

PART I



CHEMICAL AIMS IN LIGAND-FIELD STUDIES

While ligand-field theory grew up in the physics literature, it is probably within the discipline of chemistry that the subject is more widely taught and applied. In large measure, the chemist's approach to ligand-field models has been to exploit the purely group-theoretical aspects of the subject in order to establish 'finger-printing' rules by which molecules may be classified according to structure and bonding. Used in conjunction with the wide range of other physical techniques available to chemistry over the years, this approach has enjoyed some measure of success and, in earlier days at least, inspired fresh appreciation of theories of chemical bonding. However, a marked decline of interest in the ligand-field properties of single-centre systems has taken place in the past 15 years. Lest it seem perverse, therefore, to present yet another book in this area, it must be said at the outset that many of the efforts of the past decade or so can now be seen as having paved the way towards a contemporary exploitation of ligand-field theory which begins at last, and almost for the first time, to fulfil the explicitly *chemical* promise, hoped and claimed for the subject as long ago as the 1930s. In order to appreciate the sea change brought about by the contemporary synthesis, it is necessary to understand the reasons for the chemists' disenchantment with ligand-field theory in the recent past. In chapter 1, therefore, we begin with a little history.

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1.1 The promise

The developments of the theories of paramagnetism and ligand fields have been inextricably linked from the beginning.^[1,2] Understanding magnetic moments was one of the first aims and successes of quantum theory in the late 1920s and, by 1935, Howard had published^[3] one of the earliest studies of single-crystal magnetic anisotropy – on potassium ferricyanide. On the other hand, it was probably the delayed development of sufficiently sensitive spectrophotometers that held up recognition and assignment of spin-allowed bands in optical $d-d$ spectra till the early 1950s, despite the group-theoretical basis for ligand-field theory as a whole having begun with Bethe^[4] in 1929. Probably for this reason as much as any other, the first and, for a long time, only, exploitation of the subject matter of ligand-field theory by a chemist was that by Pauling in 1932 in his seminal papers,^[5] ‘The nature of the chemical bond’. We must refer here to the ‘subject matter of ligand-field theory’ – specifically, paramagnetism – for, in several papers throughout the early 1930s, Pauling was at pains to disassociate his views of the bonding and magnetism of transition-metal complexes from the crystal-field theories of Van Vleck and of Penney & Schlapp. It was Van Vleck, however, who rationalized^[6] Pauling’s hybrid-bonding orbitals and crystal-field theory under the umbrella of Mulliken’s molecular-orbital theory.^[7] That synthesis still provides the basis for so much discussion of ligand-field theory and transition-metal complex bonding that we take it as our point of departure.

Figure 1.1 provides a schematic review of the σ bonding in octahedral symmetry in terms of molecular-orbital theory for a first-row transition-metal ML_6 complex. The bonding a_{1g} , t_{1u} and e_g orbitals are completely

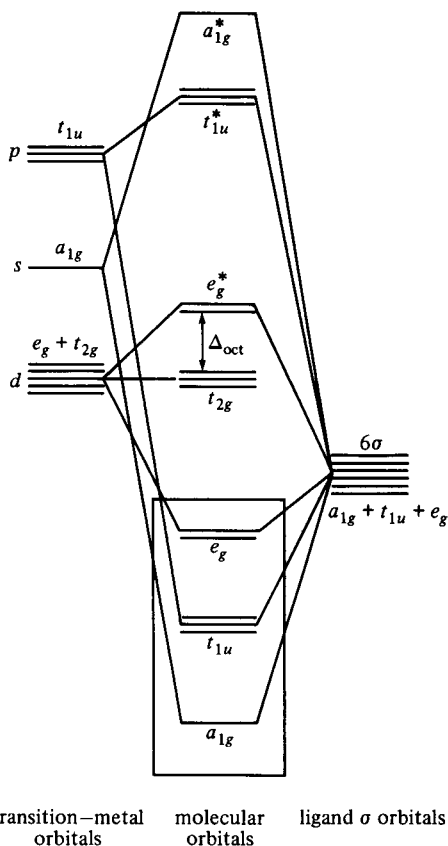


Fig. 1.1. Metal-ligand σ bonding in an octahedral complex: but see also figure 11.1.

