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## SYMMETRY VERSUS SPLITTING PARAMETERS

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Symmetry plays a central role in the interpretation of transition metal  $d-d$  spectra. The information contained in these spectra may conveniently be considered under the three headings of splitting patterns, absolute energy differences, and intensities and polarizations. Only absolute energy differences are independent of symmetry. Intensities, though largely determined by non-symmetry factors, do have a qualitative aspect insofar as selection rules, derived from group theory, may be involved. Spectral splitting patterns, especially of highly symmetrical molecules, are very largely symmetry-based features. In a similar way, the orders of magnitude for magnetic moments successfully predicted by the 'spin-only' formula and the principles of crystal-field orbital quenching derive largely from group-theoretical considerations. Even early qualitative estimates of the magnitudes of magnetic anisotropies were made directly from a knowledge of formal ground term degeneracies.

Our understanding of the *magnitudes* of spectral splittings and of the detailed behaviours of magnetic moments and anisotropies, however, rests on theories owing little or nothing directly to symmetry. The size of the spectral splitting factor  $Dq$ , for instance, is not determined by group theory. Also, interpretations of the electronic properties of molecules with less than cubic symmetry involve many more such parameters, of which  $Cp$ ,  $Dt$ ,  $Ds$ ,  $D\sigma$  and  $D\tau$  are perhaps the best known. The nature and use of such quantitative parameters form the subject matter of this book.

The origin and first examples of the use of crystal-field theory concerned magnetic moments and their dependence on the quenching of orbital angular momentum.<sup>e</sup> Thus, while it was realized that lanthanide ions in crystal lattices cannot be completely indifferent to their environment, it was found empirically in the late 1920s that Hund's formula,

$$\mu_{\text{eff}} = g\sqrt{J(J+1)}, \quad (1.1)$$

where

$$g = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}, \quad (1.2)$$

<sup>e</sup> References marked with a letter are to be found at the end of the chapter.

a formula derived for free-ions, satisfactorily explained the observed magnetic moments in lanthanide compounds. Crystal-field theory grew out of the discovery that this simplicity did not extend to the magnetic properties of compounds of the main transition block. Van Vleck had derived a complementary formula to (1.1), describing the magnetic moments of free-ions of the first-row transition series where, in first order, spin-orbit coupling effects might reasonably be ignored:

$$\mu_{\text{eff}} = \sqrt{[L(L+1) + 4S(S+1)]}. \quad (1.3)$$

Accordingly, the magnetic moments of ions with a Russell–Saunders  ${}^3F$  ground term,  $\text{Ni}^{2+}$  for example, should have values of  $\sqrt{20} = 4.47$  Bohr magnetons. Experimental values for octahedral compounds of nickel(II), however, are typically *ca.* 3.2 Bohr magnetons. The explanation of these and similar discrepancies came independently in general terms from Stoner and in comprehensive detail from Bethe.<sup>7</sup>

It was recognized that, in compounds, the metal electrons are no longer subject only to the attractive nuclear and the repulsive inter-electron coulombic (and exchange) forces, but also to the influence of neighbouring atoms in the molecule or crystal lattice. Without specifying the nature of this influence, electrostatic or covalent bonding for example, some important conclusions may be made by recourse only to symmetry. Thus we know that eigenstates transforming as  $F$  terms in spherical symmetry transform as  $A_2 + T_2 + T_1$  terms in cubic symmetry. As discussed below, we also know the relative ordering of the energies of these terms, barring a sign, from symmetry considerations alone. In its most elementary form, crystal-field theory serves to establish this sign by depicting the influencing ligands as negative charges. So it is that crystal-field theory, but mostly group theory, establishes a  ${}^3A_{2g}$  ground term for octahedral nickel(II) compounds, for example. The orbital non-degeneracy of this ground term reduces Van Vleck's formula (1.3) to the well-known 'spin-only' formula,<sup>81</sup>

$$\mu_{\text{eff}} = \sqrt{[4S(S+1)]} = \sqrt{[n(n+2)]}, \quad (1.4)$$

where  $n$  is the number of unpaired electrons, and the phrase 'orbital quenching' was coined. We do not make it part of our task to further discuss aspects of crystal-field theory which are the substance of most conventional text-books in the subject: a few are listed at the end of this chapter. While assuming familiarity with these matters, we wish to highlight some important development points in crystal-field theory and to emphasize the differing roles played by group theory on the one hand and 'quantitative' theories on the other.

