Coordination Chemistry Reviews, 99 (1990) 117–136
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THE ROLES OF *d* ELECTRONS IN TRANSITION METAL CHEMISTRY: A NEW EMPHASIS

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(Received 16 May 1989)

CONTENTS

A. INTRODUCTION

Students of inorganic chemistry must be struck by the marked change of tone that accompanies the passing from main group to *d* block chemistry. A large part of introductory courses to the transition metal area is given over to ligand field theory and the rationalization of spectral and magnetic properties. It is not simply that the pretty colours of most transition metal complexes define an aesthetic imperative or even, for the more theoretically inclined, that ligand field theory provides wide opportunities for the exercise of symmetry and group theories. We discern, rather, a central plank in the teaching of transition metal chemistry as one which exalts the possibilities for further covalency and overlap afforded by *d* orbitals that are essentially unavailable in main-group metals. I wish to challenge this emphasis upon a "natural break" between main group and *d* block. Instead, I develop the theme that it is not that transition metal chemistry and bonding need be so different from those of the main block but that there exists a different

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quality of interaction for certain types of transition metal compounds. We should point to a natural break between high and low oxidation state transition metal chemistry instead.

Let us begin by identifying some of the more important features that are, and are not, characteristic of *d* block chemistry: we shall focus on the first transition series throughout.

(1) Simple binary and ternary compounds are as common inside the *d* block as outside and, remembering the importance of ionic and covalent radii, crystal structures of compounds in both groups do not mark out transition metal systems as of special interest.

(2) The formation of Werner-type complexes of great variety is not the sole preserve of *d* block metals, notwithstanding the historical focus in that area. The thermodynamic stabilities of complexes of zinc or magnesium, for example, are frequently comparable with those of iron or cobalt.

(3) Perhaps the most obvious characteristic of the transition metals is their extensive and facile redox chemistry. It is somewhat unusual to observe more than two commonly occurring oxidation states for a main-group metal. By contrast, the existence of complexes of vanadium in all oxidation states from $-$I to $+$V is quite typical of the *d* block elements. An important subclass of transition metal redox reactions are those which involve neither bond rupture nor ligand rearrangement.

(4) Equally typical of the transition block is the formation of carbonyl and related complexes. Carbonyl complexes of the main-group metals are virtually unknown while they have been prepared in their hundreds for the *d* block metals. It makes no difference to argue that it is essentially only the existence of zero or other very low oxidation states for the transition metals that establishes this carbonyl chemistry or, alternatively, that these low oxidation states are brought about only by carbonyl and other π-acid ligands. Either way, carbonyl and zero (low) oxidation state chemistry is a distinguishing characteristic of the *d* block metals.

(5) A clear difference exists between carbonyl-type complexes and those Werner-type species of higher oxidation states. Carbonyls are almost exclusively diamagnetic and the valence shells of their metal atoms are well considered in terms of the 18-electron rule. By contrast, there is no empirical requirement to fill the *d* subshell in Werner-type systems which commonly exhibit the paramagnetism associated with unpaired *d* electrons. Of central importance here is the stability of these open *d* shells. There is no evidence of the sort of free-radical reactivity that is associated with similarly incomplete shells in main-group chemistry.

(6) While the common occurrence of planar coordinated species of especially d^8 transition metals has long been held to provide evidence for covalent bonding—most usually invoking *d* orbital participation in ap-

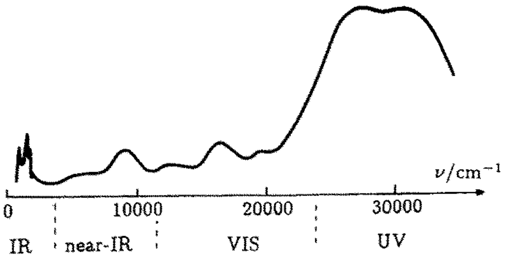


Fig. 1. A typical absorption spectrum for a transition metal complex.

propriate hybrids—it is the case that one of the more successful simple models in structural chemistry can accurately account for the angular coordination geometries of essentially all but these planar species solely in terms of repulsive forces. Over several years, Kepert [1] has applied a most simple approach to transition metal coordination geometry based upon the notion that monodentate ligands and chelates of fixed bite move over the surface of a sphere subject only to a repulsive $1/r^n$ power law between them. While the absolute energies calculated for the favoured configurations depend upon the power n assumed, the geometries yielding minimum energy essentially do not. He has successfully rationalized or predicted the angular geometries of some 2500 disparate complexes to within two or three degrees. Judged simply by results, Kepert's model cannot be ignored. Its success requires explanation as well as its inevitable failure to account for planar coordination in d^8 species.

(7) By and large, transition metal complexes are coloured. Typical features of the absorption spectra of transition metal complexes are summarized schematically in Fig. 1.

Absorptions are broadly of three types: (a) fairly sharp transitions, associated with molecular vibrations, that are of low frequency within the IR region below say 5000 cm^{-1}; (b) a number of weak, broad features spanning energies from the near-IR into the UV; and (c) frequently quite intense, broad envelopes at higher energies. Overlap between the energy ranges of these three types often occurs but the summary sketched in Fig. 1 is not untypical. The weaker, mid-range features are called "*d–d*", ligand field transitions, for reasons we shall investigate, and the higher energy ones are dominated by so-called "charge transfer" transitions.

