cl_2^+$	−2,580	50,757	5,438	597	57,191	37,888	−1305	450	0.11	6	As_4Cl_2	30

[a] Coordination number. [b] Microstoichiometry. [c] R = ligand abbreviations: py, pyridine; tempa, 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; 2MeIm, 2-methylimidazole; dtp, ethyl dithiophosphate; RAsO, diphenylmethylarsine oxide; en, ethylenediamine; das, *o*-phenylenebis(dimethylarsine); CR, 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene; CTH, *meso*-5,5,7,12,12-14-hexamethyl-1,4,8,11-tetraazacyclotetradecane.

Since this Hamiltonian is indeed applicable to *all* D_{2d} systems, including T_d, at the T_d limit, (15) may be written

$$|A_{1g}i|_{O_h} + |E_g\theta|_{O_h} = |A_1 i|_{T_d} \tag{16}$$

The standard axes used here pass through the metal–ligand bonds in the square-planar, D_{4h} stereochemistry. Distortion to a tetrahedron leads to a figure in which the x and y axes will not coincide with the S_4 axes of T_d, which is the standard choice for the latter stereochemistry. The former nonstandard choice for T_d requires the Hamiltonian

$$|A_1 i|_{T_d} = (\sqrt{7}/\sqrt{12})C_4{}^0 - (\sqrt{5}/\sqrt{24})(C_4{}^4 + C_4{}^{-4}) \tag{17}$$

Using eq 3 and 17 and inserting into (16) we derive the relationship

$$\begin{aligned} &DQ((\sqrt{7}/\sqrt{12})C_4{}^0 + (\sqrt{5}/\sqrt{24})(C_4{}^4 + C_4{}^{-4})) + \\ &\quad DT(-(\sqrt{5}/\sqrt{12})C_4{}^0 + (\sqrt{7}/\sqrt{24})(C_4{}^4 + C_4{}^{-4})) = \\ &\quad DQ'((\sqrt{7}/\sqrt{12})C_4{}^0 - (\sqrt{5}/\sqrt{24})(C_4{}^4 + C_4{}^{-4})) \end{aligned} \tag{18}$$

where DQ' is appropriate for tetrahedral symmetry. A unique solution to (18) only occurs when

$$\begin{aligned} DT &= -(\sqrt{35})DQ \\ DQ' &= 6DQ \end{aligned} \tag{19}$$

Thus a tetrahedral set of eigenvalues and eigenvectors is obtained using the D_{4h} Hamiltonian when the conditions in (19) are met. The splitting pattern so obtained is identical with the one which would be obtained if one were to begin with a tetrahedron having a field strength 6 times greater than the value of DQ used with the D_{4h} Hamiltonian. These relationships may be generalized to include DT and DS, *via*

$$\begin{aligned} DT' &= (\sqrt{35}DQ + DT)/6 \\ DQ' &= (DQ - \sqrt{35}DT)/6 \\ DS' &= DS \end{aligned} \tag{20}$$

The implication of this approach is that the Hamiltonian in (3) may be used for both the D_{2d} and T_d groups, as well as D_{4h}. Thus if we consider a D_{2d} molecule to be derived from a molecule of D_{4h} symmetry through a tetrahedral distortion, the unprimed parameters should be used. If on the other hand it is more convenient to consider such a molecule to be derived through the flattening of a tetrahedral molecule, the primed parameters should be employed. In either case the bases should be symmetry adapted to D_{2d}.

Experimental Correlations

Table I comprises a selection of data for tetragonal chromium(III), cobalt(II), and nickel(II), analyzed to illustrate the use of Hamiltonian (2). We have restricted the selection to those complexes where the experimental data are particularly good; where possible, single-crystal data are used. Moreover the selection only includes those complexes where the assignment of the spectra seems unambiguous. These assignments are considered correct for the purposes of this analysis. No account is taken of vibrational or of spin–orbit coupling. While neglect of these factors will cause an error in the determination of absolute values of the various parameters, consideration of relative changes in the magnitudes of the parameters should not be affected. Discussion of these data will be limited to those aspects of the problem not covered by previous authors.