<sup>7</sup> References marked with a number are to be found on pages 229–32.

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The ‘spin-only’ formula and its embellishments with ‘orbital contributions’ [which are only a reverse way of describing a situation intermediate between those of (1.3) and (1.4)] go far in explaining room-temperature average magnetic moments. Also based on the symmetry-predicted ground state orbital degeneracies is Van Vleck’s early explanation<sup>112</sup> of the sizes of magnetic anisotropies observed in transition-metal complexes. Magnetic anisotropies are concerned with spatial anisotropy in molecules (as opposed to spin anisotropy) and so, in first order at least, with the orbital part of the ground term wave-functions. A slight departure from cubic symmetry removes the degeneracy of an orbital-triplet or doublet term, different components being associated with different spatial directions in the molecule. In molecules with formal orbital-triplet ground terms, then, unequal thermal population of these components may lead to large magnetic anisotropies. Ions with orbital-singlet ground terms, however, should display no magnetic anisotropy, at least in first order, as distortion has no orbital degeneracy to remove. This purely symmetry-based theory satisfactorily explains, for example the < 1 % anisotropy† for high-spin iron(III) compounds with formal  ${}^6A_{1g}$  ground terms and the typically 30 % anisotropy for near octahedral ions of cobalt(II) with  ${}^4T_{1g}$  ground terms. It is, however, the business of the quantitative side of crystal-field or other theories to explain why these cobalt(II) compounds exhibit 30 % anisotropies rather than, say, 80 %. It is the basis of the quantitative aspects of these theories that we shall be discussing.

We mentioned above how symmetry rules dictate more than just which term may arise for an ion in a molecular or crystal environment. It is instructive to examine this powerful use of symmetry further. The free-ion ground terms in the transition metals are  ${}^2D$   ${}^3F$   ${}^4F$   ${}^5D$   ${}^6S$   ${}^5D$   ${}^4F$   ${}^3F$  and  ${}^2D$  for the  $d^1$  to  $d^9$  configurations, respectively. The group-theoretical transformation rules of lowering the symmetry from spherical to octahedral give

$$D \rightarrow E_g + T_{2g}, \quad F \rightarrow A_{2g} + T_{2g} + T_{1g}, \quad S \rightarrow A_{1g}$$

and are well known. The relative ordering of these terms for the lowest energy Russell–Saunders free-ion terms are shown in figure 1.1. Let us remind ourselves of the basic steps in the argument which allows group theory to derive most of the information in figure 1.1.

In octahedral symmetry a set of five  $d$  orbitals splits into a triplet

† Expressed say, as anisotropy of susceptibility versus mean susceptibility, i.e.  $\Delta\chi/\bar{\chi}$ .

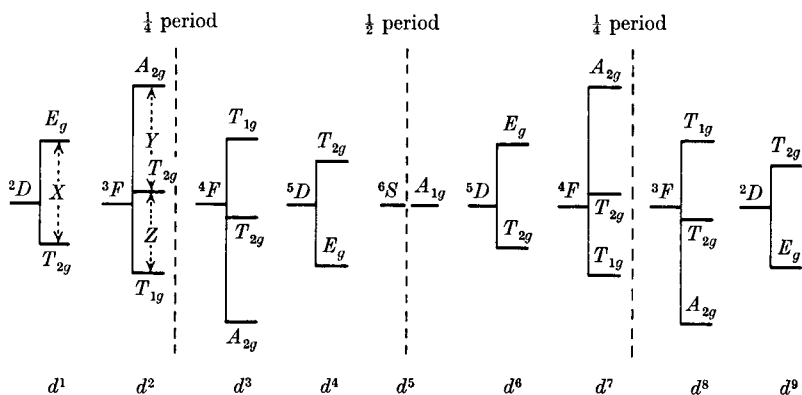


Figure 1.1. Splitting diagrams for  $d^n$  configurations in  $O_h$  crystal fields, showing inversions in  $\frac{1}{2}$  and  $\frac{1}{4}$  periods.

