

Complementary Spherical Electron Density Model for Inorganic Stereochemistries

D. Michael P. Mingos and Jeremy C. Hawes

Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, U.K.

The inert gas rule has been reformulated in terms of complementary and complete sets of central atom and ligand sphere wave-functions with s, p, and d nodal characteristics.

The inert gas rule¹ has served as an important unifying feature in organometallic chemistry,² but its theoretical justification has been limited to an analysis of the bonding characteristics of the metal valence orbitals in specific molecules (usually octahedral).³ In this communication a new theoretical model is developed which not only provides justification for the inert gas rule, but also illustrates for the first time its stereochemical implications.

If a molecule is viewed initially as a central atom surrounded

by a spherical shell of electron density representing the ligand sphere, then the derivation of the inert gas rule is trivial. The atomic orbitals of the central atom and the wave-functions of the spherical shell are both expressed in terms of spherical harmonics, $Y_{l,m}(\theta,\phi)$, and are governed by the same l and m quantum numbers. If the wave-functions of the valence orbitals of the central atom overlap effectively with those of the spherical shell then a set of matching bonding molecular orbitals is generated. For example, a transition metal atom

Table 1

(a) Deltahedra

<i>N</i>	Structure	S^{σ}	P_0^{σ}	P_{1c}^{σ}	P_{1s}^{σ}	D_0^{σ}	D_{1c}^{σ}	D_{1s}^{σ}	D_{2c}^{σ}	D_{2s}^{σ}	F_0^{σ}	F_{1c}^{σ}	F_{1s}^{σ}	F_{2c}^{σ}	F_{2s}^{σ}	F_{3c}^{σ}	F_{3s}^{σ}
10	Bicapped square antiprism	[shaded]															
9	Tricapped trigonal prism ^a	[shaded]															
8	Dodecahedron	[shaded]															
7	Pentagonal bipyramid	[shaded]															
6	Octahedron	[shaded]															
5	Trigonal bipyramid	[shaded]															
4	Tetrahedron	[shaded]															
3	Trigonal planar	[shaded]															
2	Linear	[shaded]															

^a For $N = 6-9$ there are alternative polyhedra, which are solutions to the packing problem (ref. 5), with closely related sets of ligand combinations (see Figure 1).

(b) Bipyramids and 3-connected polyhedra

<i>N</i>	Structure	S^{σ}	P_0^{σ}	P_{1c}^{σ}	P_{1s}^{σ}	D_0^{σ}	D_{1c}^{σ}	D_{1s}^{σ}	D_{2c}^{σ}	D_{2s}^{σ}	F_0^{σ}	F_{1c}^{σ}	F_{1s}^{σ}	F_{2c}^{σ}	F_{2s}^{σ}	F_{3c}^{σ}	F_{3s}^{σ}
9	Heptagonal bipyramid	[shaded]															
8	Hexagonal bipyramid	[shaded]															
7	Pentagonal bipyramid	[shaded]															
6	Octahedron	[shaded]															
5	Trigonal bipyramid	[shaded]															
10	Pentagonal prism	[shaded]															
8	Cube	[shaded]															
6	Trigonal prism	[shaded]															
4	Tetrahedron	[shaded]															

with nd , $(n+1)s$, and $(n+1)p$ valence atomic wave-functions interacts exclusively with S^{σ} , P^{σ} , and D^{σ} wave-functions of the spherical shell with identical l and m quantum numbers. If the nine molecular orbitals are fully occupied the resultant electron density is spherically symmetric and approximates to that of an inert gas atom.

If the spherical shell is now concentrated into N regions of electron density corresponding to the ligand positions of an ML_N complex then the linear combinations of ligand lone pair orbitals, σ_i , can be expressed in terms of the following spherical harmonic expansion;⁴

$$\begin{aligned}\Phi(l, m) &= \sum_i c_i \sigma_i \\ &= N' \sum_i Y_{lm}(\theta_i, \phi_i) \sigma_i \\ &= L_m^{\sigma} \quad m = 0, 1c, 1s, \dots \quad L = S, P, D, \dots\end{aligned}$$

