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An Equivalent Orbital Description of the $Re_3Cl_{12}^{3-}$ Anion and Related Species

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In a discussion of the bonding between the atoms composing a large but symmetric molecule there are usually several molecular orbitals to consider, transforming as irreducible representations of the appropriate point group. The final picture of the bonding between adjacent atoms is then usually far from clear. So, although there is invariably a bonding molecular orbital which does not contain a nodal surface between any two atoms there are usually others which do. In such cases it is useful to have an equivalent orbital description of the bonding [*11*]. It has recently been shown that the equivalent orbital method can be applied to molecules containing an octahedron of metal atoms [*10*] and it is the purpose of this communication to similarly describe some molecules which contain three rhenium atoms arranged at the corners of an equilateral triangle.

This arrangement has been found for $Re_3X_{12}^{3-}$, $Re_3X_{11}^{2-}$, Re_3X_9, $Re_3X_9M_3$, (X = Cl or Br, M = a monodentate ligand), and $Re_3Br_{10}^{-}$ [*1, 2, 5, 6, 8, 9*]. In addition to the rhenium atoms in all of these compounds there are bridging halogen atoms along each edge of, and in the plane of, the triangle. Small differences in Re-Re bond lengths occur but they are not sufficient to indicate any significant change in the bonding interactions.

The electronic structure of the triangle has been discussed by Fergusson, Penfold and Robinson in terms of valence bond theory [*9*]. Molecular orbital descriptions have been given qualitatively by Bertrand, Cotton and Dollase [*2*], quantitatively by Cotton and Haas [*4*], and by Cotton [*3*]. Cotton and Haas have shown that the molecular orbitals responsible for the Re-Re bonding have A_1', A_2'', E' and E'' symmetries (in D_{3h}). The corresponding set of equivalent orbitals are shown in Fig. 1 as solid lines. These orbitals are the basis of a reducible representation with A_1', A_2'', E' and E'' components with relative energies $\alpha + 2\beta + \beta'$, $\alpha + 2\beta - \beta'$, $\alpha - \beta + \beta'$ and $\alpha - \beta - \beta'$ within a Hückel approximation, α being a coulomb integral and β and β' being resonance integrals between adjacent orbitals on one side of the ring and related by a σ_h operation respectively. This order of energies is in agreement with the calculations of Cotton and Haas [*4*] for most internuclear distances provided $\beta < \frac{2}{3}\beta'$. Following the work on metal octahedra [*10*], it appears that the bridging chlorine groups should be included in the bonding scheme. This adds molecular orbitals of A_1' and E' symmetry and suggests that a characteristic of the equilateral triangular arrangement of metal atoms is that it is an eighteen electron structure, these electrons filling the nine orbitals shown in Fig. 1.

The Re-Re equivalent bonding orbitals shown as solid lines in Fig. 1 may be combined to give orbitals which are respectively symmetric and antisymmetric with respect to reflection in the molecular plane. Of these, the symmetric combination cannot be of σ symmetry since it must be orthogonal to the (bent) σ bond shown dotted in Fig. 1. It is, in fact, a bond of the type shown in Fig. 2. The latter is a combination of σ and π bonds; when the z axes of each atom are not parallel there will also be a δ component (the bent σ bond in Fig. 1 may be resolved into σ and π components). This type of bond has been discussed by CRAIG, MACCOLL NYHOLM, ORGEL and SUTTON [7], who called them "schedo-σ" or "pretty-nearly-σ" bonds. As they are of potential importance whenever planar arrangements of transition metal atoms occur* it may be useful to give them a simpler name.

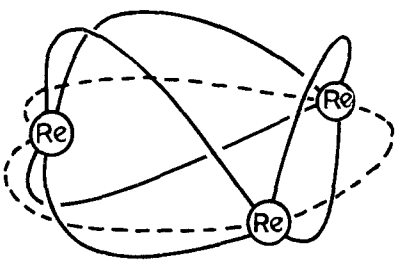

Fig. 1

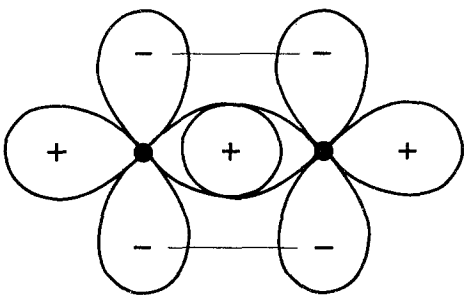

Fig. 2

Particularly appropriate would be 'ξ bonds'. The bonding between each pair of rhenium atoms in the trinuclear species would then consist of a (bent) σ, a (bent) π and a (bent) ξ bond, each being orthogonal to the other two.

* In complexes such as Ni $[S_2C_2(CN)_2]_2^{2-}$, where the four sulphur atoms are co-planar, this type of bond may also occur.

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