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A Topological Equivalent-Orbital Approach to the Bonding in some Tetrahedral Molecules

By

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The electronic structures of the tetrahedral molecules P_4, $Be_4(OAc)_6O$, $[PtMe_3Cl]_4$, $[Cu\ I\ As\ Me_3]_4$, $[Tl\ OR]_4$, $[Li\ Me]_4$ and B_4 are discussed using a simple topological equivalent-orbital approach.

Die Elektronenstrukturen der tetraedrischen Moleküle P_4, $Be_4(OAc)_6O$, $[PtMe_3Cl]_4$, $[Cu\ I\ As\ Me_3]_4$, $[Tl\ OR]_4$, $[Li\ Me]_4$ und B_4 werden diskutiert unter Benutzung einer einfachen Näherung topologisch äquivalenter Orbitale.

Les structures électroniques des molécules tétraédriques P_4, $Be_4(OAC)_6O$, $[PtMe_3Cl]_4$, $[Cu\ I\ As\ Me_3]_4$, $[Tl\ OR]_4$, $[Li\ Me]_4$ et B_4 sont discutées en usant d'une approche simple par des orbitales équivalentes topologiques.

One of the most interesting aspects of inorganic chemistry of recent years has been the information which has become available on the occurrence of compounds containing metal to metal bonds [*13*]. In contrast, the theoretical description of these compounds is still at an early stage of development. One particular point which is still rather unclear is the extent to which bridging ligands need to be included in the discussion. They have been commonly ignored; so, for example, despite the fact that for every metal orbital combination there is at least one ligand orbital combination of the same symmetry, only the electrostatic effect of the acetate anions in cupric acetate has been included in calculations published to date — and none of these appears completely satisfactory [*19*]. It is perhaps significant that a theoretical discussion of the metal-metal interactions in two molecules which contain metal octahedra, $Mo_6Cl_8^{4+}$ and $Ta_6Cl_{12}^{2+}$, lead to quite different bonding schemes [*1*], but these become unified when the chloride anions are included [*9*].

Because of the close structural relationship of a tetrahedron and an octahedron it is of interest to see whether the electronic structure of molecules which contain metal tetrahedra can be determined using the topological arguments applied to metal octahedra [*9*], and this is the topic we shall consider in this paper.

We associate with each edge of the tetrahedron a bonding equivalent orbital [*16*] bonding two atoms. With each face of the tetrahedron we associate a (three centred) bonding equivalent orbital which bonds three atoms. These two types of bond we shall for convenience call types *A* and *B* respectively [*10*]. The antibonding counterpart of type *A* we shall call type *C* (in this there is a nodal plane between the two atoms). It should be noted that these orbitals do not actually lie in the faces and along edges of the tetrahedron — this is not possible with the basis set available — but merely that these geometric features are associated with the presence of the corresponding orbitals. The orbitals form a basis for reducible representations of the T_d group, the relative energies of the components, within a Hückel approximation, being given in Tab. 1, α and β being coulomb and resonance integrals respectively, different integrals of the same type being distinguished by dashes.

We shall use these orbital sets as a basis for a discussion of the electronic structures of several molecules drawn from widely different parts of the periodic table.

The P_4 *Molecule.* The structure of the P_4 molecule was determined by MAXWELL, HENDRICKS and MOSLEY [*14*] by electron diffraction and found to be tetrahedral. If bonds of type A and B are present a total of twenty electrons will be needed to fill them, the number of valence electrons available. If it is assumed that the phosphorus $3s$ electrons do not contribute appreciably to the bonding then the twelve remaining electrons are allocated to type A orbitals. This is the more probable case and we conclude that the bonding molecular orbitals are of $A_1 + E + T_2$ symmetries.

