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Theoretical analysis of cluster compounds with cylindrical topologies

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Abstract

The wave functions of columnar metal cluster compounds can be expressed as an expansion based on the particle on the cylinder problem. Main group columnar clusters are characterised by $n+1$ skeletal and $2n-1$ 'unavailable' molecular orbitals. Transition metal columnar clusters also have $2n-1$ 'unavailable' molecular orbitals with a high proportion of p orbital character and additional 'unavailable' orbitals from the d_δ set of atomic orbitals. The number of these orbitals and their symmetries have been derived from a particle on a cylinder analysis. This bonding analysis has been applied to clusters containing columns of triangles and squares.

The Tensor Surface Harmonic Theory developed by Stone [1] has proved to be particularly useful for defining the closed shell requirements of main group and transition metal cluster compounds [2]. Although this methodology was initially applied to *closo*-, *nido*- and *arachno*-deltahedral molecules it has been subsequently extended to three- and four-connected polyhedral molecules, and condensed and polyspherical high nuclearity cluster compounds [3–7]. This free electron model which is based on the solutions of the Schrödinger equation for the particle on a sphere problem has proved to be so successful because it correctly identifies the nodal characteristics of the relevant molecular orbitals and simplifies the complex valence problem substantially by using the pseudo-spherical symmetry of the polyhedra. From these analyses it is also apparent that the *isolobal* analogies [8] between main group and polyhedral molecules exist because they both have characteristic 'unavailable' molecular orbitals which have a high proportion of p orbital character and are unsuitable either for skeletal bonding or accepting electron pairs from ligands. For a deltahedral metal cluster there are $(2n-1)$ of these orbitals and in the Stone notation they are described as L^σ_{sp} $(L \geqslant 2)$ and $\overline{L^\pi_{pd}}$ $(L \geqslant 1)$.

The metal cluster compounds illustrated in Fig. 1 do not have analogues in main group chemistry, and their closed shell requirements are not satisfactorily explained within the Tensor Surface Harmonic Methodology. It is apparent from Fig. 1 that

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the topologies of these clusters more closely resemble cylinders than spheres, and therefore it is inappropriate to attempt to describe them in terms of a spherical electron density model. We have thus developed the solutions in the Schrödinger equation for the particle on the cylinder problem in order to account for the bonding in this type of cluster. Complete details of this theoretical analysis will be given elsewhere and only the important chemical implications of the model will be discussed in this paper [9].

The wave functions for a particle on a cylinder can be derived by taking the products of the wave functions for a particle on a circle and those for a particle on a line [9]. The resultant wave functions $\psi_{k\lambda}$ are characterised by two quantum numbers k and λ which define the number of phase changes along the length of the cylinder and perpendicular to the cylindrical face respectively. The following notation has been used to describe the wave functions:

$k\Lambda = \psi_{k\lambda}$

($k = 1, \ldots, n_z$, where n_z is the number of layers of atoms;

$\lambda = 0, \pm 1, \pm 2 \ldots n_r/2$

for n_r even and

$\lambda = 0, \pm 1, \pm 2, \ldots$

$\pm (n_r - 1)/2$ for n_r odd, where n_r is the number of atoms in the cycle.

Total number of atoms in cluster $n = n_r \times n_z$).

The skeletal molecular orbitals can be expressed as an expansion of the basis function orbitals ρ:

$$\begin{aligned} k\Lambda^{\rho} &= \sum_{l=1}^{n_z} \sum_{j=1}^{n_r} c_{lj} \rho_{lj} \\ &= \sum_{l=1}^{n_z} \sum_{j=1}^{n_r} \psi_{k\lambda}(\phi, z) \rho_{lj} \\ &= \left(\frac{2}{n_r(n_z + 1)} \right)^{1/2} \sum_{l=1}^{n_z} \sum_{j=1}^{n_r} \sin\left(\frac{kl\pi}{n_z + 1} \right) e^{i\lambda\phi_{lj}} \rho_{lj} \end{aligned}$$

where ϕ_{lj} now represent the positional coordinates of the atom j in the lth layer of the cylinder. The basis function ρ bear the following correspondence to the orbital designations used in the spherical problem:

$p_{\sigma} = p_{\sigma}$

$p_{\pi} = p_z$ and p_{ϕ}

$d_{\sigma} = d_{\sigma}$

$d_{\pi} = d_{\sigma z}$ and $d_{\sigma\phi}$

$d_{\delta} = d_{z\phi}$ and $d_{z^2 - \phi^2}$

The coordinate system and the basis functions for the cylindrical problem are defined in Fig. 2.

