

1024. *Bonding in Tervalent Rhenium $\text{Re}_3\text{X}_{9+n}^{n-}$ Anions*

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A semiquantitative bonding scheme is presented for the trinuclear trivalent rhenium halogeno-anions. The bonding is divided into σ - and π -components. The principal structural features and magnetic properties of the anions can be explained by the theory.

THE recent developments in the chemistry of trivalent rhenium show that, under certain experimental conditions, salts containing the trinuclear halogeno-anions $\text{Re}_3\text{Cl}_{12}^{3-}$, $\text{Re}_3\text{Cl}_{11}^{2-}$, $\text{Re}_3\text{Br}_{12}^{3-}$, $\text{Re}_3\text{Br}_{11}^{2-}$, and $\text{Re}_3\text{Br}_{10}^{-}$,¹⁻⁷ can be isolated, as well as neutral complexes $\text{Re}_3\text{X}_9(\text{unidentate})_3$ and $\text{Re}_3\text{X}_6(\text{bidentate})_3$.⁷⁻⁹ The structures of these compounds, and of the entities Re_3Cl_9 and Re_3Br_9 , have been shown from crystal structure^{1-3,6,10,11} and spectral^{3,8} evidence to be based on a triangle of bonded rhenium atoms. The Table presents relevant structural data at present available on certain of the trinuclear species.

A molecular orbital approach to the bonding in $\text{Re}_3\text{Cl}_{12}^{3-}$ was made by Cotton and Haas.¹² Their method is also of general applicability to other cluster structures, $\text{M}_6\text{X}_8^{4+}$ ($\text{M} = \text{Mo}$ or W) and $\text{M}_6\text{X}_{12}^{2+}$ ($\text{M} = \text{Nb}$ or Ta), but was not specifically used to explain the fact that the metal-metal bonds are much shorter in the trimeric structures than in the cage structures. Bearing in mind these very short Re-Re bonds, we present a different approach.*

Bond lengths (\AA) and angles in trinuclear rhenium species

	$\text{Re}_3\text{Cl}_{12}^{3-2}$	$\text{Re}_3\text{Cl}_{11}^{2-13}$	$\text{Re}_3\text{Br}_{11}^{2-10}$	$\text{Re}_3\text{Cl}_9^{11}$	Re_3Br_9^6
Re-Re	2.48	2.48, 2.43 *	2.49, 2.43 *	2.49	2.465
Re-X (terminal in-plane)	2.52	2.57	2.72	(2.66)	
Re-X (terminal off-plane)	2.36	2.30, 2.29 *	2.48, 2.38 *	2.40, 2.29	2.45
Re-X (bridge)	2.39	2.35	2.54	2.46	2.54
X-Re-X (terminal off-plane) ...	158°	158°, 151° *	159°, 134° *	163°	155°
Re-X-Re (bridge)	62°	62°	58°	61°	58°

* Values associated with the halogen-deficient Re atom.

The bonding in $\text{Re}_3\text{Cl}_{12}^{3-}$ can be resolved into two components, *viz.*, a σ -bond framework and a π -molecular orbital encompassing the triangle of rhenium atoms.

The σ -bond framework can be considered either as a distorted pentagonal bipyramid³ of five chlorine and two rhenium atoms around each rhenium, or more generally, as σ -molecular orbitals incorporating two Re-Re bonds and five Re-Cl bonds for each rhenium. In the former case the hybrid scheme would be d^3sp^3 (using d_{z^2} , $d_{x^2-y^2}$, and d_{xy} orbitals in D_{5h} symmetry). (The Figure gives the arrangement of axes with respect to the bonds.) This involves a postulate of bent bonds, which is not unreasonable when it is taken into account that each bonded pair of rhenium atoms subtends an angle of 60° at its bridging chlorine atom. The bonds from bridging chlorines must therefore be considerably bent.

* Footnote added in Proof.—A recent Paper by F. A. Cotton (*Inorg. Chem.*, 1965, **4**, 334) emphasises the bond order changes in the various metal clusters.

¹ W. T. Robinson, J. E. Fergusson, and B. R. Penfold, *Proc. Chem. Soc.*, 1963, 116.