Table 1. *Tetrahedral orbitals and relative energies*

Equivalent Orbital Type	Corresponding Molecular Orbitals	Energies
A	A_1	$\alpha + \beta + 4\,\beta'$
	E	$\alpha + \beta - 2\,\beta'$
	T_2	$\alpha + \beta$
B	A_1	$\alpha' + 3\,\beta''$
	T_2	$\alpha' - \beta''$
C	T_2	$\alpha - \beta + 2\,\beta'''$
	T_1	$\alpha - \beta - 2\,\beta'''$

It appears that the Hückel energies of combinations of metal orbitals can be a useful guide to the symmetries of the bonding molecular orbitals of polyhedra [*2*] so it is encouraging to note that such a calculation also indicates that the bonding molecular orbitals of the P_4 molecule are of $A_1 + E + T_2$ symmetries, the $3s$ orbitals again being ignored.

The oxides P_4O_6 and P_4O_{10} also contain tetrahedra of phosphorus atoms [*5*]; in these molecules the type B bonds are filled by electrons which may be considered to originate from the oxide anions. The sulphides $P_4\,S_3$ [*7*] and $P_4\,S_7$ [*20*] contain distorted tetrahedra of phosphorus atom; in them type A bonds are filled either by 'phosphorus' or 'sulphur' electrons.

Zinc and Beryllium oxyacetates. These molecules have similar structures in which a tetrahedron of metal atoms has an oxygen atom at its centre and acetate groups along each edge [*15*, *12*].

In each acetate group there are two oxygen atoms co-ordinated to metal atoms; the symmetric combination of oxygen atoms donates electrons into a type A bonding orbital and the antisymmetric combination donates electrons into a type C bonding orbital. The type B bonds are filled by 'oxygen' electrons from the central oxygen atom; the metal atoms formally having no valence electrons.

It appears, then, that seven sets of bonding molecular orbitals, of symmetries A_1 (2), E, T_1 and T_2 (3), are responsible for the stability of the molecule. It is interesting to note that the sixteen valence orbitals of the metal atoms also transform as A_1 (2) + E + T_1 + T_2 (3)*.

Trialkyl Platinum Halides. The crystal structure of trimethyl platinum chloride has been determined by RUNDLE and STURDIVANT [*17*] and found to contain a tetrahedron of platinum atoms, each face of the tetrahedron being centred by a chlorine atom. The positions of the methyl groups was not established but it is generally accepted that they complete the 'octahedral' coordination of each platinum atom. The corresponding triethyl compound appears to have a similar structure [*11*].

A total of six electrons are involved in extra-tetrahedron bonding at each platinum atom, three of which originate from the metal. Each chlorine atom attains a closed shell structure at the expense of a platinum atom, so that each platinum contributes six electrons to the cage bonding. Adding two (σ) electrons from each chloride anion we find that there are a total of thirty two electrons available for bonding within the polyhedron. These presumably fill orbitals of types A, B and C. The filling of an A and C orbital in the absence of a bidentate ligand implies the presence of a pair of non-bonding electrons on each of the atoms which the A and C orbitals span. In the present example we conclude that there are five sets of essentially non-bonding orbitals, of symmetries $A_1 + E + T_1 + T_2$ (2). The orbitals responsible for the stability of the cage are of type B and are filled by 'chlorine' electrons. There are two pertinent comments at this point. Firstly it is perhaps surprising that molecular stability should require the presence of coordinated anions when non-bonding platinum electrons are available. However, platinum trimethyl has been reported [*4*] and appears to have a polymeric structure [*8*]. Secondly, there is no obvious reason why the chloride anions should not be replaced by a group such as CH_3^- to give platinum tetramethyl, a compound reported by GILMAN and LICHTENWALTER [*4*], but the existence of which now appears in doubt**.

Cuprous Iodide — Trimethylarsine Complex. The tetrameric structure of this molecule was established by WELLS [*22*].