For the moment we should focus on two crucial features of the "*d–d*" spectrum. Firstly, these transitions are weak. They are typically a thousand times weaker than the most intense charge transfer bands and often much weaker still than absorptions characterizing dyestuffs. A molar solution of copper sulphate, for example, is seen as obviously blue. Diluted a thousand times, it appears colourless, while a millimolar solution of, for example, potassium permanganate, whose visible spectrum is dominated by charge transfer transitions, is still quite strongly pink. Secondly, the number of bands in the "*d–d*" spectrum of a transition metal complex with given coordination number and geometry is characteristic of the number of electrons in its *d* shell; where exceptions occur, they are well understood and do not detract from this central point. This feature of a constant pattern of transitions in "*d–d*" spectra is one very important reason why transition metal complexes are discussed in terms of their d^n configuration. That contrasts with the usual vocabulary we use for main-groups bonding where *s*, *p*, *sp*, sp^2, sp^3 and, indeed, sp^x with x fractional are more useful bases.

B. THE VALENCE SHELL

This provides a point of departure for rationalization of transition metal spectra, bonding and chemistry. One typically focuses, for transition metal bonding, on the possibilities for overlap presented by the *d* shell. I believe this to be a false exaggeration of the true state of affairs and prefer, for higher oxidation state complexes at least, to emphasize the minimal participation of *d* orbitals in the valence shell. The development of this viewpoint throughout the following sections has been occasioned by a desire to provide a qualitative understanding of transition metal bonding that does not conflict with "*d–d*" spectroscopy and ligand field theory. It is difficult to comprehend the structure of ligand field theory, let alone the detailed significance of its parameters unless the *d* orbitals are largely unmixed with other orbitals: though not obvious perhaps, this thesis has been fully defended in the literature [2,3]. It is similarly hard to rationalize the weakness of "*d–d*" transitions unless those *d* functions are fairly pure. It is known, for example, that the direct mixing of 3*d* and 4*p* orbitals of free ions in a crystal field is trivially small: an early calculation [4] of spectral intensity, ultimately deriving from this mixing, yielded a result orders of magnitude smaller than that observed. Intensity actually arises in complexes primarily via covalency and overlap; that is, from the mixing of the metal *d* orbitals with appropriate ligand functions. So we admit at once that metal *d*–ligand mixing does occur. That Laporte's rule, denying the possibility of electric-dipole transitions between states of the same parity, is so well obeyed in ligand field spectra, however, is strong evidence that such mixing is small. I therefore propose that a sensible beginning in transition metal bonding theory for Werner-type complexes (higher oxidation state) is one that envisages bond formation in terms of overlap between metal *s* (and/or *p*) orbitals and appropriate ligand functions: in short, that the valence shell largely excludes the 3*d* functions.

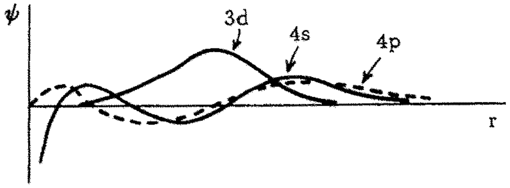


Fig. 2. Schematic radial forms for orbitals of first transition series ions in higher oxidation state complexes. The outermost, valence, regions of the 4*s* and 4*p* functions maximize further out from the metal than does the 3*d*.

Consider this position in terms of two factors that are important in the construction of molecular orbitals from metal and ligand atomic orbitals. These concern the energy matching between the interacting functions and their overlaps. In Fig. 2 are sketched typical radial forms of 3*d*, 4*d* and 4*p* orbitals of first-row transition metal ions in oxidation states appropriate for Werner-type complexes, say, +II or more. The 3*d* orbitals in such ions have much more "inner" character than the valence regions of 4*s* or 4*p* and so overlap less well with the ligand functions. However, the energy difference between typical ligand donor orbitals and metal orbitals is less for 3*d* than for 4*s* than for 4*p*. In a rough and ready way, we might represent the contributions to bonding arising from these two factors by the sketch in Fig. 3. Open circles indicate the increasingly poor energy matching between metal and ligand orbitals along the series 3*d*–4*s*–4*p* and filled circles show the poorer overlap associated with 3*d* orbitals. Taking account of both factors in a multiplicative fashion, we conclude that the major bonding contribution arises from interactions between the ligands and the metal 4*s* orbital. A minor role for the 3*d* orbitals derives from their poor overlap possibilities and a small role for the 4*p* orbitals because of their poor energy match with the ligand functions. Similarly little hybridization between the metal *d* orbitals and either other metal functions or ligand orbitals has been

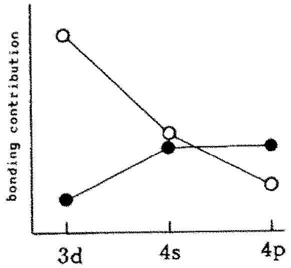


Fig. 3. An illustration of the diminishing M–L bonding contribution along the series 3*d*–4*s*–4*p* due to increasing orbital energy mismatch (open circles) and a lesser contribution for the 3*d* than 4*s* or 4*p* due to overlap (filled circles).

demonstrated by the ab initio CI calculations of Hillier and coworkers [5] on VCl_4, $CoCl_4^{2-}$ and CrO^{3+}. Actually, the hypothesis advanced in this article is not only supported by the computational chemist but is really not new. Introductions to ligand field theory and to the conventional molecular orbital accounts of it always emphasize the weak interaction between metal *d* orbitals and the ligands. Yet somehow the early emphasis gets forgotten.