For a cylindrical cluster of main group atoms with s and p valence orbitals the in-pointing sp^{σ} hybrid orbitals give rise to one very strongly bonding $1\Sigma^{\sigma}$ radial

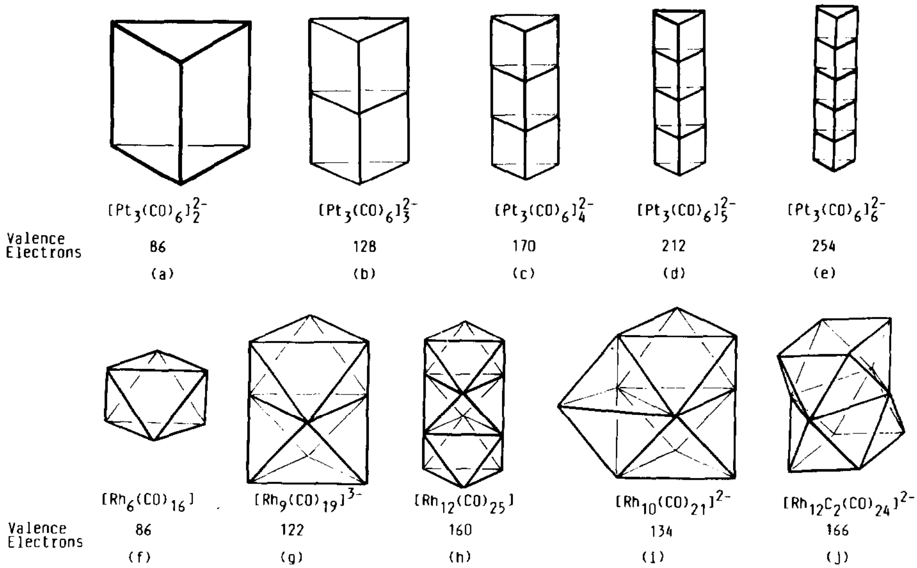

Fig. 1. Some examples of columnar carbonyl clusters and their characteristic valence electron counts.

molecular orbital, which has neither vertical nor horizontal nodes. The tangential *p* orbitals, which for the cylinder problem are defined as p_z and p_ϕ give after the relevant orbital mixings are taken into account [9] *n* bonding and *n* antibonding skeletal molecular orbitals localised predominantly on the surface of the cylinder. Although p_z and p_ϕ have been separated the molecular orbitals derived from them are still related by the parity transformation ($\hat{P}$) involving a local rotation of 90° at each atom and along the σ axis. The energies of parity related molecular orbitals are approximately equally bonding and antibonding as long as $\beta_\sigma \simeq \beta_\pi$. Consequently for a cylindrical cluster of this type there are a total of $(n+1)$ bonding and $(2n-1)$ 'unavailable' skeletal molecular orbitals, i.e. the same number as that observed for spherical deltahedral clusters. The nodal characteristics of the radial and tangential

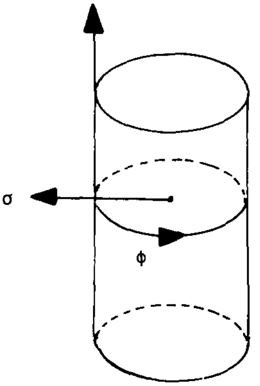

Fig. 2. Coordinate system for the particle on the cylinder problem.