occupied by the six ligand σ -donor electron pairs, so that their relative energies are unimportant in the present qualitative description. Pauling's d^2sp^3 valence hybrids can be related to the block of bonding molecular orbitals, shown in the box of figure 1.1, when we take note of the metal orbital parentage as involving two d atomic functions (d_{z^2} and $d_{x^2-y^2}$); the valence electrons, formally belonging to the metal atom, are distributed between the t_{2g} and e_g^* molecular orbitals exactly as prescribed in elementary crystal-field theory. The whole scheme brings together the positive aspects of Pauling's hybrids and crystal-field theory while simultaneously avoiding the more problematic features of these one-sided models. The primary property of the hybrid-bond approach was its concern with chemical bond formation. The less successful aspects of Pauling's formalism – being the loss of d orbitals available after hybridization in

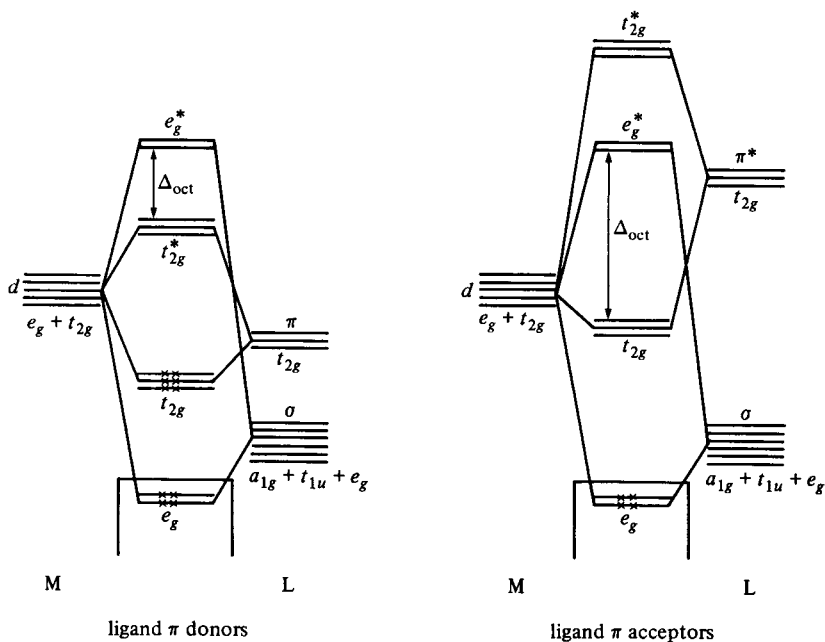


Fig. 1.2. The effects of π bonding on Δ_{oct} .

which to place the 'metal' electrons, and its general inability to describe excited-state properties and hence spectral transitions – are all adequately dealt with by reference to the non-bonding and antibonding MOs of the ligand-field region of the diagram. Similarly, the original introduction^[4] of crystal-field theory in terms of the relative *repulsive* energies between metal orbitals and ligand charges is now much better represented in terms of the antibonding energies of the e_g^* molecular orbitals. The magnitude of Δ_{oct} thus refers to the antibonding energy shift of the metal e_g orbitals and, as this might be expected to change with ionization energies, overlap and resonance integrals somewhat similarly to that of the bonding counterparts, a qualitative association of Δ_{oct} values with bond 'strength' is apparent. The approach thus relieves crystal-field theory of the embarrassment of having to rationalize Δ_{oct} values in terms of the magnitudes of actual ligand charges.

As it stands, however, the model represented in figure 1.1 does not provide even a qualitative rationalization of the phenomenological variation of Δ_{oct} values we call the spectrochemical series. That can be remedied though, in outline at least, by the introduction of ligand π function into the MO scheme. The well-known diagrams in figure 1.2

illustrate the situation for the cases of ligands acting as π donors or π acceptors towards the central metal atom. On the left, the low-lying, filled π orbitals of the ligand donate three electron pairs to the metal, filling up the t_{2g} molecular orbitals: Δ_{oct} here refers to the energy splitting between t_{2g}^* and e_g^* MOs. On the right, the high-lying, empty π^* orbitals of the ligand acceptors interact with the metal t_{2g} orbitals, leaving the t_{2g} and e_g^* molecular orbitals to hold the 'metal' electrons of the ligand-field model. There follows the idea that ligand π donors tend to reduce the magnitude of Δ_{oct} relative to the value deriving from σ bonding alone, while ligand π acceptors tend to increase Δ_{oct} . If we write the contributions to Δ_{oct} from σ and π bonding as Δ_{σ} and Δ_{π} , taking the convention that positive values correspond to an upward (antibonding) energy shift in the appropriate metal orbitals, we have the relationship