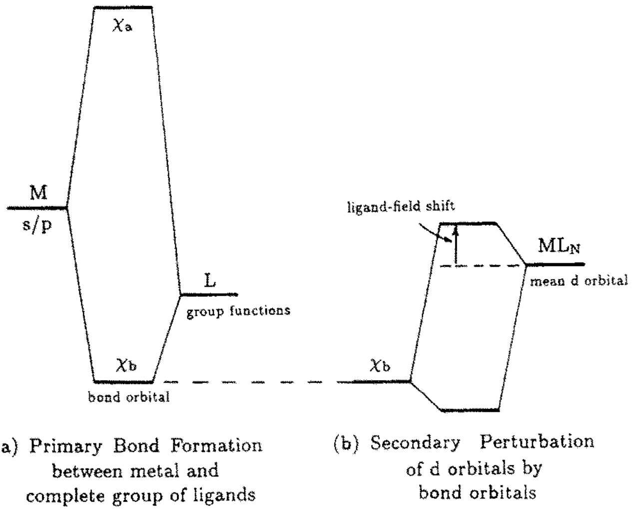
One reason for the success of Kepert's model for coordination geometry follows directly from the dominance of the metal 4*s* orbital. Thus we observe how attractive forces dominated by interactions of ligand orbitals with the spherical 4*s* orbital are non-directional and so bequeath to (secondary) repulsive forces, the determinacy of angular geometry.

While emphasizing the role of metal 4*s* orbitals, we should not disregard the *d* electrons. They do affect the bonding electrons and are, in turn, affected by them. We now consider these two aspects separately as best we might.

C. THE RESPONSE OF THE *d* ELECTRONS

The *d* electrons in a complex are no longer subject to the central field of a free ion and so lose their degeneracy. There follow all the manifestations of spectroscopy and magnetochemistry that form the stuff of ligand field theory. Recent years have seen enormous strides in the theory and application of the ligand field method. While cubic fields and the spin-only formula occupied so much attention years ago, contemporary ligand field analysis is now able to model and reproduce *d–d* transition energies, anisotropic ESR g^2 and paramagnetic susceptibility tensors [6] and, most recently, the intensity distributions [7] in transition metal spectra, for complexes of any d^n configuration, any coordination number and any coordination geometry. Careful theoretical studies [2] of the underlying structure upon which these applications depend have provided the basis for the views presented in this article. A simple summary of the nature of the ligand field method provides the background for the present thesis.

First, let us recall the usual steps involved in building up molecular states. We begin with the overlap between metal and ligand functions to produce molecular orbitals. Then, after populating these molecular orbitals with electrons according to the Aufbau principle, we recognize electron–electron repulsions and so determine the many-electron states of the molecule. However, interpretations of ligand field parameters are always made by reference to orbitals rather than states and so we are obliged to construct a scheme that retains a focus upon orbitals while implicitly including a proper account of electron–electron repulsions. This has been done [2,6] along the lines summarized in Fig. 4. In (a) is represented the formation of bond

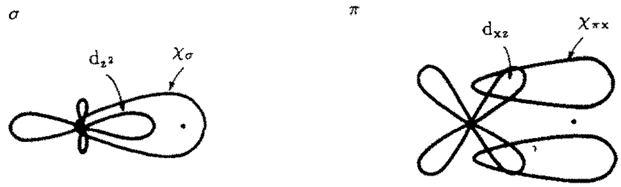


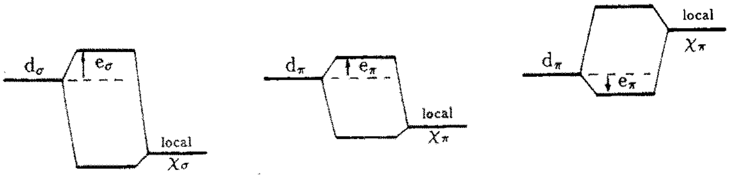
(a) Primary Bond Formation between metal and complete group of ligands

(b) Secondary Perturbation of d orbitals by bond orbitals

Fig. 4. An illustration of the two-step approach to ligand field perturbations.

orbitals in a transition metal complex. In the limit, overlap between the metal *d* orbitals and others is disregarded. However, the bond orbitals χ_b are considered to be those resulting after account has been taken of electron rearrangement in response to all interelectron repulsion (except amongst the *d* electrons). Then, in (b), is illustrated the secondary weak interaction of the metal *d* orbitals with the bond orbitals formed in step (a). The energy shifts suffered by the *d* electrons in this second step are represented as ligand field parameters. As a result of the redistribution of charge between metal and the complete set of ligands that accompanies bond formation, and the notional construction of the χ_b, the effective nuclear charge to which the *d* electrons are exposed changes. As some ligand electron density ends up in the more penetrating metal *s* and *p* orbitals, the effective nuclear charge decreases and the *d* charge cloud expands. This is the so-called "central-field covalency" aspect of the nephelauxetic effect as is discussed further in the next section. The important point for the moment, however, is to recognize that the exact radial form of these so-called "mean *d* orbitals" will vary from complex to complex and, in the absence of any enormously difficult computations, is unknown to us. The same remark pertains to the precise description of the bond orbitals also. Both mean *d* orbitals and bond orbitals are the constructs of a process that includes all interelectron repulsion (except *d–d*). So the brief summary above refers to a notional, self-consistent treatment designed to provide a basis for the qualitative interpretation of ligand field parameters. It is not to be approximated by a molecular orbital scheme relating to an interaction between metal ion *d* orbitals and functions





(a) for ligand σ donors (b) for ligand π donors (c) for ligand π acceptors

Fig. 5. Upward energy shifts are defined by positive locally defined e parameters, downward ones by negative e values.

of free ligands, as described, for example, in the angular overlap model (AOM).

