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A Topological Approach to the Electronic Structures of some Polynuclear Zinc Species

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The topological equivalent orbital approach is applied to a variety of polynuclear zinc species, all zinc 3d *electrons being included in the discussion. In all cases, the orbital energy level patterns obtained appear reasonable and lead to closed shell ground states.*

Polynuclear compounds occur widely in the chemistry of the metals, and whilst they often come within a formal definition of cluster compounds such as Cotton's,[1] there are many such systems where metal-metal bonding contributes little, if anything, to the molecular stability. In many of the molecules the symmetry of the aggregate is much greater than that of any individual atom. The presence of such symmetry elements invariably simplifies a detailed discussion of the interactions responsible for the stability of a molecule at any level of approximation. Where there is a polyhedral skeleton, therefore, it is desirable to explore ways in which the inherent symmetry may be exploited in a simple discussion of the molecular monding. Further, since at the present time detailed calculations on polynuclear species are scarcely possible there is a need for a simple approach which reasonably accurately anticipates the results of such calculations.

Commonly, the structure of such molecules has been discussed in terms of the hybridization of the key atoms involved (usually metal atoms), the object being to establish a closed shell structure and a physically reasonable network of chemical bonds. As an alternative approach to the bonding in such compounds the equivalent-orbital concept[2] has proved applicable to molecules built of atoms as disparate as lithium and platinum.[3] The detailed results are in agreement with calculations on the polyhedral boron hydrides using an explicit atomic orbital basis[4] and more recently comparison with a semi-empirical analysis has shown the method to provide the simplest qualitatively accurate picture of the binding in P_4,[5] although the part played by *d*-orbitals remains unclear.[6]

A distinction between the hybridization and the equivalent-orbital approach lies in the fact that the former considers only those orbitals which are extensively involved in bonding (and these are, often, those in which a chemist is particularly interested). However, the results of ESCA, photoelectron spectroscopy and of detailed calculations on small molecules indicate that electrons in non-valence shells may be considerably perturbed as a consequence of the formation of molecules. The equivalent-orbital method may be extended to include some, at least, of these electrons and it is the purpose of the present paper to investigate the application of the method to some polynuclear zinc compounds, the ten 3*d* electrons of each zinc atom being included in the discussion. Although these electrons are, formally, non-bonding we shall see that they behave differently in the various molecules and this difference is presumably reflected in the one-electron molecular orbital energies.

We consider first the molecule $Zn_4O(CH_3CO_2)_6$ which has essentially the same structure (T_d) as that of $Be_4O(CH_3CO_2)_6$.[7] The 4*s* and 4*p* orbitals of the four zinc atoms transform as

$$2A_1+E+T_1+3T_2$$

while the 3*d* orbitals transform as

$$A_1+2E+2T_1+3T_2$$

The 2*s* and 2*p* orbitals of the oxide residue transform as

$$A_1+T_2$$

and the σ orbitals of the acetate residues (one orbital on each oxygen) as

$$A_1+E+T_1+2T_2$$

It is evident that the 4*s* and 4*p* orbitals of the zinc atoms match exactly the available ligand orbitals. Further, a count of valence electrons indicates that there are just enough electrons (thirty-two) to fill $2A_1+E+T_1+3T_2$ molecular orbitals. That is, formally, there is no need to include the zinc *d*-orbitals in order to 'explain' either the molecular geometry or stability. The *d*-electrons comprise a closed shell which, if completely unaffected by the formation of molecular orbitals, has spherical symmetry about each zinc atom. The correlation between the local C_{3v} symmetry of each zinc atom and molecular T_d sym-

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[1] F.A. Cotton, *Quart. Rev., 20,* 1966, 389.
[2] J.A. Pople, *Quart. Rev., 11,* 273 (1957).
[3] S.F.A. Kettle, *Theor. Chem. Acta, 4,* 150 (1966).
[4] S.F.A. Kettle and D.J. Reynolds, *Theor. Chem. Acta,* (In the press).
[5] R.M. Archibald and P.G. Perkings, *Chem. Comm.,* 569 (1970).
[6] I.H. Hillier and V.R. Saunders, *Chem. Comm.,* 1233 (1970).
[7] H. Koyama and Y. Saito, *Bull. Chem. Soc. Japan, 27,* 112 (1954).

metry is

Local C_{3v}		Molecular T_d
$2z^2-x^2-y^2$	$A_1 \longrightarrow$	A_1+T_2
(xz,yz) (xy,x^2-y^2)	$E \longrightarrow$	T_1+T_2+E

There are two distinct correlations possible between the zinc *d*-orbital basis and the topological basis orbitals. Either a combination of face bonding (A_1+T_2) together with two face antibonding sets ($2E+2T_1+2T_2$) or an edge-bonding set (A_1+E+T_2) together with face antibonding ($E+T_1+T_2$) and edge antibonding sets (T_1+T_2) is acceptable. Although the situation has not yet been analysed in detail, it is probable that the second correlation is the more appropriate since it is not possible to span an edge basis orthogonal to the face with atom-based *s* and *p* functions. The addition of *d*-orbitals, however, makes such a spaning possible.

It seems probable, therefore, that the zinc *d*-orbitals exert a mild antibonding effect on a tetrahedral zinc cluster, although a much more detailed analysis than we give in the present paper would be needed to establish this with certainty.