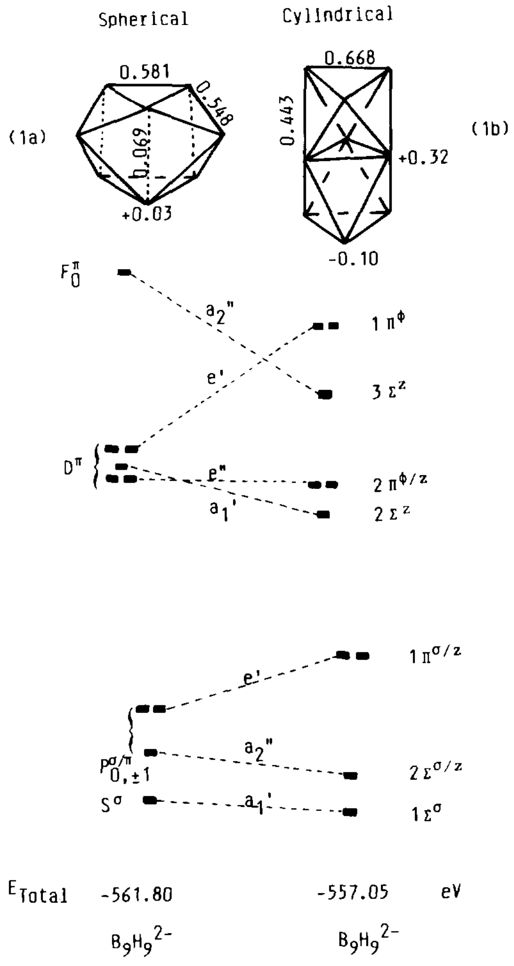

Fig. 3. Comparison of the total energies, overlap populations and charges for $B_9H_9^{2-}$ with spherical and cylindrical geometries.

molecular orbitals also are related to those for a spherical cluster with the same number of atoms. This relationship can be illustrated by reference to specific calculations on $B_9H_9^{2-}$ with either a spherical (**1a**) or cylindrical (**1b**) topology. The tricapped trigonal prism (**1a**) and the face sharing octahedra (**1b**) both belong to the D_{3h} point group and their bonding skeletal molecular orbitals span the same irreducible representations (see Fig. 3). In this Figure the pseudo-symmetry labels of these molecular orbitals based on the solutions to a particle on a sphere and a particle on a cylinder are also given in order to give a correlation between the alternative methodologies.

In Fig. 3 the computed total energies, overlap populations and computed atomic charges (derived from extended Hückel molecular orbital calculations) are summarised. Although both **1a** and **1b** are characterised by a total of $(n+1)$ skeletal bonding molecular orbitals their computed total energies differ by more than 4.5 eV. The spherical geometry is the more stable because it permits more favourable bonding interactions for the radial and tangential molecular orbitals and a more even distribution of charge density and bonding electron density. The latter conclusions are clearly supported by the computed atomic charges on the boron atoms and the overlap populations. In the light of these calculations it is not surprising that main group polyhedral molecules do not in general adopt cylindrical topologies.

The stacked platinum triangular clusters **a**–**e** in Fig. 1 provide a reasonable approximation to the bonding situation described above because although they have d valence electrons their d^{10} configurations lead to a cancellation of the bonding effects associated with the d shell. All the clusters $[Pt_3(CO)_6]_n^{2-}$ ($n = 2$–6) [10] are characterised by a total of $42n + 2$ valence electrons which corresponds to the $(n + 1)$ skeletal electron pairs calculated for main group cylindrical molecules. Detailed calculations on these clusters [11–12] have indicated that the primary bonding interactions occur within the triangles (3 bonding molecular orbitals per triangle). Between the triangles the bonding is much weaker and the resulting single bonding molecular orbital is an in-phase combination of platinum $6p_z$ orbitals $(n\Sigma^z)$ with a substantial contribution from the carbonyl π^* orbitals. These weak interactions slightly outweigh the repulsive interactions between the ring arising from the filled d shells.

The $[Pt_{19}(CO)_{22}]^{2-}$ has three pentagonal rings of platinum atoms, two interstitial platinum atoms and two capping atoms. The presence of the capping and interstitial atoms means that this cluster is more appropriately described as a bi-spherical cluster with two interstitial atoms. Such a bonding analysis has been presented in some detail elsewhere [13].

Stronger interactions between rings of transition metal atoms are achieved by depopulating some of the d band and thereby reducing the repulsive effects between the rings. For a spherical transition metal carbonyl cluster although the L_d^δ and $\overline{L_d^\delta}$ molecular orbitals derived from d_{xy} and $d_{x^2-y^2}$ are both filled by a total of $4n$ valence electrons their respulsive effect is not large because the overlap integrals between the d orbitals on adjacent metals on the spherical surface are not large and furthermore the $\pi^*(CO)$ orbitals of the carbonyl ligands mitigate the antibonding effects by interacting more strongly with $\overline{L_d^\delta}$.