² J. A. Bertrand, F. A. Cotton, and W. A. Dollase, *Inorg. Chem.*, 1963, **2**, 1166.

³ J. E. Fergusson, B. R. Penfold, and W. T. Robinson, *Nature*, 1964, **201**, 181.

⁴ J. E. Fergusson and B. H. Robinson, *Proc. Chem. Soc.*, 1964, 189.

⁵ F. A. Cotton and S. J. Lippard, *J. Amer. Chem. Soc.*, 1964, **86**, 4497.

⁶ F. A. Cotton and S. J. Lippard, *Inorg. Chem.*, 1965, **4**, 59.

⁷ J. E. Fergusson and B. H. Robinson, *J.*, 1964, 5683.

⁸ F. A. Cotton, S. J. Lippard, and J. T. Mague, *Inorg. Chem.*, 1965, **4**, 508.

⁹ F. A. Cotton and J. T. Mague, *Inorg. Chem.*, 1964, **3**, 1094.

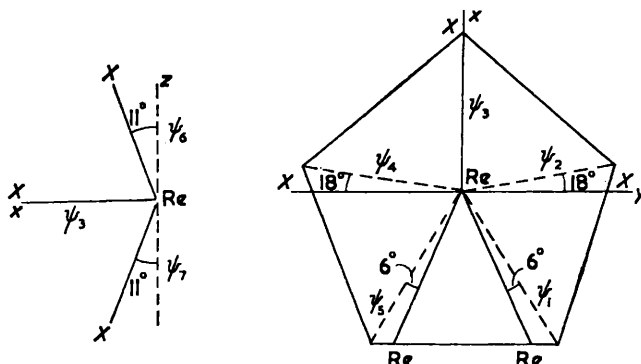
¹⁰ M. Elder and B. R. Penfold, *Nature*, 1965, **205**, 276.

¹¹ F. A. Cotton and J. T. Mague, *Inorg. Chem.*, 1964, **3**, 1402.

¹² F. A. Cotton and T. E. Haas, *Inorg. Chem.*, 1964, **3**, 10.

¹³ B. R. Penfold and W. T. Robinson, unpublished results.

The σ -bond molecular-orbital description considers the local symmetry around each rhenium as C_{2v} , and the seven bonds transform as the reducible representation $\Gamma_\sigma = 4A_1 + B_1 + 2B_2$. The orbitals of the metal that transform as the irreducible components of Γ_σ are: $A_1: p_x, d_{z^2}, s, d_{x^2-y^2}$; $B_1: p_z, d_{xz}$; $B_2: p_x, d_{xy}$. The σ -bonds are made up of two Re-Re bonds, $\Gamma_{\sigma}^{\text{Re-Re}} = A_1 + B_2$, and five Re-Cl bonds, $\Gamma_{\sigma}^{\text{Re-Cl}} = 3A_1 + B_1 + B_2$. From a consideration of the disposition of the orbitals listed above, relative



Continuous lines represent lines of closest approach between bonded atoms, and broken lines are directions of pentagonal bipyramid hybrids

to these bonds, we have selected the following sets: Re-Re bonds $A_1: s$; $B_2: d_{xy}$; Re-Cl bonds $A_1: p_x, d_{z^2}, d_{x^2-y^2}$; $B_1: p_z$; $B_2: p_y$. Molecular orbitals of the ligands, which transform as the above irreducible representations, can easily be determined by use of group theoretical methods.¹⁴

This leaves two unused atomic orbitals on each metal, *viz.*, d_{yz} , which does not appear in the above, and d_{zz} , which was not used. The same two orbitals are unused in the pentagonal bipyramid hybrid σ -bonding. The total of six atomic orbitals can be combined by the LCAO-MO approach, to give six π -molecular orbitals, three bonding ($A_1' + E'$) and three antibonding ($A_2' + E'$) in the point group symmetry D_{3h} .¹⁵

The complete structure $\text{Re}_3\text{Cl}_{12}^{3-}$ has therefore a possible total of eighteen σ - and three π -bonding orbitals. If we consider that each terminal halogen donates two electrons, and each bridging halogen donates four, this will leave three σ - and three π -bonding orbitals to accommodate the d -electrons of the metal atoms. Each rhenium atom in the anion has a formal charge of $+3$ and hence will have the d^4 configuration. The total of twelve d -electrons will therefore be successfully accommodated in the remaining bonding molecular orbitals.