$$\Delta_{\text{oct}} = \Delta_{\sigma} - \Delta_{\pi}. \quad (1.1)$$

The effects of σ and π donors as monitored by Δ_{oct} are opposed, therefore. The high position of the carbonyl ligand in the spectrochemical series^[8] is thus rationalized in terms of a strong π acceptor or acid property of this ligand. Foreshadowing much later discussion, particularly that in chapter 11, it is worth commenting here on the relationship between the description we have outlined and the synergic, 'back-bonding' model^[9,43,44] of Dewar & Chatt. It is commonly argued that the $-\text{CO}$ ligand might not be considered an especially good σ donor or π acceptor, *a priori*, in view of its rather modest role as a Lewis base with non- π -bonding acids. The adjective 'synergic' was coined to express the mutual augmentation of σ -donor and π -acceptor properties of this and similar ligands when provided with the appropriate orbital pathways by a metal, a basic theme in the model being the operation of the electroneutrality principle. Incorporation of these ideas within a molecular-orbital calculation means that the process of bond formation requires changes in the relative valence-orbital, ionization potentials for the metal and ligand orbitals, which in turn alter the degree of overlap and electron distribution. We take the diagrams in figures 1.1 and 1.2 to represent the *final situation* in a self-consistent molecular-orbital calculation: this means, not only that metal and ligand energies are different from those of the unbonded species, but also that appropriate modification of the basis orbitals has been made to describe electron polarization effects. For a first-row transition-metal ion then, we avoid labelling the metal orbitals as $3d, 4s, 4p$, since the identification of the energy splitting $t_{2g} - e_g^*$ with the ligand-field parameter Δ_{oct} requires those orbitals to conform with the

complex molecule *as it is*, rather than to refer to the free metal ion from which it was formed. We note here that the interpretation of MO diagrams like these is a matter requiring great care, no more so than when applied to the meaning of Δ_{oct} and $10Dq$: we deal with this question in detail in chapter 11, observing for the moment that the *description* given so far is only adequate for complexes possessing a d^1 configuration for the metal ion.

One feature of Pauling's original model is not reproduced by the molecular-orbital approach. His 'magnetic criterion for bond type' ascribed certain differences between high- and low-spin species to the use of inner ($3d$) or outer ($4d$) orbitals for hybrid formation. The approach implied a discontinuity of bond type between what he considered as 'mostly ionic' and 'mostly covalent'. The MO and ligand-field models, on the other hand, recognize no such discontinuity, the change from a high- to a low-spin state reflecting a smooth progression from ligands associated with small Δ_{oct} values to those with large ones. While we can no longer support Pauling's simple criterion we might reasonably identify the birth of 'magnetochemistry' with his early papers^[5], for the idea that *chemically* interesting information might be derived from a study of paramagnetism began there. Over the years, and in no small measure due to the influence of Nyholm^[10] and his school, magnetochemistry grew to the status of a routine tool within inorganic chemistry research laboratories and, indeed, one may consider it as 'the senior partner' relative to spectroscopy within the broader, chemical, ligand-field discipline up to the early 1960s. One important reason for this interest lay in the models described by Figgis^[11–14] at that time and their exploitation by Figgis, Lewis and their colleagues.^[12–14]

1.1.1 Magnetic properties of ions with formal, orbital-triplet ground states

Bringing together the work of Kotani, Bleaney and his group, and Stevens, Figgis described an approach to the interpretation of the paramagnetism of ions with formally, triply-degenerate ground terms. Although a number of systems had been studied and interpreted in a somewhat similar fashion previously, Figgis' model was the first to have rather wide application throughout the transition-metal block, with respect to variation in metal, coordination number, and ligand. The average, powder susceptibilities of some 60 complexes and their variation with temperature were measured and 'fitted' within the range 80–300 K by Figgis, Lewis and their students.