In a cylindrical cluster the d_δ overlap integrals are larger for purely geometric reasons and the d_δ orbitals of the metal atoms ($d_{z\phi}$ and $d_{z^2-\phi^2}$) belonging to inner layers experience a particularly strong interaction. The antibonding interactions between the d_δ orbitals of the inner layer atoms cannot be mitigated either by rehybridisation effects (see Fig. 4) or very effectively by bridging carbonyls, because in a cylindrical cluster the number of carbonyl ligands which can bond to the inner atoms is geometrically constrained. Therefore, a cylindrical transition metal carbonyl cluster is characterised by $(2n - 1)$ 'unavailable orbitals' with a high proportion of p orbital character and an additional set of 'unavailable' orbitals resulting from out of phase combinations of the d_δ orbitals of the inner rings of atoms.

The d_π ($d_{\sigma z}$ and $d_{\sigma\phi}$) orbitals of the metal atoms in the inner layers mix extensively with p_π (p_z and p_ϕ) to give equal numbers of in-pointing and out-pointing hybrid orbitals. The latter can either be classified as non-bonding or used in metal–ligand bonding. Since the situation is entirely analogous to that in spherical clusters the d_π orbitals of a cylindrical cluster do not generate any additional unavailable molecular orbitals.

The analysis of the particle on a cylinder problem has suggested that number and

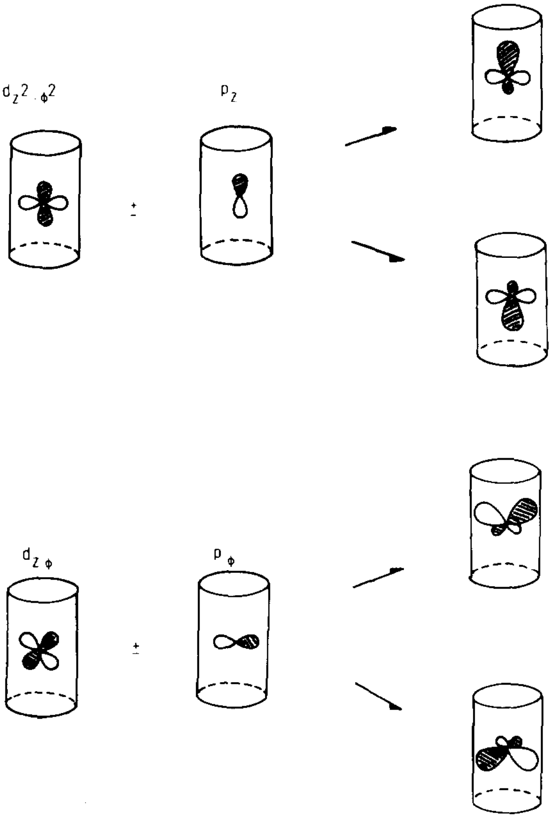

Fig. 4. Schematic representations of the possible orbital mixings between d_δ and p_π atomic orbitals for atoms in central layers of cylindrical clusters. It is noteworthy that the orbital mixings do not produce out-pointing hybrids with diminished metal–metal bonding capabilities.

symmetries of the 'unavailable' orbitals can be derived simply and follow a regular pattern. In a three layer staggered structure based on triangles of metal atoms there are three unavailable orbitals derived from d_δ $3\Sigma^{z\phi}$ and $1\ \Pi^{z^2-\phi^2}$ and for a four-layer structure there are five 'unavailable' orbitals, $4\Sigma^{z\phi}$, $1\ \Pi^{z^2-\phi^2}$ and $2\Pi^{z^2-\phi^2}$. These molecular orbitals which are illustrated in Fig. 5 are derived from the out-of-phase combinations of the d_δ orbitals on the inner triangles and are also out-of-phase with respect to the outer triangles. In the general case of n_z staggered triangles there are:

$$k\Sigma^{z\phi} \quad (k = n_z, \ldots [n_z/2] + 2)\ *$$

$$k\Sigma^{z^2-\phi^2} \quad (k = 1, \ldots (n_z - 2))$$

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* $[X]$ is the integer contribution of X, e.g. if $X = 2\frac{1}{2}$ $[X] = 2$.