The most successful ligand field models today exploit the idea of spatial superposition. That is to say that the overall d orbital energy shifts in a complex can be expressed as a sum of shifts arising from spatially local perturbations. The sum is a double one, involving discrimination of both ligands and bonding modes. Figure 5 illustrates perturbations of local d orbitals, i.e. of components expressed within the local axis frame of an individual metal–ligand interaction, of σ and π type. Local σ-bonding induced shifts of the d orbital energy are labelled e_σ and those for π bonding as e_π. The bond orbitals deriving from interactions of a metal ion and ligand donor functions are of lower energy than the metal d orbitals. Consequent ligand field shifts are then to higher energies, as shown in Figs. 5(a) and 5(b), and represented by positive values of e_σ or e_π. In Fig. 5(c) is shown the interaction of the d orbitals with bond orbitals arising out of metal bonding with (empty) higher energy orbitals that characterize ligand acceptors:these latter will normally be ligand π^* functions. The ligand field shifts are now to lower energies and represented by negative e_π parameters.

In summary, then, ligand σ and π donor functions give rise to positive, locally defined parameters e_σ and e_π. Ligand acceptor functions lead to negative e_π values. These qualitative ideas define the modern view of ligand field theory we call the cellular ligand field (CLF) model. Only the symbols e_σ and e_π are held in common with the AOM [8] now discussed in several recent texts [9]. These models differ with respect to the interpretation of e parameters. In particular, while the AOM considers interactions between free ligand and metal (ion) functions, the CLF recognizes the underlying bonding and electron density by referring to interactions between the mean *d* orbitals and the bond orbitals, as described above. The important and fundamental differences that exist between molecular orbital and ligand field approaches to spectral and magnetic phenomena are discussed more fully elsewhere [3].

D. THE NEPHELAUXETIC EFFECT

The nephelauxetic effect [10] is that the empirically determined parameters of interelectron repulsion in a complex are less than those in the corresponding free ion. The magnitude of that decrease is greater for more reducing ligands and/or more oxidizing metals: concatenating these two observations, we have *d–d* Coulomb energies that decrease as electron density is transferred from ligands to metal. The phenomenon is immediately comprehensible from our present standpoint. A greater transfer of negative charge to the central metal, via its more penetrating *s* and/or *p* orbitals in the bonds, increases the shielding of the spectral *d* electrons from the metal nucleus. The reduced effective nuclear charge to which the *d* orbitals are subject results in their expansion and, in turn, in a greater mean *d*-electron–*d*-electron separation and hence lesser repulsion energy. Values for B(complex)/B(free ion), for example, are typically observed around 0.7–0.9 for amines, say, or 0.5–0.6 for phosphorus or sulphur donor atoms. However, even greater nephelauxetic effects (lower B values) have recently been observed in some low spin complexes of cobalt(II) [11]. A brief discussion of these systems serves to illustrate current thinking in ligand field analysis.

The study [11] concerns planar coordinated, low spin cobalt(II) Schiff base complexes: its prime focus was the ligand field consequences of bent bonding and other forms of misdirected valency. For present purposes, however, we compare a subset of parameter values determined in this analysis with those typical of analogous nickel(II) complexes and—it is a fair assumption—of the putative corresponding high spin cobalt(II) species. Table 1 presents such values in a schematic way only and refers to the structure shown in Fig. 6. The ratios of F_k(complex)/F_k(free ion) for the low spin species of 0.28 and 0.82 for $k = 2$ and $k = 4$ respectively are extremely low, and while F_k integrals are necessarily positive, the linearly related Racah parameters need not be: in the present case, $B = -50\ \text{cm}^{-1}$.

The parameter sets in the table reveal aspects of the electronic structure of these complexes quite naturally. Consider the change from high to low spin electronic arrangements. The discontinuity of spin type is characterized by a rearrangement of the *d* electrons such that they avoid the bond regions more

TABLE 1

Comparison of selected ligand field parameters in high and low spin planar Schiff-base complexes of cobalt(II)

	$\bar{e}_\sigma$(N) (cm^{-1})	$e_{\pi\perp}$(N=) (cm^{-1})	F_2 (cm^{-1})	F_4 (cm^{-1})	Mean M–ligand bond length (Å)
Low spin [a]	7500	−550	400	90	1.84
High spin [b]	4000	+900	1280 [c]	95 [c]	1.97

[a] Observed [11].

[b] Estimated by comparison with related nickel(II) species [15].