The quantum numbers are no longer strictly valid because of the descent in symmetry, but they do accurately represent the nodal characteristics of the ligand linear combinations which determine the overlap preferences between ligand and central atom orbitals with the same symmetries. Since θ_i and ϕ_i now

N	Point group	8 D_{2d}	8 D_{4d}	8 C_{2v}	7 D_{5h}	7 C_{2v}
Structure		Dodecahedron	Square antiprism	Bicapped trigonal prism	Pentagonal bipyramid	Tetragonally capped trigonal prism
Ligand field splitting and occupancy for 18e species		b_2 ——— xy e ——— xz e ——— yz a_1 ——— z^2 b_1 — θ — x^2-y^2	e_3 ——— xz e_3 ——— yz e_2 ——— xy e_2 ——— x^2-y^2 a_1 — θ — z^2	b_1 ——— xz b_2 ——— yz a_1 ——— x^2-y^2 a_2 ——— xy a_1 — θ — z^2	a'_1 ——— z^2 e'_2 ——— xy e'_2 ——— x^2-y^2 e''_1 — θ — xz e''_1 — θ — yz	a_2 ——— xy a_1 ——— z^2 b_1 ——— xz b_2 — θ — yz a_1 — θ — x^2-y^2
Associated ligand sphere D^σ functions		D_0^σ D_{1c}^σ D_{1s}^σ D_{2s}^σ	D_{1c}^σ D_{1s}^σ D_{2c}^σ D_{2s}^σ	D_0^σ D_{1c}^σ D_{1s}^σ D_{2s}^σ	D_0^σ D_{2c}^σ D_{2s}^σ	D_0^σ D_{1c}^σ D_{2s}^σ

7 C_{3v}	6 O_h	6 D_{3h}	5 D_{3h}	5 C_{4v}	4 T_d
Monocapped octahedron	Octahedron	Triangular prism	Trigonal bipyramid	Square pyramid	Tetrahedron
e ——— xz e ——— yz a_1 ——— z^2 e — θ — xy e — θ — x^2-y^2	e_g ——— z^2 e_g ——— x^2-y^2 t_{2g} — θ — xy t_{2g} — θ — xz t_{2g} — θ — yz	e'' ——— xz e'' ——— yz e' — θ — xy e' — θ — x^2-y^2 a'_1 — θ — z^2	a'_1 ——— z^2 e' — θ — xy e' — θ — x^2-y^2 e'' — θ — xz e'' — θ — yz	b_1 ——— x^2-y^2 a_1 — θ — z^2 b_2, e — θ — xy b_2, e — θ — xz, yz	t_2 — θ — xy t_2 — θ — xz t_2 — θ — yz e — θ — z^2 e — θ — x^2-y^2
D_0^σ D_{1c}^σ D_{1s}^σ	D_0^σ D_{2c}^σ	D_{1c}^σ D_{1s}^σ	D_0^σ	D_{2c}^σ	None

Figure 1. Summary of complementary interactions between the ligand linear combinations and the metal d orbitals. The correspondence between the conventional representations of the d orbitals and that used to describe the ligand linear combinations is: $z^2 = d_0$; $xz = d_{1c}$; $yz = d_{1s}$; $xy = d_{2s}$; $x^2-y^2 = d_{2c}$.

Table 2. Examples of π -donor complexes with 8N and 18N valence electrons.

Molecular formula	Co-ordination geometry	Number of valence electrons
CO ₂	Linear	16
BF ₃	Trigonal planar	24
SO ₄ ²⁻	Tetrahedral	32
MnO ₄ ⁻	Tetrahedral	32
PF ₅	Trigonal bipyramid	40
TaMe ₃ (OMe) ₂ ^a	Trigonal bipyramid	40
SF ₆	Octahedral	48
WF ₆	Octahedral	48
18N Valence electrons		
[O(RuCl ₅) ₂] ⁴⁻	Linear	36
[N{Ir(SO ₄) ₂ (H ₂ O)} ₃] ⁴⁻	Trigonal planar	54

^aMes = 2,4,6-trimethylphenyl.

