

Complementary spherical electron density model for coordination compounds

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Abstract - The Complementary Spherical Electron Density Model recognises the essentially spherical nature of the majority of co-ordination and cluster compounds and expresses the relevant wave functions on this basis. In particular the linear combinations of ligand wave functions, or in the case of a cluster compound the metal wave functions, are expressed in terms of a spherical harmonic expansion with each linear combination defined by l and m quantum numbers. Interestingly not all ligand polyhedra generate linear combinations whose quantum numbers match the d , s and p valence orbitals of the central atom. Co-ordination polyhedra which are solutions of the packing and covering problems on a spherical surface generate S , P and D linear combinations in a sequential fashion which emulate those on the central atom. It follows that the Noble Gas Rule, the isolobal analogy and related generalisations can be reformulated in a quantum mechanical fashion which has precise stereochemical consequences. For example, compounds which conform to the Noble Gas Rule can be described in terms of complementary sets of ligand and metal wave functions which when taken together have a net angular momentum of zero. The model can also be extended to 16, and 14 electron situations using the particle on a hemisphere and particle on a ring solutions to the Schrödinger equation.

The great strength of the model is that it can be extended to cluster compounds which contain interstitial atoms. For example, cluster compounds of gold of the general type $[\text{Au}(\text{AuPR}_3)_n]^{x+}$ have molecular orbital characteristics which can also be expressed in terms of a spherical harmonic expansion. Consequently co-ordination compounds and high nuclearity cluster compounds with interstitial atoms both conform to the same type of electron counting rules. Furthermore this mode of analysis can be extended to high nuclearity cluster compounds where the metal atoms lie on successive shells. It is always the bonding preferences of the inner atoms which determine the preferred close shell requirements.

For cluster compounds where tangential bonding effects are important and in co-ordination compounds where π -bonding makes a significant contribution it is necessary to take into account the vector surface harmonic solutions to the particle on a sphere problem. The additional bonding molecular orbitals generated from the vector surface harmonics are particularly important for lower nuclearity clusters and complexes containing π -donor ligands.

INTRODUCTION

The renaissance of inorganic chemistry since the 1950's has owed much to the more general availability of X-ray diffractometers and n.m.r. spectrometers and the development of computer hardware and software to handle the vast amount of data which they produce rapidly. The structural characterisation of co-ordination compounds in the solid state and solution is often therefore no longer the rate limiting step in the development of a synthetic research programme. This role has been taken over by the discovery of satisfactory synthetic procedures and the isolation of single crystals suitable for the diffraction experiments. The structural data accumulated in the last three decades on co-ordination compounds has undermined the elegant simplicity of Werner's stereochemical conclusions based on rigid octahedral and square-planar co-ordination geometries. Modifications in the electronic, steric and chelating capabilities of ligands have led

to the structural characterisation of complexes with co-ordination numbers up to 12 and for each co-ordination number a wide variety of co-ordination polyhedra. The advances in the development of stereochemistries are very effectively documented and summarised in Keppert's book (ref. 1). The development of cluster chemistry has followed a similar pattern. Early studies, particularly by Dahl and his co-workers (ref. 2) suggested that cluster compounds might conform to a simple stereochemical pattern based on three connected and deltahedral arrangements of metal atoms. This idea was codified in the Polyhedral Skeletal Electron Pair Approach (ref. 3) which related the electronic characteristics of these simple cluster compounds to those of isostructural hydrocarbon and borane polyhedral molecules. The elegant synthetic studies of the Milan (ref. 4) and Cambridge (ref. 5) groups undermined this simple generalisation and suggested that many clusters are derived from the condensation of the simpler polyhedral entities by vertex, edge and face sharing. More recently Longoni *et al* (ref. 6) have developed synthetic routes into high nuclearity clusters, whose metal stereochemistries are best described in terms of fragments of hexagonal, cubic, body centred cubic and icosahedral close packing arrangements of metal atoms.

The complexity of the stereochemical problem in co-ordination and cluster chemistry briefly outlined above poses a tremendous challenge to our current valence theories. The development of high speed computers and the application of rigorous m.o. methods to valence problems have had much less of an impact than for example in organic chemistry. Indeed much of the insight into bonding problems obtained during the last ten years has not arisen from this approach, but rather from the combination of simple theoretical ideas with either group theoretical or perturbation theory concepts. In particular one can cite the following generalisations which have had a major impact on the stereochemical problem.