[c] Taken as 0.9 times the free-ion values.

effectively in the low spin situation. Now we recognize the second role of *d* electrons alluded to earlier; namely, their effects upon the bonding electrons. Thus the lessened repulsion between *d* and bonding electrons allows a closer approach of the ligands in the low spin state, as evidenced by the bond lengths quoted in the table. That closer approach increases bond strength and the electron density in the bonding region and so, via appropriate modification of the underlying bond orbitals, χ_b, increases the values of e_σ. At the same time, more negative charge is donated to the metal which, in response to the electroneutrality principle, relieves the extra charge accumulation by an expansion of its spectral *d* orbitals, as revealed by the large nephelauxetic reduction of the interelectron repulsion. Then, in order to preserve a balance so far as possible, the greater donation by the ligands is accompanied by (weak) π-acid character rather than the π donation observed in corresponding high spin species; after all, the electroneutrality principle operates for the ligand atoms just as for the metal.

This discussion illustrates two centrally important aspects of the electronic structure of transition metal complexes: (a) the interdependence of the electron density in the *d* orbitals and in the bond orbitals, and (b) the elasticity of the *d* cloud expansion in response to varying degrees of charge transfer. We shall pursue these two themes further now, and in that order.

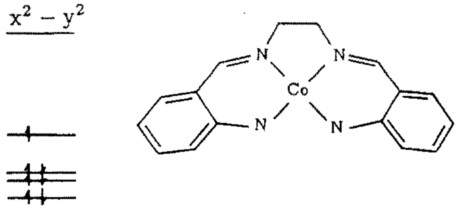


Fig. 6. The low spin electron configuration in a typical planar coordinated cobalt(II) Schiff-base complex.

E. THE STERIC ROLE OF THE *d* ELECTRONS

A recent ligand field analysis [12] of a series of trigonal bipyramidal complexes graphically illustrates the steric role of incompletely filled *d* shells. In Fig. 7 is shown the coordination geometry of molecules with the formula $LMBr^+$ where L is the tripodal ligand, tris(dimethylaminoethyl)-amine, offering one axial and three equatorial amine donors throughout this series.

Important geometrical and ligand field parameters, the latter having been determined by reproduction of experimental "*d–d*" spectral transitions, are summarized in Table 2. Ambiguities in the values of e_π(Br) described in the original paper, do not affect the present discussion, the central issue of which concerns the changes in the ratios of e_σ values for axial and equatorial sites as the central metal is varied.

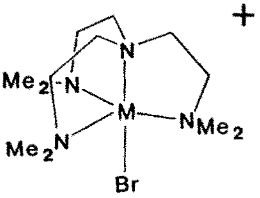


Fig. 7. The trigonal bipyramidal coordination in the species $LMBr^+$.

TABLE 2

Structural and ligand field parameters for the series $LMBr^+$

Metal	Co	Ni	Cu	Zn
M–N(ax) (Å)	2.15	2.10	2.07	2.19
M–N(eq) (Å)	2.08	2.13	2.14	2.11
M–Br (Å)	2.43	2.47	2.39	2.45
$\bar{e}_\sigma$(ax) (cm^{-1})	4000	5000	5800	
e_σ(eq) (cm^{-1})	4000	3900	3300	
[a] e_π(Br) (cm^{-1})	1000	1000	1000	
z^2	.	.	.	..
xy $x^2 - y^2$	:	:.	::	::
xz yz	::	::	::	::

[a] Fixed for the present discussion, see ref. 12.

Simple VSEPR theory suggests that the axial M–N bond be longer than the equatorial ones and such is indeed observed in the cobalt and zinc molecules. Overlying that, we observe a general contraction of bond lengths on moving to the right-hand end of the transition series, as expected from changes in the effective nuclear charge. Of particular interest, however, is the marked reduction in the axial bond lengths and, indeed, reversal in the relative magnitudes of axial and equatorial interactions in the copper analogue, with nickel occupying an intermediate position. The observed ligand field parameters similarly reflect these changes. They may be understood in terms of the steric hindrance by the d shell suffered by the bonds in the complex. Thus, from the orbital populations included in Table 2, we observe increasing occupancy of those orbitals which interact most directly with the equatorial ligands. In the d^7 cobalt complex, the repulsive interactions are effectively equal for axial and equatorial sites, one d electron associated with the z or axial direction and two with the equatorial xy plane. In the d^9 molecule, the extra d electrons increasingly repel and frustrate the equatorial bonding so that, as the electroneutrality principle operates to satisfy the local metal charge, the axial bonds contract in compensation.

Several years earlier, somewhat similar proposals about the effects of d orbital occupancy upon ligand field parameters were made by Lever and Hollebone [13]. Within the series of linear transition metal dichlorides, e_σ values were observed to decrease from d^4 (chromium) to d^6 (iron) but then increase again for d^8 (nickel): at the same time, e_π values increased unevenly throughout the same series. These changes were correlated with the configurational changes from $(\delta^2\pi^2)$ to $(\delta^3\pi^2\sigma)$ to $(\delta^4\pi^3\sigma)$. In the language of the present article, the occupancy of the d_{z^2} (σ) orbital on exchanging chromium for iron tends to frustrate the axial ligation and e_σ decreases. The larger value of e_π for the d^6 halide is to be seen as reflecting the increased effective nuclear charge on the metal together with the operation of the electroneutrality principle on the ligand. The further increase in e_σ for the d^8 complex and the more modest increase in e_π were ascribed to the underlying increase in the effective metal nuclear charge on traversing the period.