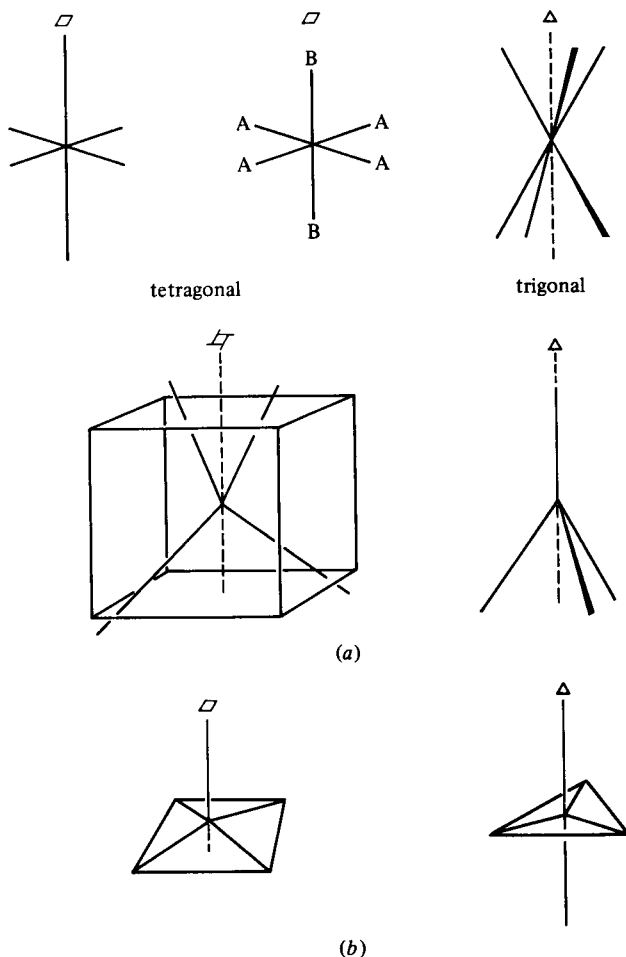


Fig. 1.3. Types of axial field: (a) tetragonal and trigonal distortions from octahedral and tetrahedral precursors, and (b) examples of four-fold and three-fold geometries which do not approximate cubic precursors.

The approach may be illustrated by its application to ions with formal 2T_2 ground terms.

The model involves the simultaneous perturbation of the six-fold degenerate 2T_2 basis by the effects of spin-orbit coupling and an axially symmetric, ligand-field distortion, using the effective Hamiltonian

$$\mathcal{H}' = \lambda \mathbf{L} \cdot \mathbf{S} + V_{\text{axial}}. \quad (1.2)$$

The exact nature of the axial field is irrelevant in this model and could

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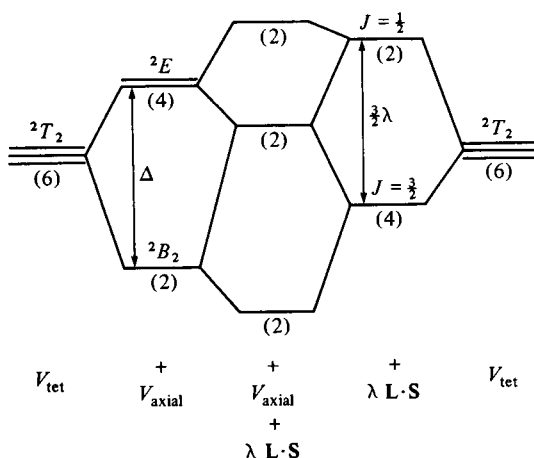


Fig. 1.4. The separate and simultaneous perturbations of a cubic-field 2T_2 term by an axial distortion and spin-orbit coupling: total degeneracies are given in parentheses.

represent any of the departures from octahedral or tetrahedral precursors shown throughout figure 1.3(a) or even, perhaps, the intrinsically lower symmetries of the types of geometry shown in figure 1.3(b). In all cases, the axial field is simply represented by a splitting Δ of the orbital-doublet and -singlet components of the T term, being defined by the energy difference,

$$\Delta = \varepsilon({}^2E) - \varepsilon({}^2B_2), \quad (1.3)$$

taking, here symmetry labels appropriate for the tetragonal distortion of the tetrahedron in figure 1.3(a). The model had emerged from the recognition that low-symmetry splittings can be comparable with those from spin-orbit coupling previously studied by Kotani^[15] and, in the middle of figure 1.4, are shown the three Kramers' doublets which arise from these two effects (1.2) together. The energies and composition of these doublets are functions of the two parameters Δ and λ . The model involves one further variable; namely, Stevens' orbital reduction factor^[16] k appearing in the magnetic moment operator,

$$\mu_\alpha = \beta_0(kL_\alpha + 2S_\alpha); \quad \alpha = \parallel, \perp. \quad (1.4)$$