Recall first that the NSH framework provides magnitudes of the empirical parameters DQ, DS, DT, etc., which may be compared directly not only within a group of complexes of the same stereochemistry but with data from complexes of other stereochemistry where the point group concerned belongs to the same subduction chain.[16] Note also that their magnitudes are independent of the choice of coordinate axis.[16] Unfortunately there is a dearth of worked examples of low-symmetry group molecules with which to make such comparisons, which will necessarily have to await the collection of further data.

The ratio DT/DQ, also noted in Table I, provides a measure of the degree of tetragonal distortion and it is satisfying to note that complexes with very weakly coordinating ligands such as the perchlorate and tetrafluoroborate ions have relatively high values for this ratio, though still fall considerably short of the theoretical maximum for a square-planar molecule (eq 9). It is satisfying that the ratios for the macrocyclic ligand complexes of nickel(II) can be relatively high when the weaker field axial ligands are used.[29] This is a consequence of the very high in-plane field of such derivatives coupled with the fact that this in-plane field is enhanced when the axial field is weak.[29]

Values of DT/DQ have been calculated for some 110 six-coordinate nickel complexes whose tetragonal distortion is sufficient to observe splitting of the first two spin-allowed transitions. We find, in general, that the magnitude of DT/DQ

lies between 0.1 and 0.2 except when very weakly coordinating axial ligands are employed. With chromium(III) complexes the ratio is generally somewhat smaller (nearer 0.1) (Table I) as a consequence of the larger *DQ* values encountered with these complexes. The large variation in the equatorial field strength of the ethylenediamine derivatives[13] as a function of the axial field is noteworthy. This variation appears unsystematic and warrants further attention. Diarsine[30] appears to have a somewhat smaller field than ethylenediamine while the magnitude of the axial field is in accord with the previous value (Table I). Considering five-coordinate nickel(II) complexes of C_{4v} square-pyramidal stereochemistry, we find a range of *DT*/*DQ* values. The presumed square-pyramidal[31] $Ni(dtp)_2PPh_3$ exhibits a *DT*/*DQ* value typical of the tetragonal complexes under discussion and has a large *DQ* value. In view of the likely π-bonding stabilization of the NiS_4 plane in this molecule, it is most probable that the metal atom lies in the basal plane. The DQ_z value for this complex seems large, implying a *DQ* value for the axially coordinated phosphine of about 30,000 cm^{-1}. There are no six-coordinate phosphine nickel(II) complexes with which to make a comparison, but an estimate of *DQ* for triphenylphosphine can be obtained by consideration of $Ni(PPh_3)_2Cl_2$ a tetrahedral complex whose single crystal polarized spectrum was analysed by Fereday, Hathaway, and Dudley.[32] Using their assignment, the average environment rule, and multiplying the resultant number by $^9/_4$ and $6(21^{1/2})$ to obtain a number appropriate for an octahedral complex in the tensor formalism, we arrive at a value close to 35,000 cm^{-1}. While it is clear that further work is necessary to analyze the spectra of $Ni(PPh_3)_2Cl_2$ itself, the axial *DQ* value observed in the five-coordinate $Ni(dtp)_2PPh_3$ is, in fact, qualitatively in agreement with previous studies. With the five-coordinate square-pyramidal nickel(II) and cobalt(II) complexes of Ph_2MeAsO, on the other hand, X-ray studies reveal[33] that the metal lies out of the plane with an axial ligand–metal–basal ligand angle near 100° (β). As commented earlier, such a displacement may lead to high *DT*/*DQ* ratios. These are indeed observed (Table I) and in fact are an indicator of the displacement of the metal atom from the basal plane. The angle β may be calculated by referring back to the crystal field model as discussed by Gerloch, *et al.*[34] It is important to note that both equatorial and especially the axial *DQ* values are markedly low, even for an MO_5 chromophore. This result is in apparent contrast to the basal and equatorial *Dq* values reported by Gerloch, *et al.*,[34] which are typical of the ligands concerned. The difference, of course, arises because the β angle dependence is absorbed into the *DQ* value, while it is explicitly factored out of the *Dq* values, making them rather artifical. The two types of parameters give a different insight into the nature of the metal–ligand bonding. The *DQ* parameter provides information concerning the totally symmetric (A_{1g}) contribution to the ligand field and indicates that in these cases the overall perturbation of the metal ion is greatly reduced relative to the tetragonal systems and very much so relative to the NiS_4P five-coordinate system previously discussed. This kind of information does not come readily from the traditional approaches to this problem.