The Angular Overlap Theory first developed by Schäffer and Jørgensen was adapted by Burdett for stereochemical problems. Despite the fact that this model is extremely simple, ignoring for example the metal s and p valence orbitals and generally π -bonding effects it can account for many features of the stereochemistries of simple co-ordination compounds. (ref. 7,8).

Walsh Diagram Methodology. Hoffmann and his coworkers (ref. 9) have demonstrated that a wide variety of stereochemical problems can be analysed using Walsh diagrams, which trace the variation of orbital energies as a function of alternative distortion pathways. This model neglects important electron and nuclear repulsion effects and is based on simple overlap and electronegativity effects and yet has proved to be a powerful technique for developing stereochemical generalizations and ligand site preferences.

Polyhedral Skeletal Electron Pair Approach. The geometries of metal cluster compounds depend particularly on the number of valence electrons associated with the cluster and the empirical rules developed by Wade and myself (ref. 10,11) have provided a unifying framework for this complicated area of chemistry. Stone's Tensor Surface Harmonic Theory has provided an elegant theoretical basis for these rules (ref. 12).

The Isolobal Concept has recognised an important relationship between the frontier orbitals of main group and transition metal fragments (ref. 13). The synthetic implications of this generalisation have been exploited most effectively by Stone (ref. 14).

These alternative approaches for explaining the bonding in inorganic compounds can be unified by the Complementary Spherical Electron Density Model since they share in common an evaluation of the angular aspects of the quantum mechanical problem. Central to each approach is the recognition that the angular parts of the wave functions as expressed in spherical harmonics play a dominant role in stereochemistry. In this paper it will be demonstrated that the ligand linear combinations can also be expressed as spherical harmonic expansions thereby simplifying the quantum mechanical analysis.

TOPOLOGICAL REPRESENTATION OF COORDINATION POLYHEDRA

It is common practice to define the stereochemistries of complexes in terms of idealised co-ordination polyhedra, but for reasons which will become apparent below it is also useful to define the topology of the ligand ensemble in the following manner:

(a) Spherical The ligands are equidistant from the central atom and are evenly distributed over the surface of an imaginary sphere, e.g. octahedral, trigonal bipyramidal, etc.

(b) Hemispherical All the ligand atoms lie on one side of the equator of the imaginary sphere. The metal carbonyl fragments $M(CO)_5$, $Mo(CO)_4$ and $Mo(CO)_3$ characterised by matrix isolation studies by Turner *et al* (ref. 15) provide examples of this co-ordination topology.

(c) Toroidal The ligands lie in a single plane, e.g. square-planar $[\text{PtCl}_4]^{2-}$.

(d) Hemi-toroidal The ligands form an incomplete ring as in the T-shaped complex $[\text{Rh}(\text{PPh}_3)_3]^+$.

In the spherical topology the ligands are capable of generating linear combinations which emulate in a 1:1 fashion those of the wave functions of the central atom. Each of the topologies (b)-(d) represent sub-groups of the spherical situation and consequently although their wave functions can still be represented in terms of those for the spherical situation the descent in topology results in a discarding of some of the spherical wave functions. This descent in topology therefore has important stereochemical consequences, which will be discussed in detail below.

SPHERICAL COORDINATION COMPOUNDS

The derivation of the linear combinations of ligand orbitals, σ_i , in a co-ordination compound using group theoretically based projection operator techniques is well documented (ref. 16):

$$\Phi = \sum_i c_i \sigma_i$$

This approach by focussing on the specific point group fails to emphasise the essentially spherical nature of the quantum mechanical problem. An alternative derivation of the coefficients, c_i , arises from the utilisation of a spherical harmonic expansion of the following type:

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

This assumes that the linear combinations of ligand orbitals can be satisfactorily expressed as solutions to the particle on the sphere problem whose wave functions are given by the spherical harmonics $Y_{l,m}(\theta, \varphi)$ summarised in Table 1. The coefficients c_i are given by the evaluation of the spherical harmonic functions at the ligand positions θ_i and φ_i as defined in spherical polar co-ordinates, i.e. $Y_{l,m}(\theta_i, \varphi_i)$.