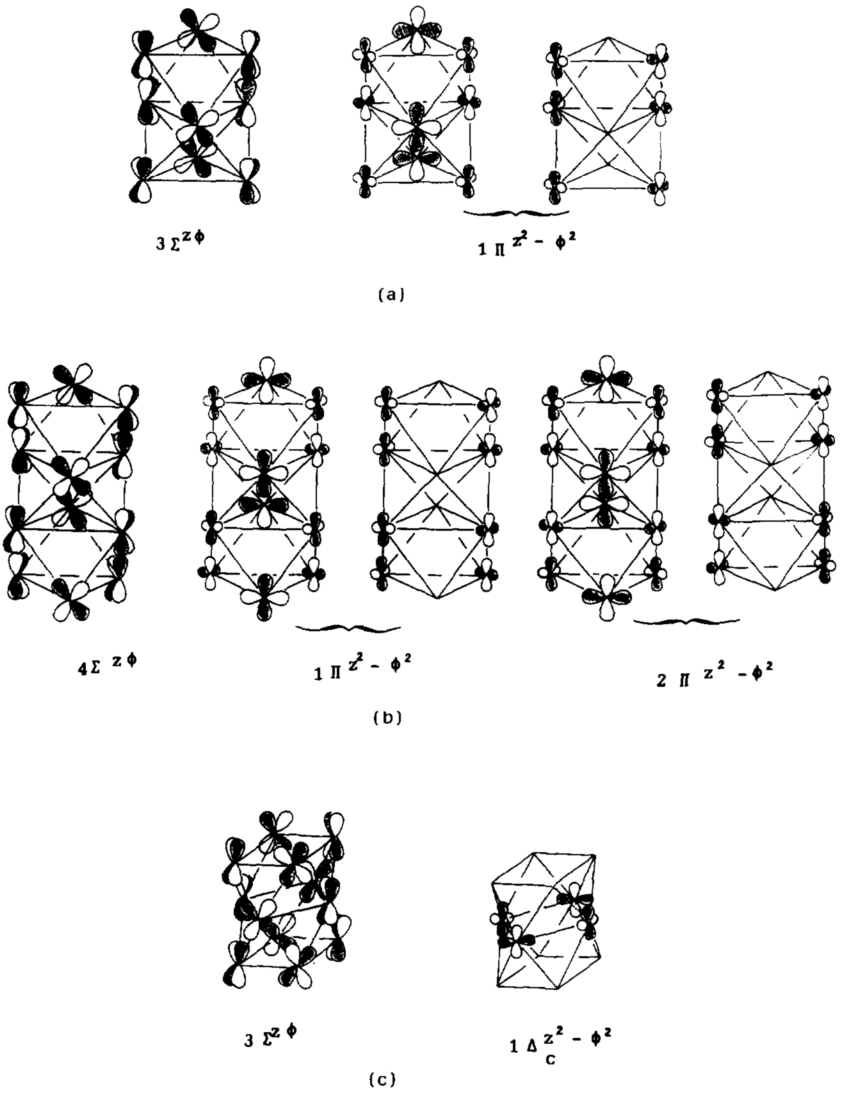

Fig. 5. Schematic illustrations of the additional 'unavailable' molecular orbitals derived from d_δ orbitals of the inner layers: (a) $n_z = 3$, $n_r = 3$; (b) $n_z = 4$, $n_z = 3$; (c) $n_z = 3$, $n_r = 4$.

Therefore, the total number of unavailable d_δ orbitals is:

$$3(n_z - 2) - [(n_z - 2)/2]$$

In summary, a transition metal carbonyl cluster with a staggered column of triangles has $(2n - 1)$ unavailable orbitals with a high proportion of p orbital character and an additional $3(n_z - 2) - [(n_z - 2)/2]$ d unavailable orbitals. Therefore these clusters are characterised by a total of:

$$14n + 2 - 6(n_z - 2) + 2[(n_z - 2)/2] \text{ valence electrons}$$

Table 1

Comparison between carbonyl- and sulphido-columnar clusters based on staggered metal triangles

Compound	Electron counts	Unavailable orbitals $2n-1+(\text{extra } d_\delta)$	Compounds	d electrons	Electron counts			Unavailable orbitals $2n-2^{b}+(\text{extra } d_\delta)$
					valence electrons	+	n electron pairs [a]	
$[Rh_6(CO)_{16}]$	86	$2\times6-1$	$[Mo_6S_8]^{4-}$	24	72	+	(12) = (84)	$2\times6-2$
$[Rh_9(CO)_{19}]^{3-}$	122	$2\times9-1+(3)$	$[Mo_9S_{11}]^{4-}$	36	102	+	(18) = (120)	$2\times9-2+(3)$
$[Rh_{12}(CO)_{25}]^{2-}$	160	$2\times12-1+(5)$	$[Mo_{12}S_{14}]^{6-}$	50	134	+	(24) = (158)	$2\times12-2+(5)$

[a] The *sp* hybridised outpointing orbital of each metal which is available for one terminal ligand is unoccupied in this series of clusters. [b] There is one more unavailable orbital ($\bar{F}_d^\delta$) in $Mo_6S_8L_6$ discussed in ref. 20.