The repulsive role of the d electrons attains significance notwithstanding the contracted nature of those orbitals and their minimal overlap with precursor ligand functions. Within the interactive scheme of Section C, their repulsive role has been included with the description of the bond orbitals that the ligand field parameters ultimately probe. One must recognize also that such repulsions imply contributions to "bonding" because the consequent changes in bond length have modified both energies and wavefunctions in the complex.

Many other examples of the repulsive role of *d* electrons, evidenced by both structural and ligand field properties, are reviewed in ref. 3. Here we focus on one further example and so address a long-standing structural issue in *d* block chemistry.

F. PLANAR COORDINATION

The common occurrence of planar coordination in d^8 complexes has been a focal point for transition metal chemistry for many years. Some have considered this stereochemistry as direct evidence of the participation of *d* orbitals in overlap and bonding in terms, for example, of Pauling's dsp^2 hybrids [14]. Planar coordination also presents an apparent embarrassment to the "repulsive theory" of Kepert [1] in that no model based on repulsions between ligands or bond pairs would favour planar over nominally tetrahedral coordination.

Let us consider then an octahedral d^8 complex. The *d* electron arrangement approximates the configuration $(t_{2g})^6(d_{x^2-y^2})^1(d_{z^2})^1$ which offers "isotropic" repulsion to the octahedral bond orbitals. So far as this role for *d* electrons is concerned, small elongations of either axial or equatorial bonds (within vibrations perhaps) are met with a restoring field: d^8 octahedral geometry, per se, is stable. Suppose, however, that we persist, as it were, and begin to draw out two *trans* ligands (let us say along *z* as the axial direction). The orbital diagram in Fig. 8 depicts the resulting ligand field splitting. Eventually the e_g orbital splitting increases to such an extent that the low spin arrangement (b) is favoured and then the repulsive role of the *d* electrons is roughly doubled in the *z* direction and removed in the *xy* plane (over and above the essentially unchanged role of the t_{2g}^6 set). There follow two consequences. The equatorial ligands may now approach the metal more

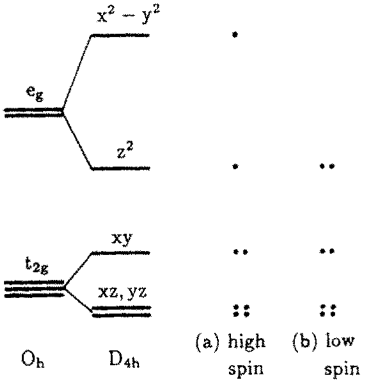


Fig. 8. High and low spin electronic arrangements in tetragonally elongated d^8 species.

closely and thereby more effectively satisfy the electroneutrality principle by compensating a metal for its loss of the axial ligands; and the return of the axial ligands (lost or very distant) is generally hindered by the doubly occupied d_{z^2} orbital. Thus d^8 planar geometry is stabilized by the repulsive role of the directed lone pair in the d_{z^2} orbital. One supposes that the path from octahedral to planar would be discontinuous in that the pairing up of electrons which accompanies the change in spin state would occur suddenly in the same way, for example, as a piece of metal "snaps" under distortion. Further, tetrahedral coordination is not favoured over planar here, again because of the steric activity of the lone pair in the d_{z^2} orbital.

The upshot is that planar coordination is not to be seen at all as a challenge to the proposed innocence of *d* orbitals in transition metal covalency and that Kepert's model merely needs to be supplemented with a recognition of the steric role of an asymmetrically filled *d* shell. In passing, there will be many occasions where that steric role will be manifested in bond length variations rather than in angular changes and this provides a further reason why the simpler approach pursued by Kepert meets with wider success than might otherwise be expected.

G. THE SPECTROCHEMICAL SERIES AND *d* ORBITAL OVERLAP

The nephelauxetic and spectrochemical series describe two different generalizations that are empirically observed of ligand field transition energies. It is an unfortunate accident of teaching methods, perhaps, that students generally feel less confident with "interelectronic repulsion" than with "ligand field splittings", for the basic features of the nephelauxetic effect are more readily comprehensible than those of the spectrochemical series. However, the discussion of cloud expansion given in Section D refers necessarily to "global" effects within a complex. Racah parameters (B, C), for example, relate to changes in central shielding in a complex, which result from the bonding of the metal to the set of ligands as a whole. There is no ready possibility of any superposition over individual M–L contributions as characterizes the ligand field potential. This follows because the physical utility of the ligand field superposition rests upon the (totally defensible [2]) notion that the sources of various spatially local potentials are actually situated locally, circumstances which are not satisfied for the interelectron repulsion terms. So the nephelauxetic series correlate nicely with chemical concepts of metal–ligand charge transfer but only in an average way that monitors the global or net effect of the ligand set as a whole.