represent the locations of the ligand atoms on the sphere this mode of expressing the linear combinations has stereochemical implications. In particular only deltahedra and closely related polyhedra generate S^σ , P^σ , and D^σ functions in a sequential fashion [see Table 1(a)]. Other classes of polyhedra, e.g. bipyramids and three-connected polyhedra which have ligand atoms located on the nodal planes of the D^σ functions utilize F^σ functions [see Table 1(b)] in preference to D^σ functions for the higher co-ordination numbers. The polyhedra in Table 1(a) more closely emulate the wave-functions of the imaginary spherical shell than those in Table

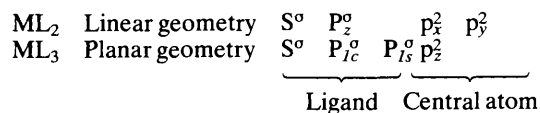
1(b), because they represent the most efficient solutions to packing and covering problems on a spherical surface.⁵ Polyhedra which do not have this property do not have wave-functions which match those of the central atom. For example, for eight co-ordination the cube and the hexagonal bipyramid are not compatible with the eighteen electron rule because they generate F^σ functions and have vacancies in their D^σ functions.

A co-ordination compound achieves a pseudo-spherical eighteen electron configuration by adopting one of the polyhedra in Table 1(a) and utilizing a complementary and complete set of S, P, and D wave-functions. As the ligand co-ordination number is reduced from nine, vacancies in the D^σ shell of ligand linear combinations are matched by filled d orbitals with complementary m quantum numbers and thereby utilize the most stable valence orbitals of the central atom. For example, in an octahedral complex the ligand-metal bonding m.o.'s S^σ (a_{1g}), P^σ (t_{1u}), D_0^σ , and D_{2c}^σ (e_g) are matched by filled d_{1c} (xz), d_{1s} (yz) and d_{2s} (xy) orbitals. The complementary nature of these interactions for other co-ordination polyhedra are summarized in Figure 1. Also given in Figure 1 are the splittings of the d orbitals arising from the ligand field.⁶

Although the complementary effects described above are defined by the pseudo-symmetry of the spherical ligand shell the inert gas rule also depends on the efficiency of overlap between the metal valence orbitals and the ligand orbitals. The contracted nature of the d wave-functions for transition metals⁷ means that the complementary metal d and ligand D^σ functions will only have comparable radial distribution functions if the metal-ligand distances are short. Therefore, it is hardly surprising that the hydrido complexes invariably

conform to the inert gas rule, e.g. $[\text{ReH}_9]^{2-}$ (tricapped trigonal prism), $\text{MoH}_4(\text{PPh}_3)_4$ (dodecahedral), $\text{OsH}_4(\text{PMe}_2\text{Ph})_3$ (pentagonal bipyramid), and $[\text{RuH}_6]^{4-}$ (octahedral).⁸ π -Acceptor ligands provide an alternative mode of achieving short metal–ligand distances and influencing the radial parts of the metal d wave-functions through back donation effects.³ There are consequently numerous examples of metal carbonyl and related compounds which conform to the inert gas rule.⁹ Furthermore they adopt the co-ordination polyhedra which give efficient coverage of the ligand sphere. These co-ordination polyhedra also tend to minimise nuclear–nuclear and electron–electron repulsion terms.

For main group ML_N ($N = 2$ or 3) molecules the valence orbitals do not share the same complementary relationships. The following sets of complementary orbitals:



represent excited state configurations unless L is a sufficiently good π -acceptor ligand effectively to lower the energies of the p orbitals below those of the s orbitals. Such geometries are indeed observed in $\text{C}(\text{CO})_2$ and OLi_2 (linear)¹⁰ and $\text{C}(\text{CN})_3^-$ (planar). Angular (e.g. OH_2 and OF_2) and pyramidal (e.g. NH_3 and NF_3) geometries are more stable when L is not a π -acceptor, because more s character is introduced into those orbitals localized on the central atoms.¹¹

π -Donor ligands have the effect of destabilising the complementary orbitals on the central atom and therefore the achievement of inert gas configurations about the ligand atoms rather than the central atom becomes the primary electronic factor.¹² Examples of π -donor compounds with $8N$ and $18N$ electrons are presented in Table 2. Ligands which do not have orbitals which overlap effectively with the metal d

orbitals can support electron counts intermediate between these extremes and have incompletely filled d shells.

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