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The Metal–Metal Bond in The Trinegative Octachloroditechnetate Ion

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The crystal and molecular structure of $(NH_4)_3Tc_2Cl_8 \cdot 2H_2O$, reported by Bratton and Cotton[1] demonstrates the presence of $Tc_2Cl_8^{3-}$ ions having a nonbridged eclipsed $Cl_4Tc{-}TcCl_4$ structure with a metal to metal bond distance very short. Such arrangement is present also in the $Re_2Cl_8^{2-}$ and $Mo_2Cl_8^{4-}$ ions. However, the charge of 3– on $Tc_2Cl_8^{3-}$ seems surprising by comparison with the charge of 2– on $Re_2Cl_8^{2-}$ and in view of the consideration that the extra electron originates an electronic open shell system and is probably antibonding in character.

This fact, together with the metal–metal bond distance, led us to investigate the electronic structure of the octachloroditechnetate(3–) ion according to molecular orbital theory within the CNDO approximations which have been just described.[2] An idealized D_{4h} symmetry has been employed with Tc–Tc and Tc–Cl bond distances of 2.13 and 2.36 Å respectively. The orbital basis set included the 5s, 5p and 4d atomic orbitals of each technetium atom and the 3s and 3p of each chlorine atom. Radial wave functions were taken from Basch and Gray[3] for the technetium atom and from Clementi paper[4] for chlorine atom. The self consistent procedure has been obtained with different molecular orbitals for electrons with different spin.

The resulting eigenvectors have been successively deorthogonalized via the $S^{-1/2}$ matrix so that Mulliken population analysis[5] has been performed. The populations of the valence orbitals of each technetium atom are reported in Table I. From inspection of the table and of the occupied eigenvectors the outer electron is essentially localized on the combination of the d orbitals which may be considered of δ^* type with respect to the Tc–Tc direction. Such possibility of the odd electron occupying the δ^* orbital was previously considered even if not taken into account seriously.[1]

TABLE I. Electronic Populations of Technetium Orbitals.

	Spin α	Spin β
5s	0.168	0.168
5p	0.085	0.085
4d	2.735	2.259

The total electronic populations of the Tc–Tc and Tc–Cl bonds have been found of 0.832 and 0.234 respectively; therefore, on assuming for the latter bond an unitary bond order, the metal–metal bond has to be viewed as a nearly quadruple bond. The electronic populations of the $4d_{Tc}$–$4d_{Tc}$ orbitals alone, reported in Table II, reveal that the major components of the Tc–Tc bond are the π bonds which are about three times as strong as the σ bond and six times as strong as the δ bond.

TABLE II. Contribution of the 4d Orbitals to the Metal–Metal Bond.

	Spin α	Spin β
d_σ–d_σ	0.081	0.081
d_π–d_π	0.230	0.230
d_δ–d_δ	–0.003	0.037

Under these aspects the results agree very well with the Cotton and Harris[6] investigation on the electronic structure of $Re_2Cl_8^{2-}$ ion on the basis of an extended Hückel scheme. However, the present calculation scheme, which explicitly introduces the two electron interactions, showed that the δ bond is indeed very weak and may be responsible of the eclipsed configuration of the ion rather than of the strength of the Tc–Tc bond.

In order to have some indications about the surprising charge of 3– a closed shell calculation on $Tc_2Cl_8^{2-}$ has been carried out. Mulliken population analysis furnished in this case the value of 0.898 and 0.302 for the Tc–Tc and Tc–Cl bonds respectively. Therefore, the bond order of the former relatively to the latter decreases on going from $Tc_2Cl_8^{3-}$ to $Tc_2Cl_8^{2-}$.

The odd electron removing indicates thus a lowering of the relative bond order Tc–Tc/Tc–Cl and provides evidence that such mechanism plays an important role in determining both the ionic charge and the oxidation products.

References

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