and a doublet – the  $t_{2g}$  and  $e_g$  sets – and these are energetically separated by a quantity we call  $\Delta_{\text{oct}}$  or  $10Dq$ . In that ‘the energy of the  $t_{2g}$  set’ refers to the energy of a single electron placed in that set, the energy separation of the  $E_g$  and  $T_{2g}$  terms which arise from the  $d^1$  ( ${}^2D$ ) configuration is also  $10Dq$ . The situation for the  $d^1$  configuration is straightforward and well-known. With one exception, all that is involved is group theory. The exception is the *sign* of the orbital or term splittings. In crystal-field terms the metal orbitals are variously repelled by negative ligands and the familiar result in octahedral geometry is that the  $t_{2g}$  orbitals lie lower than the  $e_g$  orbitals. Insofar as we are concerned with energy *splittings*, a ‘baricentre rule’ may be invoked such that a  $d^5$  configuration is unshifted energetically on forming a spin-free octahedral complex.<sup>c</sup> Thus, relative to the  $d^1$  configuration, we place the  $t_{2g}$  orbitals at  $-4Dq$  in energy and the  $e_g$  orbitals at  $+6Dq$ : the same figures pertain for the  $T_{2g}$  and  $E_g$  terms relative to  ${}^2D$ .

Conventional crystal-field text-books are extensively concerned with the more complex situation occurring for  $d$  configurations involving more than one electron.<sup>b,c</sup> Figure 1.2 shows part of the weak-field/strong-field correlation diagram for octahedral  $d^2$  ions. Only spin-triplet terms are shown. On the left side of figure 1.2 inter-electron repulsion effects split the  $d^2$  configuration into Russell-Saunders terms, Hund’s rules leaving  ${}^3F$  lowest. The nature of these terms, that is their quantum labelling as opposed to their absolute energy separations, is determined entirely by coupling coefficients which in turn derive from the commutation relations between angular

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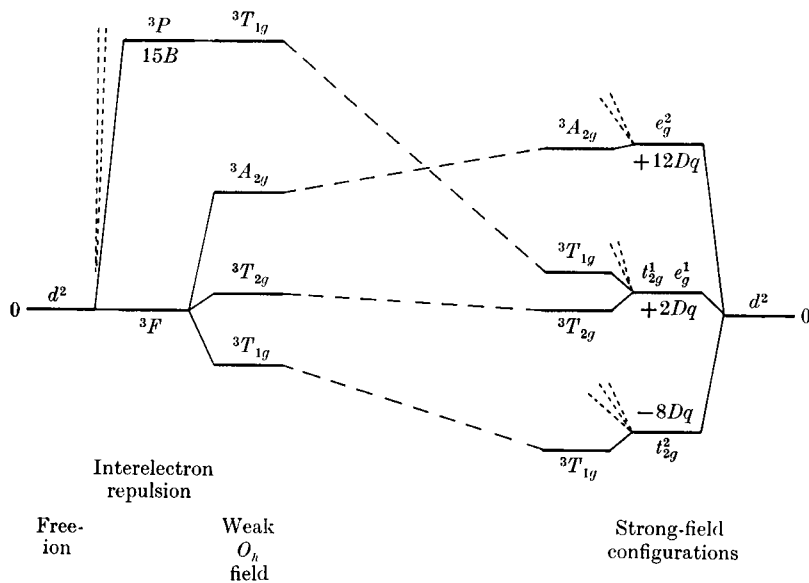


Figure 1.2. Partial correlation diagram for  $d^2$  configuration in  $O_h$  crystal field, showing spin-triplet terms only.

momentum operators. Group theory of a slightly different kind tells us that, on lowering the symmetry from free-ion spherical to complex octahedral, the Russell–Saunders terms split into the component terms shown in the figure. At this stage, the ordering and relative energies of the terms arising, say, from  ${}^3F$  are unknown. As we are considering energy splittings only, the neglect of crystal-field terms possessing full spherical symmetry means that the energy of the  ${}^3T_{1g}(P)$  term should be the same as its parent  ${}^3P$  term, in first order. Group theory alone has therefore established the qualitative nature of the left-hand side of figure 1.2.

On the right-hand side are represented the strong-field configurations in  $O_h$  symmetry, corresponding to placing two electrons in the  $t_{2g}$  orbital set, one in  $t_{2g}$  and one in  $e_g$ , or both in the  $e_g$  set. At this strong-field limit, we are supposing that there is no interaction between the pair of metal electrons. Such interaction would involve two-electron operators so that the strong-field representations as one-electron wavefunctions implicitly require the neglect of any electron *interactions*. The ordering of these strong-field configurations derives directly from the ordering of the  $t_{2g}$  and  $e_g$  orbitals used in the  $d^1$  case: not only the ordering but also the energy values with respect to the

free-ion spherical distribution represented by  $d^2$ . If electron interaction of any sort is included, the degeneracies of the strong-field configurations are lost, but in a way determined by group theory. The  $t_{2g}^2$  configuration, for example, gives rise to the terms