Table 1 Polar forms of the spherical harmonic functions normalised to 4π

Y_{lm}	Polar Form	
Y_{00}	1	
Y_{10}	$\sqrt{3} \cos \theta$	
Y_{11}^c	$\sqrt{3} \sin \theta \cos \varphi$	
Y_{11}^s	$\sqrt{3} \sin \theta \sin \varphi$	
Y_{20}	$\sqrt{5/4} (3 \cos^2 \theta - 1)$	$Y_{l,m}^c = 1/\sqrt{2} [(-1)^m Y_{l,m} + Y_{l,-m}]$
Y_{21}^c	$\sqrt{15} \cos \theta \sin \theta \cos \varphi$	
Y_{21}^s	$\sqrt{15} \cos \theta \sin \theta \sin \varphi$	$Y_{l,m}^s = 1/i\sqrt{2} [(-1)^m Y_{l,m} - Y_{l,-m}]$ For $m > 0$
Y_{22}^c	$\sqrt{15/4} \sin^2 \theta \cos 2\varphi$	
Y_{22}^s	$\sqrt{15/4} \sin^2 \theta \sin 2\varphi$	
Y_{30}	$\sqrt{7/4} (5 \cos^3 \theta - 3 \cos \theta)$	
Y_{31}^c	$\sqrt{21/8} \sin \theta (5 \cos^2 \theta - 1) \cos \varphi$	
Y_{31}^s	$\sqrt{21/8} \sin \theta (5 \cos^2 \theta - 1) \sin \varphi$	
Y_{32}^c	$\sqrt{105/4} \cos \theta \sin^2 \theta \cos 2\varphi$	
Y_{32}^s	$\sqrt{105/4} \cos \theta \sin^2 \theta \sin 2\varphi$	
Y_{33}^c	$\sqrt{35/8} \sin^3 \theta \cos 3\varphi$	
Y_{33}^s	$\sqrt{35/8} \sin^3 \theta \sin 3\varphi$	

The advantage of this mode of designating the linear combinations is that they can be assigned "pseudo-spherical" quantum numbers L and m and therefore it becomes a simple matter to qualitatively evaluate their interactions with the valence orbitals of the central atom which are also expressed in terms of spherical harmonics, i.e.

$$\Psi(r, \theta, \varphi) = R_{n,l}(r) \cdot Y_{l,m}(\theta, \varphi)$$

Although the L and m quantum numbers are no longer strictly valid in a co-ordination compound because it has less than spherical symmetry, they do accurately represent the nodal characteristics of the ligand linear combinations. It is these pseudo-spherical symmetry characteristics which determine the overlap preferences between the ligand and metal orbitals. In particular if differences in the radial parts of the wave functions are neglected then ligand linear combinations and metal orbitals with matching L (l) and m quantum numbers have much larger overlap integrals and contribute most to bonding.

Since θ_i and φ_i represent the locations of the ligand atoms on the spherical surface this mode of expressing the ligand linear combinations has important stereochemical implications. In particular it can be shown (ref. 17) that only ligand polyhedra which represent solutions to the packing and covering problems on a spherical surface generate S, P, and D functions in a fashion which emulate the spherical harmonic wave functions of the central atom. These polyhedra are summarised below in Table 2.

TABLE 2

No. of Vertices	Best Covering Polyhedron	Best packing Polyhedron
3	Triangle	Triangle
4	Tetrahedron	Tetrahedron
5	Trig. Bipy.	Square Pyramid
6	Octahedron	Octahedron
7	Pentagonal Bipy.	Capped Octahedron
8	Dodecahedron	Square Antiprism
9	Tricapped trig. prism	Capped Square Antiprism

The manner in which these polyhedra generate S^σ , P^σ , and D^σ ligand linear combinations is illustrated in Figure 1. Other general classes of polyhedra, e.g. three-connected polyhedra and bipyramids, are less spherical and generate F^σ linear combinations before the D^σ shell is completely filled because they have atoms located on the nodal planes of the D^σ functions. These polyhedra are not generally adopted by transition metal complexes because the F^σ functions are not matched by the valence orbitals of the central atom.