In conventional ligand field models it is only the ligand field potential that carries information on the molecular geometry and point group. In the manner of Section C, the ligand field may be subdivided, under reasonable

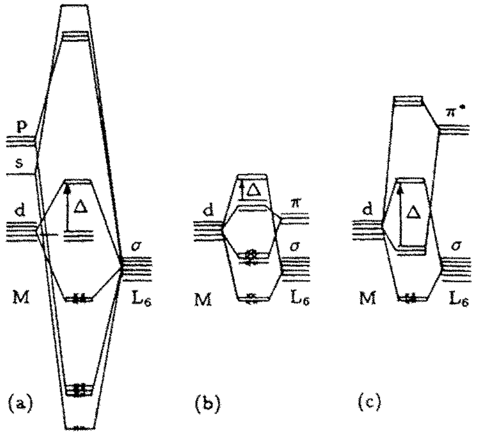


Fig. 9. Molecular orbital diagrams for bonding in an octahedral complex: (a) with ligand σ bonding only; (b) the additional contribution from ligand π donors; (c) from ligand π acceptors.

physical approximation, into separate M–L contributions of varying symmetry type (local σ, π_x, π_y). A local d_{z^2} orbital is shifted by an energy e_σ and local $d_{xz,yz}$ orbitals by e_π. As described in Section C, donor ligations give rise to positive e parameters, and acceptors to negative ones. Hence, locally, the splitting $E(d_\sigma) - E(d_\pi)$ is less for π donors and greater for π acceptors. Transformation of this result into a global reference frame, together with superposition over other ligands in the complete complex, automatically ensures [10(b)] in the octahedron, for example, that the (now global) $d_{x^2-y^2}$, d_{z^2} orbital pair lies higher in energy than the $d_{xz,yz,xy}$ trio with the usual splitting $\Delta_{\text{oct}} = 3e_\sigma - 4e_\pi$. Again, Δ_{oct} is less for π bases (e_π, positive) and more for π acids (e_π, negative). This line of reasoning is used to rationalize the occurrence at the low end (small Δ_{oct}) of the spectrochemical series of say the halogens, of ammonia in the middle ($e_\pi = 0$), and of say phenanthroline towards the high end.

It should be noted that this little discussion was made totally within the framework of modern ligand field theory and as such is wholly compatible with the notion that d orbitals are largely uninvolved in overlap with precursor ligand functions. Let us compare the more conventional approach to the spectrochemical series offered by molecular orbital theory. Figure 9 illustrates the formation of molecular orbitals for ligands entering into σ and π bonding with the metal in an octahedral complex. The rules for combining orbitals of similar symmetry are well known as are the broad concepts that suggest the typical ordering of molecular orbitals shown in the figure. Let us concentrate here on just two aspects of these diagrams which are often insufficiently emphasized.

First, in (a) for the σ bonding case, the metal orbital parentage of the filled bonding e_g, a_{1g}, t_{1u} molecular orbitals is d^2, s, p^3, so pointing to the relationship with Pauling's (purely bonding) d^2sp^3 hybrids. These observations are not to be seen, of course, as suggesting that the d orbital must make a 33% contribution to the molecular orbital or even a 33% contribution to the metal part of the molecular orbital. The diagram merely indicates connections of levels with the same symmetry and that the d orbital contribution is probably less than that of the metal s and p. After all, bonding between ligand σ orbitals and the metal 1s core orbital is also symmetry allowed but surely not considered as of any importance here.

Secondly, the scheme in Fig. 9(c) is that usually advanced to explain the large octahedral field splitting observed in complexes with strong π-acid ligands like carbonyl. The "backbonding" scheme of the Dewar–Chatt model is well known, of course, but important to review here. Carbon monoxide is not a good base towards metals outside the d block but forms literally hundreds of complexes with transition metals: the vast majority of these involve the metal in a very low, quite often zero, oxidation state. The model proposes that donation of electrons from the metal to empty π^* orbitals on the carbonyl group notionally induces a polarity M^+–CO^- that is, in turn, removed by enhanced electron σ donation from the carbonyl. Two strands of thought are evident in this argument: the acquisition of near neutrality and the existence of two (or more, in principle) pathways to effect this. The final result is that the transition metal has become a much better acceptor than the non-transition metal by virtue of its ability, in low oxidation states at least, to escape charge accumulation by passing the charge back to the carbonyl group. The e_g d orbitals are raised in energy and the t_{2g} set lowered, yielding a large value of the spectrochemical splitting parameter Δ_{oct}. So much else of transition metal carbonyl chemistry is explained by this model that there can be no doubting its essential validity. However, the "backbonding" process very much involves overlap of metal d orbitals with the ligands and so contrasts dramatically with the bond type advanced for the higher oxidation state species discussed thus far. We are to recognize, therefore, that the metal–carbonyl and similar interactions define a different, discrete limiting type of bonding in transition metal chemistry. Clearly, it would be a mistake to suppose that what is surely right for the carbonyl-type case must be right for all others—any more than the reverse.

H. OXIDATION STATE AND *d* ORBITAL OVERLAP

The usual occurrence of transition metal carbonyl chemistry with very low oxidation states is surely the key to this issue. In complexes with metals in higher oxidation states, we should recognize the relative radial compactness of the (3)*d* orbitals relative to the (4)*s* and *p*. The latter define the valence shell, and the bond orbitals they form with the ligand functions now lie at lower energies than the relatively "uncoupled" metal *d* functions. Therefore there is no tendency to fill up the *d* shell here even if the free-ion (3)*d* shell energy were comparable with or even less than that of the free ligand orbitals. The somewhat buried *d* orbitals, rather like the 4*f* orbitals in the lanthanides, expand in response to the overall electron donation by the ligand set into the metal *s* and/or *p* functions and that elasticity acts to reduce local charge concentration. In those complexes involving metals in very low oxidation states, the radial parts of the *d* orbitals are now much more like those of the *s* and *p* in extent and so all three types are to be considered as valence orbitals. While an open *d* shell and unpaired *d* electrons are perfectly stable in the higher oxidation state complexes, there being no tendency towards normal "free radical" behaviour, the exposed nature of the *d* shell in zero or other low oxidation state systems introduces the 18-electron rule as a guiding principle.

