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The Bonding within the $Mo_6Cl_8^{4+}$ and $Ta_6Cl_{12}^{2+}$ cations

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The cations $Mo_6Cl_8^{4+}$ and $Ta_6Cl_{12}^{2+}$ have related structures [*1*, *6*] in which the metal ions are at the corners of an octahedron and the chlorine atoms are either above the faces of the octahedron ($Mo_6Cl_8^{4+}$) or above the edges ($Ta_6Cl_{12}^{2+}$). Discussions of the bonding within these molecules have been almost entirely concerned with the metal octahedra and they have therefore usually been considered together [*2*, *3*, *4*] although quite different bonding schemes have been suggested for the two cases. It is the purpose of this communication to point out that the bonding within these structures is, in fact, very similar. Indeed, in a sense, they are isoelectronic.

The twelve metal-metal bonds in $Mo_6Cl_8^{4+}$ are directed along the edges of the octahedron. These localized bonds form a basis of a representation which spans the A_{1g}, E_g, T_{1u}, T_{2g}, and T_{2u} irreducible representations of the octahedral group O_h. It is generally agreed that the molecular orbitals responsible for bonding within the octahedron also have these symmetries [*2*, *3*]. The energies of these orbitals are, according to the Hückel approximation, $\alpha + 4\beta$, $\alpha - 2\beta$, $\alpha + 2\beta$, α and $\alpha - 2\beta$ respectively, α and β being coulomb and resonance integrals. For small internuclear distances this ordering of orbital energies is in reasonable agreement with the calculations of Cotton and Haas [*2*]. These are symmetry-based combinations of the equivalent orbitals, all of which are filled. A negative β value indicates that the orbital is less stable than the parent equivalent orbital, not that it is antibonding.

The eight metal-metal bonds in $Ta_6Cl_{12}^{2+}$ are three-centre (triangular) bonds of the type commonly found in the higher boron hydrides [*5*]. Each orbital has a threefold rotation axis and this coincides with a threefold axis of the metal octahedron, so that there is a one to one correspondence between the orbitals and the faces of the octahedron. These localized bonds form a basis for a representation which spans the A_{1g}, A_{2u}, T_{1u} and T_{2g} irreducible representations of the octahedral group. The orbitals which are responsible for the metal-metal bonds in this molecule also have these symmetries [*2*, *3*]. The calculated energies, $\alpha + 3\beta$, $\alpha - 3\beta$, $\alpha + \beta$ and $\alpha - \beta$ respectively, again agree fairly well with the results of Cotton and Haas [*2*] at short internuclear distances.

In both structures the edges and faces of the metal octahedron define the position of bonding orbitals. Metal-metal bonding occurs along octahedral edges in $Mo_6Cl_8^{4+}$ whilst the faces may be considered as containing empty three-centred orbitals into which chlorine atoms donate σ electrons to give a σ bonding orbital. Conversely, the faces define the metal-metal bonds in $Ta_6Cl_{12}^{2+}$ and along the edges are empty orbitals into which σ electrons are donated by chlorine atoms. It follows, then, if one considers the metal electrons and chlorine σ electrons only, that the two structures are isoelectronic. For $Mo_6Cl_8^{4+}$ there are twenty-four metal and sixteen chlorine electrons, a total of forty, whilst for $Ta_6Cl_{12}^{2+}$ there are sixteen metal and twenty-four chlorine electrons. The simplest description of the bonding within these *cations* (as opposed to that within the metal octahedron) would then require twenty bonding molecular orbitals, of symmetries A_{1g} (2), A_{2u}, E_g, T_{1u} (2), T_{2g} (2) and T_{2u}. It is evident that the problem left unresolved by Cotton and Haas [2] — that 'no graphic or pictorial explanation of (the qualitative difference in the arrangement of molecular orbitals for the metal octahedra in $Mo_6Cl_8^{4+}$ and $Ta_6Cl_{12}^{2+}$) is evident to us' — is a consequence of taking a restricted basis set of wave functions.

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