N	Structure	S	P _o	P _{1c}	P _{1s}	D _o	D _{1c}	D _{1s}	D _{2c}	D _{2s}	F _o	F _{1c}	F _{1s}	F _{2c}	F _{2s}	F _{3c}	F _{3s}
10	Bicapped Square Antiprism	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█
9	Tricapped Trigonal Prism	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█
8	Square Antiprism	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█
8	Dodecahedron	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█
7	Pentagonal Bipy.	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█
7	capped Octahedron	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█
7	Capped Trig. Prism	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█
6	Octahedron	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█
5	Trigonal Bipyramid	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█
5	Square Pyramid	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█
4	Tetrahedron	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█
3	Trigonal Planar	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█
2	Linear	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█

Fig. 1. Summary of linear combinations for polyhedra which are solutions to the packing and covering problem on a spherical surface.

N	Structure	S	P _o	P _{1c}	P _{1s}	D _o	D _{1c}	D _{1s}	D _{2c}	D _{2s}	Examples
9	Tricapped Trig. Prism	■	■	■	■	■	■	■	■	■	[ReH ₉] ²⁻
8	Square Antiprism	■	■	■	■	■	■	■	■	■	[H ₄ W(CN) ₈]
8	Dodecahedron	■	■	■	■	■	■	■	■	■	K ₄ [W(CN) ₈], [MoH ₄ (PMe ₂ Ph) ₄]
7	Pentagonal Bipy.	■	■	■	■	■	■	■	■	■	[OsH ₄ (PMe ₂ Ph) ₃]
7	Capped Octahedron	■	■	■	■	■	■	■	■	■	[W(CO) ₄ Br ₃]
7	Capped Trig. Prism	■	■	■	■	■	■	■	■	■	[Mo(CNBut) ₇] ²⁺
6	Octahedron	■	■	■	■	■	■	■	■	■	[Mo(CO) ₆]
5	Trigonal Bipyram.	■	■	■	■	■	■	■	■	■	[Fe(CO) ₅]
5	Square Pyramid	■	■	■	■	■	■	■	■	■	[Ni(CN) ₅] ³⁻
4	Tetrahedron	■	■	■	■	■	■	■	■	■	[Ni(CO) ₄]




Fig. 2. Illustration of the complementary interactions which occur in co-ordination compounds which conform to the Noble Gas Rule. In each instance the ligand linear combinations and the filled orbitals localised on the metal generate a complete set of S, P and D functions.

COMPOUNDS WHICH CONFORM TO THE NOBLE GAS RULE

Those compounds which conform to the Noble Gas Rule adopt the polyhedra in Table 2 and have filled d orbitals which precisely match the vacancies in the D shell of the linear combinations. The complementary nature of the ligand linear combinations and filled metal orbitals which result in the attainment of a pseudo-spherical electron distribution based on a total of 18 valence electrons and effective net angular momentum of zero are illustrated in Figure 2. The examples of compounds which illustrate these complementary interactions generally have hydride or π -acid ligands co-ordinated to the metal. This ligand dependence arises from differences in the radial distribution functions of the nd, (n+1)s and (n+1)p valence orbitals. Since the nd valence orbitals have maxima in their radial distribution functions relatively close to the nucleus only ligands which can achieve short metal-ligand bond lengths can involve them sufficiently in bonding for this generalisation to be valid. Hydride achieves this by virtue of its size and π -acid ligands by means of multiple bond formation which shorten the metal-ligand internuclear distances.

COMPOUNDS WHICH DO NOT CONFORM TO THE NOBLE GAS RULE

Ligands which are capable of forming strong multiple bonds with the metal by π -donation effects also involve the metal d orbitals extensively in bonding, but since these ligands are generally more electronegative than the metals the bonding components of these interactions are more localised on the ligands. Consequently these complexes are generally characterised by d⁰ configurations, e.g. [MnO₄]⁻. If the ligands are neither strong π -donors or acceptors then the metal d orbitals remain essentially core-like and can accommodate variable numbers of d electrons. Examples of such complexes are given in Table 3. Often the bonding in such complexes has a considerable electrostatic component and the adoption of a spherical polyhedron reflects a minimisation of ligand repulsion effects. Complexes with fewer than 18 valence electrons are far more numerous than those which exceed the Noble Gas configuration.