Spin Isomerism in Tetragonal Complexes. Some diethylthiourea complexes of nickel, $Ni(detu)_4X_2$ (X = Cl, Br), were the first six-coordinate nickel(II) complexes observed[35] to exhibit spin isomerism. Holt and coworkers made some calculations of the magnetic behavior of these complexes on the basis of a simple model possessing a $^1A_{1g}$ ground state with a thermally accessible $^3B_1$ excited state. Five-coordinate spin-isomeric nickel(II) complexes have been discussed in a similar vein.[36] In the former case, assuming diamagnetism for the $^1A_{1g}$ state and a moment of 3.2 BM for the spin triplet state, attempts were made to fit the observed magnetic behavior. Not unexpectedly agreement between observed and calculated paramagnetism could only be achieved if the singlet–triplet energy separation was considered to be temperature dependent. This is a not uncommon observation.[37] Use of the ground-state energy space diagrams reveals that such a simple model is quite inadequate. While there are indeed reasons for believing that the singlet–triplet energy separation might well be temperature dependent, use of the simple Maxwell–Boltzmann statistics between the two states is insufficient to justify such a conclusion.

To emphasize this point consider the $Ni(detu)_4X_2$ complexes and place them into an appropriate ground-state energy space diagram. The *DQ* value is expected to be fairly low because of the position of thiourea in the spectrochemical series. The parameter dσ can be safely assumed to be negative, it being certain that the existence of the spin singlet ground state arises through a greatly reduced interaction along the Cl–Ni–Cl axis, consistent with the known structure of[38] $Ni(tu)_4Cl_2$. The sign of dπ is likely to be negative for the same reason.

The knowledge that the system has a spin-singlet ground state relatively near a spin-triplet excited state can be used, while referring to Figure 4, to deduce that the complex must lie in the range defined by

$$-7200 \leqslant d\sigma \leqslant -5600$$

$$-5000 \leqslant d\pi \leqslant 0$$

Reference to both Figures 4 and 5 will show that the interface between $^3B_{1g}$ and $^1A_{1g}$ is independent of *DQ* and thus dσ is known within close limits independently of *DQ*.

It is evident from Figure 4 that the excited state above $^1A_{1g}$ is not necessarily $^3B_{1g}$ but could easily be $^3A_{2g}$, or ^3E_g. Further, one of these two states will always lie relatively close to the ground state in this region. This condition will render the $^1A_{1g}$ ground state paramagnetic, since both states can couple thereto by spin–orbit coupling. Such coupling may be responsible, for example, for the residual paramagnetism in a range of "diamagnetic" square-planar nickel complexes, such as[39] $Ni(TAAB)(BF_4)_2$, a macrocyclic derivative. Moreover the presence of these states near $^3B_{1g}$ will give rise to a zero field splitting of the $^3B_{1g}$ levels whose magnitude is likely to be large enough that the assumption of a fixed magnetic moment for this state over a wide temperature range is quite unjustified. Hence the utility of appropriate ground-state energy space diagram in any discussion of the magnetism of spin-crossover system is clearly demonstrated; *e.g.*, see ref 40. Any calculation must take into account *all* states lying relatively close to the ground state (within 20,000 cm^{-1}, at least) and not just the pair of relevant spin states, if it is to be definitive and not totally misleading. We have attempted such a calculation of the magnetic properties of the detu complexes, using our own data which agree well with those of Holt, *et al.*[35] Unfortunately the electronic spectra are not sufficiently well resolved to allow an unequivocal determination of the various empirical parameters. The data are still ambiguous with respect to the question of the temperature dependence of the singlet–triplet separation, and detailed publication must await a single crystal polarized absorption study which hopefully will clarify the issue.