$${}^1A_{1g} + {}^1E_g + {}^1T_{2g} + {}^3T_{1g}.$$

Figure 1.2 shows the spin-triplet terms which arise in this way. The next step in the argument is to correlate the terms on the two sides of the diagrams. This is straightforward for the  ${}^3A_{2g}$  and  ${}^3T_{2g}$  terms as these occur only once each. There are two  ${}^3T_{1g}$  terms, however, and these must be correlated with due regard to the 'non-crossing rule' (ref. 17, p. 200). If the abscissa in figure 1.2 is taken to measure free-ion electron interaction effects, the crystal-field or one-electron operator effects being held constant, then the energy separation between the  ${}^3A_{2g}$  and  ${}^3T_{2g}$  terms stays constant throughout the figure as  $10Dq$  – the energy separation of the parent strong-field configurations. The two  ${}^3T_{1g}$  terms, however, have a variable separation due to a fixed, finite crystal-field matrix element between these terms separated by (assumed) variable interelectron repulsions. The calculation of the off-diagonal crystal-field matrix element  $x$  may be made without recourse to the specific nature of the crystal-field operator. The process involves the setting up of the  ${}^3T_{1g}$  energy matrix, as follows:

$$\begin{array}{c} {}^3T_{1g}(F) \\ {}^3T_{1g}(P) \end{array} \begin{array}{c} {}^3T_{1g}(F) \\ {}^3T_{1g}(P) \end{array} \begin{array}{c} -6Dq - E \\ x \end{array} \begin{array}{c} x \\ 15B - E \end{array} \quad (1.5)$$

where  $15B$  is the  ${}^3F - {}^3P$  energy separation due to interelectron repulsion and  $E$  is the energy of either  ${}^3T_{1g}$  term under the combined perturbation of crystal-field and interelectronic repulsions. The diagonal elements are taken with respect to the energy of the  ${}^3F$  term. In the limit of no interaction between  ${}^3T_{1g}$  terms, the baricentre rule fixes the energy of the  ${}^3T_{1g}(F)$  term as  $-6Dq$ , relative to  ${}^3F$ . The interaction between the two  ${}^3T_{1g}$  terms is represented by the off-diagonal element  $x$ . This matrix represents the situation anywhere across the abscissa in figure 1.2 as both crystal-field and electron interaction effects are involved. In order to solve this general secular problem, we consider the special case where we know the solutions already; namely, the strong-field limit. Thus, at the right-hand side of the figure, interelectron repulsions are assumed to vanish and hence also  $B$  in (1.5). This leads to the quadratic equation:

$$E^2 + 6DqE - x^2 = 0. \quad (1.6)$$

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In the strong-field limit, however, we know the roots to be  $-8Dq$  and  $+2Dq$ . Putting  $E$  equal to either of these values in (1.6) gives

$$x = \pm 4Dq. \quad (1.7)$$

In summary then, we see how the ordering of the  $A_{2g}$ ,  $T_{2g}$  and  $T_{1g}$  terms arising from a free-ion  $F$  term and their relative energy separations are determined by group-theoretical considerations. Symmetry even tells us that, relative to  $X$  in figure 1.1 being  $10Dq$ ,  $Y$  and  $Z$  for the  $d^2$  case are  $10Dq$  and  $8Dq$  respectively. Further, symmetry also relates the splitting patterns for all the  $d^n$  configurations, giving rise to the familiar inversions in the half and quarter periods as shown in figure 1.1. These inversion rules may be arrived at *via* the hole formalism. Thus, being concerned here with terms of maximum spin multiplicity, we note that six  $d$  electrons will arrange themselves with one electron of one spin per orbital plus a single electron of the other spin. The distribution of this 'extra' electron amongst the five orbitals of 'other spin' will be identical to the distribution of the single electron of the  $d^1$  configuration. The splitting patterns for a  $d^{5+n}$  configuration should be identical, therefore, to those for a  $d^n$  configuration. In addition, the arrangements of  $10-n$  electrons in the whole  $d$  spin-orbital set will be like the arrangements of  $n$  electrons but inverted energetically, as arrangements of  $10-n$  electrons are equivalent to arrangements of  $n$  holes, i.e. particles of opposite charge. Accordingly, the splitting patterns for  $d^{10-n}$  configurations are the inverse of those for  $d^n$ . This rule is responsible for the inversion in the half period of figure 1.1 and, in conjunction with the similarity of  $d^n$  to  $d^{5+n}$ , for the inversions in the quarter period. An alternative way of deriving the  $d^2 - d^3$  inversion, for example, would be to set up a correlation diagram like figure 1.2. The left-hand side would be qualitatively identical, in that symmetry alone at first does not appear to determine the relative orderings of  $A_{2g}$ ,  $T_{2g}$  and  $T_{1g}$  terms. But, on approaching the problem from the strong-field side, we note that the ordering of strong-field configurations, with the usual single assumption of negatively charged (or dipolar) ligands, is