Table 3

Examples of co-ordination compounds which do not conform to the Noble Gas Rule			
N	d ⁿ	Co-ordination Geometry	Examples
8	d ₁ ⁰	Bicapped Trig. Prism	[ZrF ₈] ⁴⁻
8	d ¹	Dodecahedron	[NbCl ₄ (diars) ₂]
7	d ⁰	Pentagonal Bipyramid	[ZrF ₇] ³⁻
7	d ⁰	Capped Trigonal Prism	[NbF ₇] ²⁻
7	d ₂ ²	Pentagonal Bipyramid	[V(CN) ₇] ⁴⁻
7	d ₂ ²	Capped Octahedron	[MoBr ₄ (PMe ₂ Ph) ₃]
6	d ₀ ⁰	Octahedral	[TiF ₆] ²⁻
6	d ₄ ²	Octahedral	[OsF ₆]
6	d ₄ ²	Octahedral	[PtF ₆]
6	d ₈ ⁰	Octahedral	[Ni(NH ₃) ₆] ²⁺
5	d ₁₀ ⁶	Square-pyramid	[RuCl ₂ (PPh ₃) ₃]
5	d ₁₀ ⁶	Trigonal Bipyramid	[CdCl ₅] ³⁻

NON-SPHERICAL COORDINATION COMPOUNDS

Figures 3 and 4 illustrate the solutions of the Schrödinger equation for the particle on a hemisphere and the particle on a ring. For the particle on a hemisphere the spherical harmonics $Y_{l,m}(\theta, \varphi)$ are also the solutions to the Schrödinger equation, but the boundary conditions on the rim of the hemisphere ($\theta = \pi/2$) differ. If ligands are allowed to lie on the boundary of the hemisphere the appropriate boundary conditions arise from:

$$\partial \Psi / \partial \theta = 0 \quad \text{at} \quad \theta = \pi/2$$

for which the only permitted wave functions are the spherical harmonics with $l+m = \text{even}$. These are illustrated in the bottom half of Figure 3. The alternative boundary condition of

$$\Psi = 0 \quad \text{at} \quad \theta = \pi/2$$

permits only those spherical harmonics with $l+m = \text{odd}$ as solutions. This condition is appropriate to complexes where the ligands are all clearly in one half of the sphere and the electron density is zero at the rim. The two sets of wave functions are orthogonal and when taken together regenerate the complete set of spherical harmonic wave functions. Consequently the $l+m = \text{odd}$ functions are illustrated in Figure 3 for the upper (Northern, N) hemisphere.

Similarly the particle on the ring can be expressed as a special case of the spherical problem with the condition:

$$\Psi = 0 \quad \text{unless} \quad \theta = \pi/2$$

This restricts the solutions to those spherical harmonics which have $l=m$. These are illustrated in Figure 4.

The important corollary of this analysis is that when the spherical symmetry is reduced the resulting topologies have a more limited set of suitable spherical harmonic solutions. Therefore, both topologies provide the opportunity of using fewer valence electrons in metal-ligand bonding and localising electron pair holes in orbitals which are orthogonal to the occupied metal-ligand bonding molecular orbitals.

In hydrido- and π -acid complexes which generally conform to the Noble Gas Rule the loss of a ligand creates an electron pair hole in what was initially a spherical electron distribution. Given the usual ordering of valence orbitals $nd \gg (n+1)s \gg (n+1)p$ for transition metal atoms it is energetically favourable to localise that electron pair hole in the highest lying $(n+1)p$ valence orbitals. If a spherical ligand topology is retained in the 16 electron complex, ML_{N-1} , this cannot be achieved and the electron pair hole is localised in a metal d orbital. In contrast the adoption of either a toroidal or hemi-spherical co-ordination topology affords the possibility of localising the electron pair hole in an orbital which has either pure p orbital character (toroidal) or a high proportion of p orbital character (hemi-spherical).