Summary and Conclusions

This paper has described how the magnitudes of the linearly independent parameters *DQ*, *DS*, and *DT* may be derived from analysis of the electronic spectra of tetragonal D_{4h} and C_{4v} complexes, through use of the normalized spherical harmonic Hamiltonian. The critical reader may regard the advantage of using the NSH Hamiltonian, rather than the classical Hamiltonian for tetragonal complexes, to be marginal. It is pertinent therefore to summarize here the real value of this approach.

One of its more important aspects is the standardization it offers to the study of the electronic spectra of noncubic molecules as a whole. Such standardization is vital, especially where rhombic systems are concerned, if real progress in our understanding of noncubic complex electronic spectra is to be made and if useful chemical information is to be derived therefrom. There can be little doubt that the lack of such standardization in the study of molecules whose symmetry is less than tetragonal has inhibited the development of the area. NSH Hamiltonians provide a unique and unambiguous solution to this problem.[16] The data discussed in this paper provide a basis for comparison of the results to be obtained in the future with less symmetric systems. Indeed it is the fact that the parameters are linearly independent of each other and of the coordinate axis of choice, which provides a means by which data from molecules of two different symmetry groups may be directly related.[16] From a computational point of view the procedure offers ease and simplicity in setting up the Hamiltonian itself and, perhaps more importantly, provides a framework in which sign (phase) ambiguities do not exist.[16]

The ground-state energy space diagrams constitute not only a means of answering specific questions concerning possible ground states of the molecule but also provide a challenge to the synthetic chemist.

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Supplementary Material Available. A complete listing of the matrices of Hamiltonian (2) for all spin states of d^2 and d^3 will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number AIC40389D.

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Contribution from the Chemistry Department,
York University, Downsview, Ontario M3J 1P3, Canada

Higher Oxidation Level Phthalocyanine Complexes of Chromium, Iron, Cobalt, and Zinc. Phthalocyanine Radical Species

J. F. MYERS, G. W. RAYNER CANHAM, and A. B. P. LEVER*

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Radical phthalocyanine(1−) complexes of chromium(III), iron(III), cobalt(III), and zinc(II) are reported and characterized by electronic and vibrational spectroscopy, magnetism, electron spin resonance, and Mössbauer spectroscopy and through oxidative titrations. Further elucidation of the reaction of iron(II) and of cobalt(II) phthalocyanine with the hydrohalic acids is presented. It is suggested that most of the previously reported manganese(III) phthalocyanine derivatives are five-coordinate. A survey of the first-row transition metal phthalocyanines reveals that only the above-mentioned metal ions will form radical phthalocyanine species under the conditions used.

In recent years there has been considerable interest in high oxidation level porphyrin complexes, as such species may well occur in biological environments.[1-20] There is interest concerning the nature of the oxidized species, *i.e.*, oxidation of metal or ligand, and in the latter case concerning the nature of the electronic configuration[16,18] so produced. Evidence that radical porphyrin cations with different ground states have quite different chemical properties[18] leads to a belief that porphyrin radical species have a dominant role to play in biological electron transfer, *e.g.*, in photosynthesis.[18]

The phthalocyanines, while of similar structure to the porphyrins, exhibit nevertheless characteristic differences which may be ascribed to differing electronic structure and "hole" size.[21] Previous studies have characterized a wide range of