In passing, we might well consider why carbonyl complexes of non-transition metals seem not to exist. As emphasized above, the principal distinction between low oxidation state transition metals and non-transition metals, in this context, is that the former are capable of acting as very good acceptors, but in the special synergic way. Certainly the removal of surplus negative charge by π backbonding confers a strong σ acidity on the metal. Then why do we not find carbonyl complexes of highly positively charged metal atoms? Presumably because the demands of the electroneutrality principle are to be satisfied on the ligands as much as on the metal. Without the transition metal π basicity, the carbonyl group would be unable to take advantage of the increased metal σ acidity. In short, synergism establishes that the roles of *both* ligand and metal are enhanced by the mutual processes of the Chatt–Dewar model. Non-transition metals cannot pay their dues, for they have no readily available π orbitals that may overlap *well enough* with the ligands. The same argument applies to transition metals in their higher oxidation states. Of course, some degree of π bonding between metal and ligand is envisaged in Werner–type complexes but that presumably involves less-effective p_π–p_π overlap much more than d_π–p_π. Thus Werner-type complexes and carbonyl-type complexes might be viewed as extremes in a "continuum" of bond type in transition metal chemistry.

Actually, "continuum" is not a wholly apposite adjective here. The range of formal oxidation states is sampled roughly integrally and it is not proposed that the nephelauxetic effect operates sufficiently to change the radial extent of a higher oxidation state ion to that of a lower. Rather, "bands" of behaviour are to be envisaged within each oxidation state. The different extremes of behaviour described above can be seen to originate in the following way.

In the neutral atoms, say of the first transition series, the energies and radial extents of the 3*d* and 4*s* orbitals are roughly comparable. As discussed, both functions are to be included in the valence shell and the 18-electron rule will tend to be obeyed. Removal of electrons to form higher oxidation states may notionally be considered to involve depletion of either 4*s* or 3*d* shells. If 4*s* electrons are removed, the occupation of the 3*d* shell is confirmed by the increased effective nuclear charge they suffer on removal of shielding associated with the more penetrating parts of the 4*s* orbital. If 3*d* electrons are removed initially, the reduced interelectron repulsion within the 3*d* subshell will result in a contraction and stabilization with respect to the 4*s* shell followed by electron rearrangement and "collapse" into the *d* shell. The result, either way, is loss of electrons from the 4*s* shell preferentially, together with contracted 3*d* orbitals and their effective removal from the valence shell, with all that follows. Reduction of a higher oxidation state complex involves increasing the *d* electron count by integral steps, together with a greatly increased interelectron repulsion and expansion that ultimately returns the *d* orbitals into the valence shell. However, a lesser electron donation from the ligands towards a higher oxidation state metal increases the shielding properties of the inner parts of the bonding orbitals and produces the relatively secondary expansion of the *d* subshell that we monitor in the nephelauxetic effect. Further electron donation from the ligands, for example, as we replace bromine atoms by iodine atoms in a halocopper complex, produces the stepwise (as opposed to continuous) change of placing an extra electron into the *d* shell itself and so results in

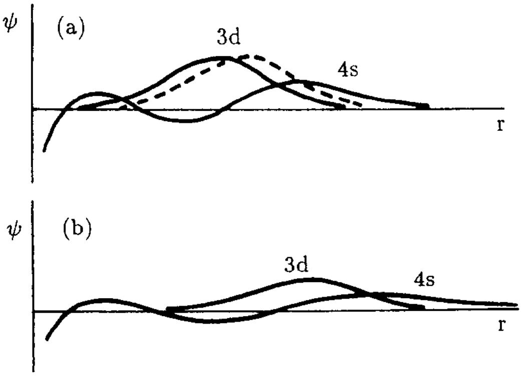


Fig. 10. Schematic radial waveforms for (a) higher oxidation state complexes; and (b) for lower oxidation state systems. The dotted curve represents the range of nephelauxetic expansion within the given oxidation state.

chemical reduction. Overall, therefore, the radial parts of the 3*d* and 4*s* orbitals in high and low oxidation state transition metal complexes are summarized in Fig. 10.

I. CONCLUDING REMARKS

I have described in this article how many aspects of transition metal chemistry and bonding can be well comprehended in terms of the workaday extremes of contracted *d* orbitals on the one hand and of expanded ones on the other. We can also see where and why these limiting cases arise. The thesis has arisen from the necessity to provide a basis for those phenomena we deal with by ligand field theory that does not conflict with broader chemical issues. In focusing too strongly upon the symmetry matching of metal *d* orbitals with ligand function sets, traditional teaching schemes have underplayed the elasticity of transition metal *d* orbitals which sets high and low oxidation state species at opposite ends of a bonding structure that brings all the rich variation so characteristic of *d* block chemistry.

ACKNOWLEDGEMENTS

I am most grateful to the following members of this laboratory for their critical reading of the manuscript: Professor The Lord Lewis, Drs. E.C. Constable, J.E. Davies and Melinda J. Duer; Neil D. Fenton, Sarah J. Essex and Kathleen M. Jupp.

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