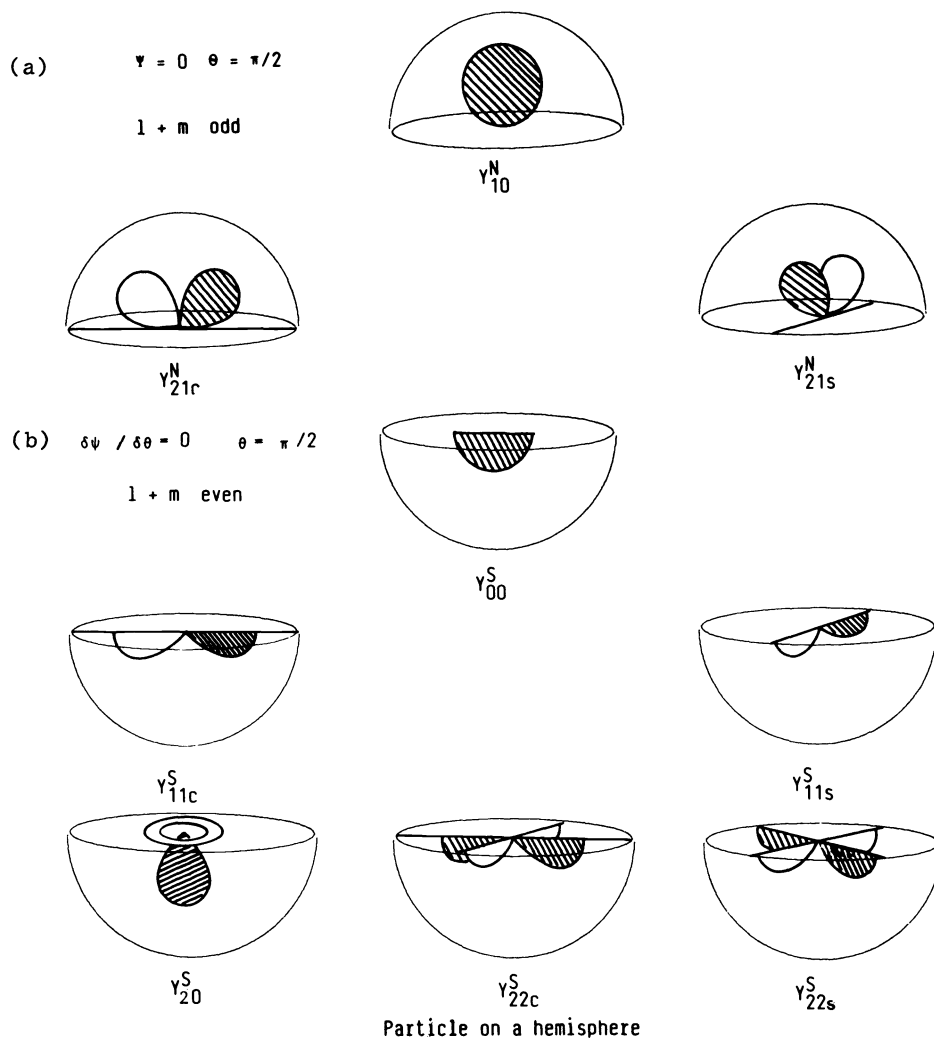


Fig. 3. Solutions to the particle on a hemisphere problem, based on the following boundary conditions : (a) Top half of the Figure, that the electron density is zero at the boundary and (b) bottom half of the Figure, the electron density reach a maximum at the rim. To illustrate the complementary nature of these functions (a) is shown for the Northern (N) and (b) for the Southern (S) hemispheres.