This description accounts for the short metal-metal bond (0.3 \AA shorter than in rhenium metal) in terms of one σ - and one π -bond per Re-Re bond. In addition, the bonding scheme accounts for the observed diamagnetism of the tervalent anions. It would also account for the one unpaired electron per triangle found in the neutral quadrivalent $\text{Re}_3\text{Cl}_{12}$.¹⁶ There are here only three electrons to distribute among the A_1' and E' π -molecular orbitals.

It is clear that the bonding in the $\text{Re}_3\text{X}_{11}^{2-}$ anion is basically the same as for $\text{Re}_3\text{Cl}_{12}^{3-}$ the only difference being that one σ -orbital on one rhenium atom (centrifugally directed from the triangle) is vacant. However, comment is necessary on the observation that the two Re-Re bonds involving the halogen-deficient metal are significantly shorter than the other one.

The orbital on the halogen-deficient rhenium atom most likely to be affected by the

¹⁴ C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, 1962.

¹⁵ F. A. Cotton, "Chemical Applications of Group Theory," Interscience, New York, 1963.

¹⁶ R. Colton and R. L. Martin, *Nature*, 1965, **205**, 239.

loss of the terminal-in-plane halogen is the p_x . This orbital (in C_{2v} symmetry) transforms as the A_1 representation and may be considered to form a hybrid with, say, the $s(A_1)$ orbital of the same rhenium atom. The sp -hybrid pointing into the triangle will be expected to give greater overlap than a simple s -orbital in the metal-metal σ -bonding, leading to a shortening of the two bonds to the halogen-deficient metal atom. This process would be assisted by the increased positive charge developed on this atom.

This mixing of the p_x and s -orbitals is not ruled out even for $\text{Re}_3\text{Cl}_{12}^{3-}$. However, whereas it may give stronger bonding in an already tightly bound metal triangle it would not necessarily, by replacing a p_x orbital with an sp -hybrid, give much improvement for the terminal-in-plane Re-Cl bond. Any advantage is in fact apparently lost since, for steric reasons, these Re-Cl bonds are unusually long.

This explanation offered for the shortening of Re-Re bonds in $\text{Re}_3\text{X}_{11}^{2-}$ leads naturally to an enquiry into the result of removing further in-plane terminal halogen atoms from the trimeric system. No dimensions are yet available for any $\text{Re}_3\text{X}_{10}^-$ ion, and Re_3Cl_9 ,¹¹ with its strong intermolecular interactions possesses, as expected, the same size Re_3 triangle as in $\text{Re}_3\text{Cl}_{12}^{3-}$. The Re_3Br_9 entity in $(\text{QnH})_2\text{Re}_4\text{Br}_{15}^6$, however, apparently exists in comparative isolation in the crystal and therefore should reveal whether Re-Re bond shortening is cumulative. (There will, of course, be no charge effect in the symmetrical Re_3Br_9 to contribute to such shortening.) In fact, the mean Re-Re length of 2.465 Å is not significantly shorter than any of the "long" bonds in species so far examined, but neither is it significantly longer than 2.45 Å, the mean length in both $\text{Re}_3\text{X}_{11}^{2-}$ ¹⁰ anions. The evidence then is that in $\text{Re}_3\text{X}_{11}^{2-}$ the limit to the reduction in overall size of the Re_3 triangle has been reached. Clearly, a structure analysis of a salt of $\text{Re}_3\text{Br}_{10}^-$ is much to be desired. The detailed dimensions of $\text{Re}_3\text{Br}_{12}^{3-}$ would also be highly relevant, and a structure analysis of $\text{Cs}_3\text{Re}_3\text{Br}_{12}$,¹⁰ at present in progress in this laboratory, should provide these.

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