$$(t_{2g})^3 < (t_{2g})^2(e_g)^1 < (t_{2g})^1(e_g)^2 \text{ etc.}$$

The group-theoretical transformation of these configurations on recognizing electron interactions then determines the ordering of the terms,  ${}^4A_{2g}$  being lowest.

We have reviewed the construction of splitting patterns and correlation diagrams in some detail, partly to provide a basis for later



discussions, but mainly to re-emphasize the role of symmetry in these 'crystal-field' arguments. There is one more well-known feature of these diagrams which is neither group-theoretical nor a quantitative feature like  $\Delta_{\text{oct}}$  or  $10Dq$ . It is the famous  $-\frac{4}{9}$  relationship between the theoretical magnitudes of the splitting parameters in octahedral and tetrahedral geometries. At the most elementary level, the inversion implied by the minus sign is conventionally demonstrated by inscribing an octahedron and a tetrahedron in cubes with common axes and examining the relative proximity of  $d_e$  ( $t_2$  or  $t_{2g}$ ) and  $d_y$  ( $e$  or  $e_g$ ) orbital sets to negatively charged ligands. The  $\frac{4}{9}$  factor assumes identical natures for the metal and ligands in the two geometries and equal 'bond lengths'. Although the origin of the  $-\frac{4}{9}$  factor is not directly group theoretical, it does derive from geometry. It may be seen as due partly to a change in coordination number and partly to the change in size of the cubes in which one inscribes tetrahedra or octahedra with equal bond lengths. As discussed later in this book, the  $-\frac{4}{9}$  factor is not a quantitative factor on the same footing as the splitting parameters  $Dq$  etc., and as such may be referred to as a geometrical factor.

So we appreciate the strength of simple crystal-field theory. In cubic symmetry, a single parameter is sufficient, in first order at least, to represent the splitting patterns of all  $d$  configurations in octahedral, tetrahedral (or other cubic) geometries and to establish orders of magnitude for magnetic properties which are consequential on ground term multiplicities. This power largely derives from group theory. However, when we are interested in absolute energy splittings, in correlations between spectra, magnetism, chemistry and structure, our attention turns to the magnitudes of the splitting factors for which symmetry and group theory have nothing to say.

Perhaps the most celebrated of early discussions on the magnitude of crystal-field splittings was that concerning high- and low-spin iron(III) compounds. Pauling<sup>81</sup> had described his hybridization scheme for octahedral compounds in which six directed covalent bonds could be formed involving overlap of ligand ( $\sigma$ ) orbitals with central metal  $d^2sp^3$  hybrids. Six pairs of electrons donated by the ligands fill these directed orbitals. Any further electrons, equal in number to the number of  $d$  electrons on the corresponding metal free-ion, had to fit into the remaining, unhybridized  $d$  orbitals if possible. So, for iron(III) complexes with the  $d^5$  configuration, six covalent bonds implied five electrons in three  $d$  orbitals and hence one unpaired electron. The low magnetic moment of the  $\text{Fe}(\text{CN})_6^{3-}$  ion was in general agreement with



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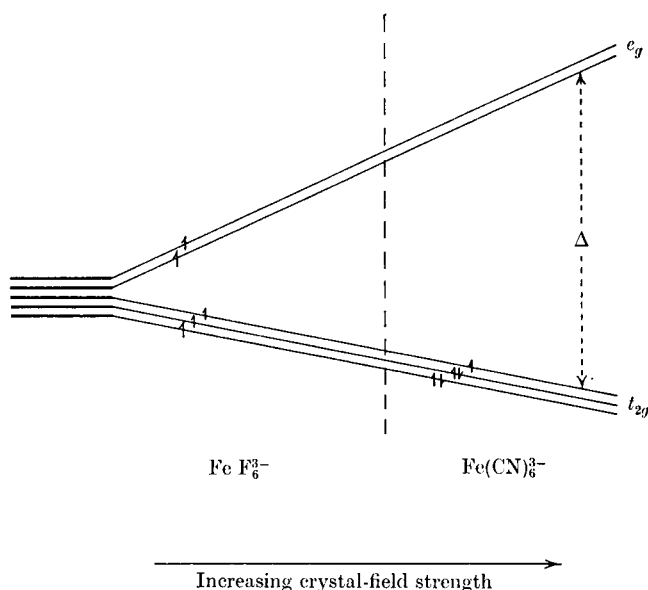