This analysis accounts for the electron counts in the following series of rhodium clusters:

$[Rh_6(CO)_{16}]$ [14] octahedral ($n_z = 2$) 86 valence electrons
$[Rh_9(CO)_{19}]$ [3–15] face sharing octahedra ($n_z = 3$) 122 valence electrons
$[Rh_{12}(CO)_{25}]$ [16] three face sharing octahedra ($n_z = 4$) 160 electrons

The structures of these clusters are illustrated in **f–h** in Fig. 1. The structure shown in Fig. 1 (i) [17] is derived from the face sharing octahedra by the introduction of an additional capping atom and is electronically related to the latter by the capping principle [18], i.e. it has a total of 122 + 12 (= 134) valence electrons.

For cylindrical clusters based on staggered arrangements of squares there are also $(2n - 1)$ unavailable orbitals with a high proportion of p orbital character and the following unavailable orbitals derived from d_δ for a cluster with three layers:

$3\Sigma^{z\phi}$ and one component of $1\,\Delta^{z^2-\phi^2}$

These orbitals are illustrated in Fig. 5. For these clusters there is in addition a pair of orbitals which are approximately non-bonding $(1\Pi^{z^2-\phi^2}(e_u))$.

$[Rh_{12}C_2(CO)_{24}]^{2-}$ has a structure based on two square-antiprisms sharing a square face (Fig. 1 (j)) [19] and has a total of 166 valence electrons. This corresponds to the 11 skeletal bonding molecular orbitals and 25 'unavailable' molecular orbitals. 23 of these (i.e. $2n - 1$) are associated with the high energy p orbitals and the additional pair correspond to $3\Sigma^{z\phi}$ and $1\,\Delta^{z^2-\phi^2}$ derived from d_δ. Clearly this suggests that in this cluster the non-bonding e_u molecular orbitals are fully occupied.

The $k\Lambda^{z\phi}$ and $k\Lambda^{z^2-\phi^2}$ molecular orbitals are related by a parity operation involving a local rotation of 45°, but their energies do not reflect this precisely because $\beta_d^\sigma \neq \beta_d^\pi \neq \beta_d^\delta$ unless n_r and n_z are very large.

Although the arguments developed above have concentrated on carbonyl clusters they can be easily extended to halide and sulphide clusters of the earlier transition metal clusters. It has been argued that the major electronic difference between octahedral clusters with π-acceptor and π-donor ligands arises from the unavailability of some components of the $\overline{L_d^\delta}$ molecular orbitals [20]. In a metal carbonyl cluster all the L_d^δ and $\overline{L_d^\delta}$ orbitals are occupied, whereas in $[Mo_6Cl_8L_6]^{4+}$ there is an additional unavailable molecular orbital $\overline{F_d^\delta}$ (a_{2u}). This molecular orbital retains its unavailable character, and is joined in the columnar clusters $[Mo_9S_{11}]^{4-}$, $[Mo_{12}S_{14}]^{6-}$, etc. [21] by an additional $3(n_z - 2) - [(n_z - 2)/2]$ d_δ unavailable molecular orbitals.

The existence of these molecular orbitals accounts for the closed shell requirements of the sulphido-columnar clusters. The conclusions based on this analysis are summarised in Table 1 and are consistent with a more detailed theoretical analysis [22].

The *isolobal* analogies which have proved so useful in correlating the structural chemistries of main group and transition metal carbonyl polyhedral molecules are based on the assumption that the molecular orbitals derived from d_δ do not make a significant contribution to skeletal bonding. Whilst this assumption is valid for clusters with spherical topologies it is necessary to evaluate the bonding effects associated with the d_δ orbitals in cylindrical clusters. The unavailable skeletal molecular orbitals derived from d_δ have been evaluated using a particle on a cylinder model.

The observed difference between spherical and cylindrical clusters has a broader significance in the interpretation of the structures of the elements themselves. Boron does not form close packed metallic structures, but prefers complex arrangements based on the linking of spherical icosahedra. In contrast transition metals adopt close packed arrangements based on face and edge shared octahedra. Clearly the d interactions between adjacent metal atoms must make a significant contribution to this observation.

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