Accepting the role of *d*-orbitals which we have suggested above, an intriguing possibility exists. The addition of an independent set of orbitals with similar transformational properties to those of the zinc *d*-orbitals could mean that the latter are stabilized to an extent which offsets any inherent antibonding nature they possess. A possible example of this is provided by the unknown species $Zn_4O(S_2CR)_6$. A well-characterised analogous molecule is $Zn_4O[S_2P(OR)_2]_6$, although only an incomplete crystallographic study has been reported.[8] The existence of bonding involving sulphur *d*-orbitals is a subject of controversy; in the present case such bonding would imply additional, formally empty, molecular orbitals of symmetry $3A_1+2A_2+5E+7T_1+8T_2$ which more than adequately cover all the topological sets spanned by the zinc *d*-orbitals. The widely differing energies and sizes of the zinc and sulphur *d*-orbitals means that any interaction between them is unlikely to be primarily responsible for the molecular stability. On the other hand, it may well be a contributing factor.

It is interesting that, of the species observed so far, when a zinc tetrahedron is not centred the ligands binding the zinc atoms together are found in the faces, and not the edges, of the tetrahedron; $[CH_3Zn(OCH_3)]_4$, $[C_2H_5Zn(OC_4H_9{-}t)]_4$ and $Zn_7O_8(CH_3)_{14}$ are examples of this.[9] It has been argued elsewhere that in this situation the complete shells of *d*-electrons on atoms at the corners of the tetrahedron are nonbonding, although a weak antibonding effect, as discussed above, is also possible. It is interesting to note that in the hypothetical species $[RZn(SR')]_4$ the transformation of the *d*-orbitals on the sulphur and zinc are identical ($A_1+2E+2T_1+3T_2$) and, if the arguments presented above for $Zn_4O[S_2P(OR)_2]_6$ molecules are valid, then their extension to $[RZn(SR')_4]$ systems suggest that in such species a small, but perhaps crucial, *d*-orbital stabilising interaction will occur.

A most interesting polyhedral species is the octamer $[CH_3Zn(SC_3H_7{-}i)]_8$ where the zinc atoms and the sulphur atoms define interlaced irregular dibisphenoids.[10] In the (idealised) point group S_4 the *s* and *p* orbitals of the zinc atoms transform as 8A + 8B + 8E (of which 2A + 2B + 2E may be regarded as involving bonding with the terminal methyl groups) and the *d* orbitals transform as 10A + 10B + 10E. The orbitals from the valence shells of the sulphur atoms transform similarly, again allowing for the terminal groups. That is, each type of atom gives rise to basis orbitals of species 16A + 16B + 16E.

Although the overall molecular geometry is approximately S_4, the zinc skeleton has D_{2d} (idealised) symmetry. Taking as a starting point a regular dodecahedral arrangement of zinc atoms the topological bases (in the S_4 point group) are:

edge bonding	5A+5B+4E
edge antibonding	4A+4B+5E
face bonding	3(A+B+E)
face antibonding	6(A+B+E).

It is to be noted that there are three independent face sets, of which two are symmetry-related in D_{2d}. In $[MeZnSR]_8$, where the zinc and sulphur atoms together contribute 128 electrons, (ten *d*-electrons from each zinc and six valence-shell electrons from each sulphur), a possible allocation of electrons is to the following topological sets

edge bonding	5A+5B+4E
edge antibonding	4A+4B+5E
face bonding	3(A+B+E)
face antibonding	4(A+B+E)

giving a total of 16A + 16B + 16E. This sum is identical with the sum generated separately by the available zinc and sulphur orbitals. It is to be noted that in suggesting the above topological occupancy we have distinguished one of the face sets - that corresponding to the four 'empty' faces - by leaving its antibonding set unoccupied. It is further worthy of comment that face 'antibonding' orbitals are only antibonding from the point of view of the atoms defining the face. When such a face is centred by a further atom, the appropriate interactions between it and those atoms defining the face may strongly bonding.

The apparent non-existence of $[R_8Zn_8(SR')_{12}]^{4-}$ species, in which all faces of the parent zinc dodecahedron are centred, finds a possible explanation in an extension of the above discussion. The 'new' sulphur orbitals, 3A+3B+3E, are to be compared with the remaining topological face antibonding, 2A+2B+2E orbitals.

Conclusions

In the present paper we have shown that it is pos-

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[8] A.J. Burn and G.W. Smith, *Chem. Comm.*, 394, 1965.

[9] H.M.M. Shearer and C.B. Spencer, *Chem. Comm.*, 194, (1966). Y. Matsui, K. Kamiya, M. Nishikawa, and Y. Tomile, *Bull. Chem. Soc. Japan*, *99*, 1828 (1966). M.L. Ziegler and J. Weiss, *Angew. Chem. Int. Ed.*, 9, 905, (1970).

[10] G.W. Adamson and H.M.M. Shearer, *Chem. Comm.*, 897 (1969).

sible to give a topological account of the bonding in a variety of polynuclear zinc compounds. We have included the zinc d-electrons and the d-orbitals on other atoms where appropriate. In the absence of detailed calculations it is not possible to make the general claim that the description we give is correct, but the internal consistency and agreement with the detailed calculation where possible indicate the applicability of our model.

Kettle has used a slightly different approach to the electronic structure of some molecules similar to those discussed in this paper.[3] The approach is isomorphic to the present approach in the same way that there is an isomorphism between faces and corners of a tetahedron.

Finally, we note the general conclusion from the discussion of this paper that zinc d-electrons exert a minor antibonding influence in polynuclear compounds. Formally, this situation may be changed when other atoms in the molecule have low-lying vacant d-orbitals. In practice, however, it is doubtful if the presence of such d-orbitals has more than a marginal effect on the molecular stability.

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