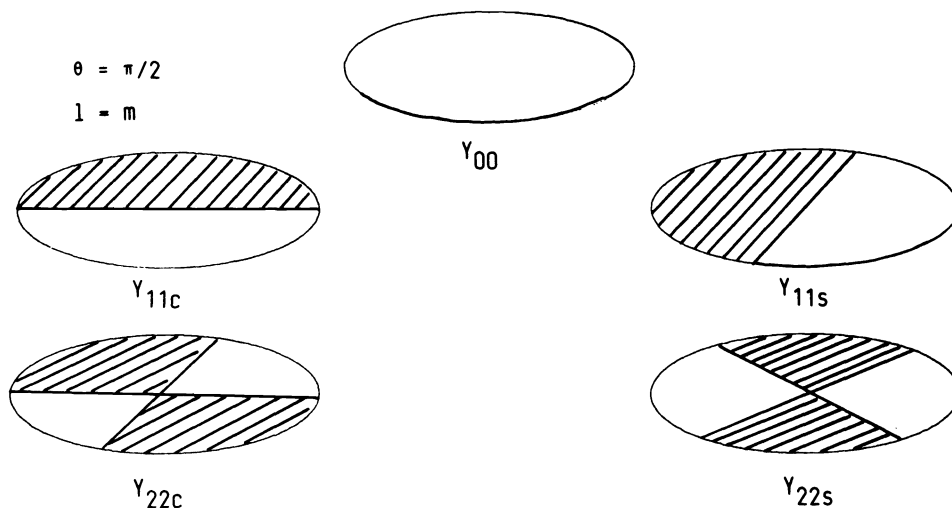


Fig.4. Solutions to the particle on the ring problem expressed in terms of the spherical harmonic functions with $l = m$.

CLUSTER COMPOUNDS

The cluster compounds of gold bear a strong resemblance to co-ordination compounds because the radial bonding between the peripheral metal atoms and the central atoms dominate. For an AuPPh_3 fragment the dominant frontier orbital is an outpointing d-s-p hybrid and the higher lying p_x and p_y orbitals make little contribution to bonding. The gold atoms have a complete x_{d10} shell which contributes little to bonding. In the clusters $[\text{Au}(\text{AuPR}_3)_m]^{x+}$ the linear combinations of gold 6s orbitals of the peripheral atoms can be derived in exactly the same way as that developed above for co-ordination compounds. The larger 6s-6s overlap integrals between adjacent gold atoms leads to a larger spread in the energies of the L linear combinations. Indeed in spherical clusters only the S and P functions are sufficiently bonding for electron occupation. These S and P linear combinations overlap strongly with the 6s and 6p orbitals of the central gold atom giving rise to a set of four stable bonding molecular orbitals. The 5d orbitals of the central atom interact only weakly with the higher lying D linear combinations of surface atoms, but their core like nature insures that they are fully occupied. Therefore, spherical gold clusters of this type are characterised by a total of $12m + 18$ valence electrons, i.e. an effective Noble Gas configuration is attained about the central atom. Although both co-ordination compounds and these gold cluster compounds achieve a Noble gas configuration the manner in which it is achieved is quite different. Figure 5 illustrates this important distinction and emphasises the observation that although high co-ordination number complexes generate D functions which contribute to the Noble Gas configuration in the cluster compounds the central metal atom d functions are always occupied and the D functions of the peripheral gold atoms are antibonding by virtue of their out-of-phase metal-metal interactions.

The analogy between co-ordination and cluster compounds can be taken further to analyse the bonding in a second class of gold cluster compounds, which have a total of $12m + 16$ valence electrons. These clusters which are illustrated in Figure 6 have toroidal geometries, with the electron pair hole localised in a p_z orbital orthogonal to the toroidal plane. These complexes are directly analogous to the square-planar 16 electron co-ordination compounds.

The examples discussed above have only metal atoms as their constituents. During the last few months the X-ray structure of $[\text{NbAs}_8]^{3-}$ has demonstrated that it has a centred crown structure analogous to that previously reported for $[\text{Au}(\text{AuPR}_3)_8]^{3+}$ (refs. 19 and 20). Interestingly both compounds have toroidal geometries and 16 valence electrons involved in Nb-As and As-As skeletal bonding. This finding suggests an alternative class of spherical clusters based on the niobium-arsenic system with a total of 18 skeletal valence electrons.