The structure is very similar to that of trimethyl platinum chloride, the arsine molecule replacing the methyl groups of the latter. If it is accepted that six electrons are to some extent involved in the bonding of an arsine molecule to each copper atom (two in σ bonds and four in π) then four of these electrons come from the copper atom. Both the molecule and the cage are then isoelectronic with the trialkyl platinum halides and their bonding identical. The extra-cage bonds transform as $A_1 + E + T_1 + T_2$ (2), which, together with the topological set, identifies A_1 (3) + E (2) + T_1 (2) + T_2 (5) molecular orbitals as responsible for the bonding of the whole molecule. If the valence orbital set on each metal atom is taken as d_σ, d_π, d_δ, s and p_σ, it is readily shown that these too transform as A_1 (3) + E (2) + T_1 (2) + T_2 (5) under the operations of the T_d point group.

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* We cannot consider just the more stable metal-orbital combinations since each combination interacts with a ligand group orbital.

** The author has several times attempted to prepare this compound without success. He understands that several other workers have similarly failed.

Thallium alkoxides. The suggestion that these molecules contain a tetrahedron of thallium atoms was first made by SIDGWICK and SUTTON [*18*] and subsequently confirmed by the work of DAHL et al. [*3*]. It is probable that above each face of the tetrahedron there is an alkoxide group. The electronic structure of these molecules follows naturally from our discussion of molecules containing platinum and copper tetrahedra. There are in this case no extra-tetrahedron bonds but since the three metal orbitals on each atom which were involved in this bonding in the other examples are still present we allocate six electrons to them. There remain twenty four 'thallium' electrons to be allocated, which we place in type A and C orbitals and which are therefore also non-bonding. Two σ electrons from the oxygen of each alkoxide group fill type B orbitals and are responsible for the stability of the molecule.

Table 2. *Relative molecular orbital energies in a* B_4 *tetrahedron*

	HOFFMANN and LIPSCOMB [*6*]	This work. The orbital type is indicated
T_2	-0.85	-0.60 (C)
T_1	-0.56	-0.90 (C)
T_2	-0.09	-0.03 (B)
E	0.03	0.07 (A)
A_1	0.04	0.10 (B)
T_2	0.75	0.75 (A)
A_1	2.16	2.11 (A)

The conclusion that there are non-bonding interactions between the platinum, copper and thallium atoms in the last three examples finds support in the crystal structures of the molecules in which the metal-metal distances vary from ca. 3.2 to 3.9 Å.

There are only two tetrahedral molecules for which detailed calculations are available in the literature. In the first, tetrameric lithium methyl, the methyl groups are above the faces of a tetrahedron of lithium atoms [*21*]. Type B bonds are evidently involved so that we predict that the bonding involves A_1 and T_2 molecular orbitals, the former being the more stable. This conclusion is in agreement with WEISS and LUCKEN's calculations [*21*]. Another test of the topological approach is provided by HOFFMANN and LIPSCOMB's work on the B_4 tetrahedron [*6*]. Their numerical results (as a function of the dimensionless energy parameter x) are given in Tab. 2 along with ours (Tab. 1) in which we have put $\alpha = \alpha' = 0$ (in conformity with HOFFMANN and LIPSCOMB) $\beta = 0.75\,x$, $\beta' = 0.34\,x$, $\beta'' = \beta'/10$ and $\beta''' = \beta/10$. The relative magnitude of these resonance integrals seems reasonable; they provide a good agreement between HOFFMANN and LIPSCOMB's results and ours, with the exception of the upper two orbital sets which are interchanged. This behaviour is similar to that found with metal octahedra [*9*], where the semi-empirical and topological approaches gave identical ordering of levels only at short internuclear distances.

Conclusions

The topological-equivalent orbital method seems capable of providing a simple description of the bonding in symmetrical polyhedral molecules and is probably preferable to the commonly used valence bond approach, since it gives, very simply, an order of orbital energies which is a reasonable approximation to that found by more detailed calculations. It may well be that a useful criterion of the accuracy of a semi-empirical molecular orbital calculation on a polyhedral molecule is whether or not it has a chemically acceptable equivalent orbital interpretation.

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