Full descriptions of the technical and numerical features of Figgis' approach, which was applied to transition-metal complexes with formal ${}^2T_{2(g)}$, ${}^3T_{1(g)}$, ${}^4T_{1(g)}$ and ${}^5T_{2(g)}$ ground terms, have been presented several times and will not be repeated here. The importance of the models lay in their promise to illuminate the nature of the bonding in the complexes

to which they were applied. Numerical values for the three parameters Δ , k , λ (together with ones for a further parameter A associated with the degree of cubic-field mixing between T_1 terms arising from the free-ion P and F terms) were determined by reproduction of the absolute values and temperature dependences of experimental, mean magnetic moments. These parameter values were to be correlated with broader chemical concepts along the following lines. Firstly the sign and magnitude of the axial-field parameter Δ should comment upon the nature of the ligand-field asymmetry with respect to the unique geometric axis. Something of the nature of the different roles played by A- and B-type ligands in a *trans*-octahedral MA_4B_2 complex, for example, should be discernible from a series of such Δ values. Secondly, some measure of the degree of covalency in the M—L bonds should derive from the values determined for λ and k . At the time these models were first proposed and applied, Stevens' orbital reduction factor was also called^[17] an 'electron delocalization factor' or 'covalency factor', being associated with the degree of overlap between metal and ligand π orbitals. The extent by which k was reduced from unity in a given complex should, it was hoped, provide a measure of the delocalization of unpaired metal electrons onto the ligands and, at the same time, comment upon the relative degrees of σ and π bonding in the complex. The effective spin-orbit coupling coefficient λ in (1.2) should also reflect the covalent nature of the bonding by providing some measure of the degree of orbital expansion which had taken place on complex formation.^[18]

Should we be less than convinced by these aspirations today, it is well to remember that Figgis' models allowed both absolute values and temperature variations of the magnetic moments of a wide variety of transition-metal complexes to be reproduced theoretically, virtually exactly and almost for the first time since the principles of the subject had been laid down in the late 1920s. This success appeared to signify that magnetochemistry had come of age and promised a rich haul, in terms of our understanding of chemical bonding, to be had from increasingly detailed and sophisticated theory and experiments. At the beginning of the 1960s the mood was certainly optimistic. It didn't last.

1.2 Larger bases

Despite its successful reproduction of the detailed paramagnetism of so many transition-metal complexes, Figgis' approach failed to yield generally acceptable interpretations of the model parameters. Actually, several

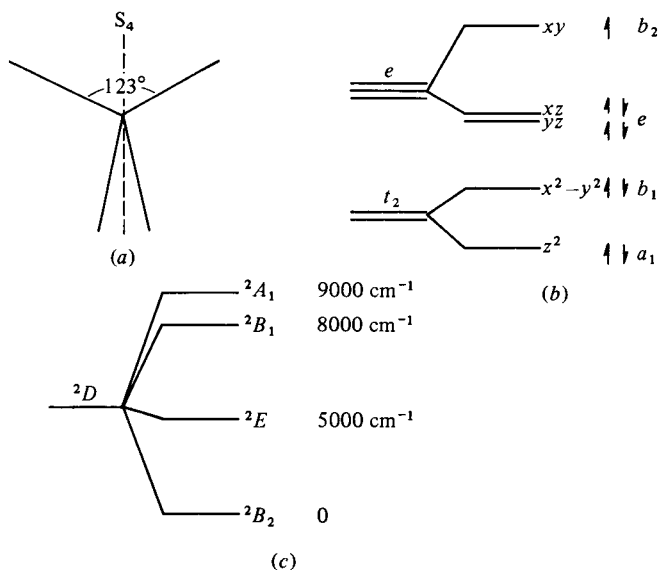


Fig. 1.5. Cs_2CuCl_4 . (a) Approximate axial symmetry of CuCl_4^{2-} ions: (b) predicted orbital ordering from compressed geometry, and (c) summary of term splitting from the polarized spectrum.^[4,21]

difficulties were recognized^[11-14] by Figgis and Lewis from the beginning. Orbital reduction factors frequently failed to correlate with accepted notions of π bonding and covalency and in due course came to be regarded as 'fudge' factors. Since then, arguments have been presented^[19] to show why direct correlations of the sort originally claimed may not obtain and in chapter 11 we shall see more of the origins of the confused state of the interpretation of orbital reduction factors. Similarly, relationships between empirical λ values and covalency or ligand-field strength were not transparent. The most serious problems, which began to emerge a little later, were to do with the fact that various parameter values estimated by the procedures above were seriously in error due to deficiencies in the model itself. The ligand-field properties^[20] of some nominally tetrahedral copper(II) complexes illustrate the point.

Crystals of Cs_2CuCl_4 contain nominally tetrahedral CuCl_4^{2-} ions, shown by X-ray crystallographic analysis to suffer the tetragonally compressed, approximate D_{2d} geometry shown in figure 1.5(a). We expect, therefore, the orbitals involving the z label to be stabilized with respect to the tetrahedral energies, as shown in figure 1.5(b) and to give rise to a 2B_2 ground term. Application of the 2T_2 model, described above, to the