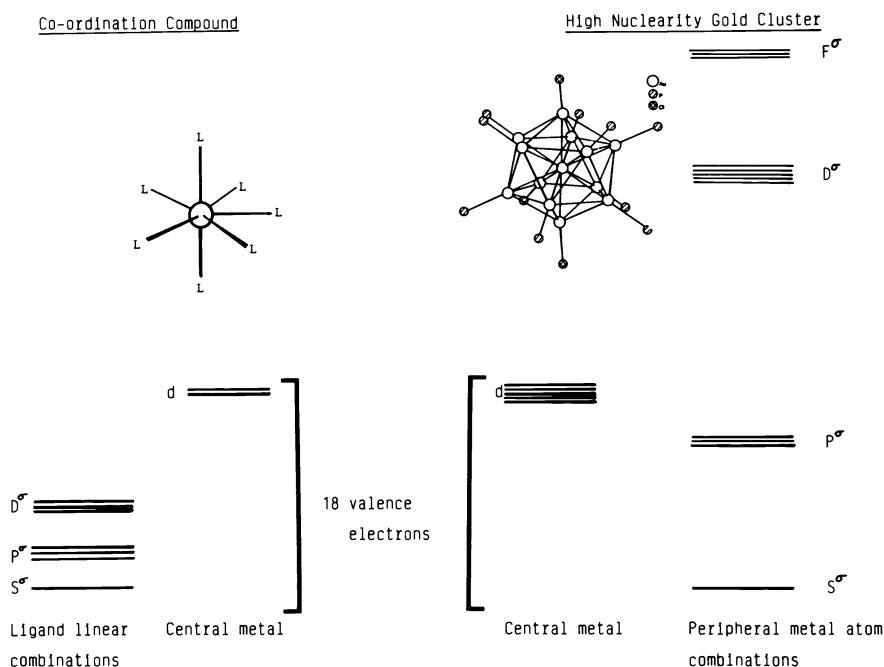


Fig. 5. Attainment of 18 electron configurations in co-ordination and cluster compounds which have an interstitial metal atom.

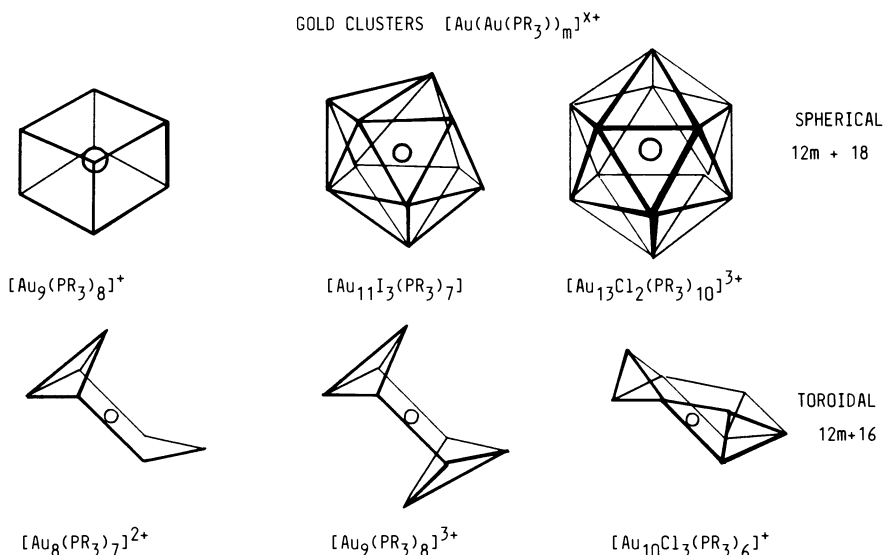


Fig. 6. Examples of spherical and toroidal gold cluster compounds.

The complementary spherical electron density model can be extended to high nuclearity clusters with several interstitial atoms. For those clusters where the radial bonding predominates the electron counts are $12n_s + \Delta_i$, where n_s is the number of surface atoms and Δ_i is the electron count characteristic of the interstitial group of atoms. Clusters with up to fifty metal atoms can be rationalised on this basis (ref. 21).

SUMMARY

The stereochemistries of co-ordination and cluster compounds can be understood in terms of free electron models which are based on the solutions to the particle on the sphere, the hemisphere and the ring. The Complementary Spherical Electron Density Model provides a powerful and flexible scheme for summarising these fundamental quantum mechanical relationships.

Acknowledgements

I should like to thank members of my research group for their stimulating contributions to the experimental and theoretical aspects of the problem and Dr. P.A. Cox for many helpful discussions on the quantum mechanical aspects of the research.

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