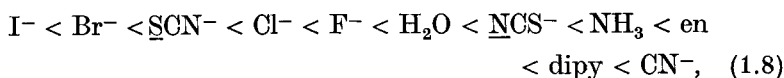
Figure 1.3. Relationship between spin-pairing and  $\Delta$  in crystal-field model.

this idea. On the other hand, the high moment of  $\text{FeF}_6^{3-}$  ions, corresponding to five unpaired electrons, implied the non-involvement of the iron  $3d$  orbitals in hybridization. Pauling therefore considered the bonding in the complex fluoride to be weaker than in the hexacyanide, more ‘ionic’ in character and, following the later ideas of Huggins, to involve  $sp^3d^2$  hybrids in which the outer, rather than inner,  $d$  orbitals participate. In Pauling’s view, the change in spin-multiplicity implied a change of bond type.

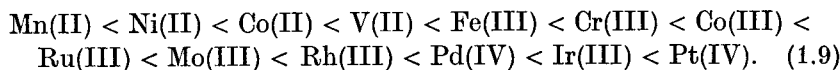
Van Vleck’s<sup>111</sup> approach to the problem was to consider the cyanide ligands as producing a stronger crystal-field than the fluorides, so much so that the ground state involved paired electrons even at the cost of increased interelectron repulsion energy, as in figure 1.3. Pauling<sup>81</sup> found this view unappealing in that fluorine, being the most electronegative element, might be expected to provide a greater electrostatic crystal-field perturbation. However, Van Vleck chose to regard  $\Delta$ , the splitting factor, as a *parameter* of the system, not necessarily determined solely or largely by purely electrostatic effects. At the same time he showed<sup>111</sup> the relationships between Pauling’s hybridization valence-bond method, Bethe’s crystal-field model, and Mulliken’s molecular-orbital approach,<sup>71</sup> and we shall have more to say about this shortly. The important concept to emerge from the

$\text{FeF}_6^{3-}/\text{Fe}(\text{CN})_6^{3-}$  work is that all ligand influences, whether electrostatic or covalent, could be parameterized within the crystal-field framework by the splitting factor,  $\Delta$ . Actually, this does not need to be within a crystal-field framework specifically, i.e. electrostatic, for as discussed earlier, octahedral symmetry requires only one parameter to describe spectral term splittings (neglecting second-order effects involving interelectron repulsion parameters) so that the idea of parameterizing all forms of ligand influence by a single  $\Delta$  factor is no more than a statement of symmetry. The notion has permeated the chemical literature, however, that electrostatic and covalent bonding effects are somehow both 'surprisingly' compatible with crystal field theory. We shall return to this point also.

And so we come to that remarkable collection of data called the 'Spectrochemical Series'. This is an empirical ordering of metals and ligands according to the size of  $\Delta$  values their spectra possess.<sup>d</sup> For a given metal it is found that  $\Delta$  values increase along the series



where en = ethylenediamine and dipy = dipyridyl, and that this series is approximately independent of the central metal ion. A second series, approximately independent of the ligand is:

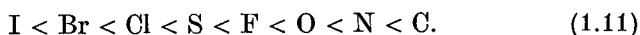


The way these two series may be written in terms of only ligands or only metals may be put in the more revealing and remarkable way expressing  $\Delta$  as a product of a purely ligand function  $f$  and a purely metal function  $g$ :

$$\Delta \sim f(\text{ligands}) \cdot g(\text{metal}). \quad (1.10)$$

Empirical values of  $f$  and  $g$ , derived from a large number of observed spectra of octahedral compounds are given in table 1.1. There are irregularities, but the values in the table are widely applicable.

One feature of series (1.8) noted earlier, is the way  $\Delta$  values increase with decreasing size of the donor atom on the ligand:



This seems reasonable on the basis of a simple electrostatic origin for the splitting  $\Delta$ , as smaller ligands imply smaller bond lengths. On a simple electrostatic model, involving no penetration of metal orbitals