Metal–Metal Bonding in [Re₂X₈]²⁻ Ions and Other Metal Atom Clusters[1]

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The metal–metal bonding in the $[Re_2X_8]^{2-}$ ions is treated by a simple MO method similar to that previously used for other metal atom cluster compounds. A quadruple bond between the rhenium atoms is proposed and it is shown that this accounts for the eclipsed rotomeric configuration. The assignment of the absorption spectrum of $[Re_2Cl_8]^{2-}$ species is discussed. Finally, the consistency of observed bond lengths with the calculated bond orders for all of the known halo metal atom cluster compounds is demonstrated.

Introduction

In the two preceding papers,[2,3] the preparation,[2] constitution,[2] and structure[3] of $[Re_2X_8]^{2-}$ compounds have been discussed. With this information available, it is of interest to consider the electronic structure of a $[Re_2X_8]^{2-}$ ion, particularly the Re to Re bonding, and also to consider possible relationships between the structure and bonding in such a binuclear metal atom cluster (the simplest type in principle) and the structures and metal–metal bonding in other known metal atom cluster compounds.

Treatment of Bonding

The metal–metal bonding in the $[Re_2X_8]^{2-}$ ions, which is clearly very strong since the Re–Re distance[3] is extremely short, 2.24 Å., can be treated in a first approximation by a molecular orbital method similar to that used recently for other metal atom clusters.[4,5] It was previously observed that, for the $[Nb_6X_{12}]^{2+}$, $[Ta_6X_{12}]^{2+}$, $[Mo_6X_8]^{4+}$, and Re_3Cl_9 metal atom cluster systems, the structures could be considered to be built up of square MX_4 units with some (or all) of the X atoms being shared between two or more such units. The $[Re_2X_8]^{2-}$ species fit very well into this scheme. They stand at the extreme where there is no sharing of X groups, since they consist simply of two parallel ReX_4 units connected by a Re to Re bond; there is some distortion from planarity in order to reduce $X \cdots X$ repulsions. The fact that the molecular symmetry is D_{4h} rather than D_{4d}, that is, that the two ReX_4 halves are in an eclipsed rather than a staggered rotomeric relationship,[3] is of the highest importance.

As before,[4] we set aside the $d_{x^2-y^2}$, p_x, p_y, and s orbitals of the valence shell of each rhenium atom for use in σ-bonding to the atoms X; we are then left with the d_{z^2} and p_z orbitals, which are of σ symmetry relative to the Re–Re line, the d_{xz} and d_{yz} orbitals, which, analogously, have π symmetry, and the d_{xy} orbital, which has δ symmetry. A σ-bond between the rhenium atoms

can be formed by overlap of σ orbitals on each rhenium atom. Presumably the atomic orbitals so used are d_{z^2}–p_z hybrids, but in carrying out overlap calculations only pure d_{z^2} orbitals have been used. A pair of π bonds can be formed by overlap of the two sets of π atomic orbitals. Finally, a δ bond can be formed by overlap of the δ atomic orbitals. The σ, π, and δ overlaps were computed and orbital energies estimated in the manner previously described.[4–6] The results are presented in Figure 1. Since there are eight electrons to occupy these MO's, the ground state configuration will be $\sigma^2\pi^4\delta^2$. Thus, a closed shell electronic structure is obtained. This is in agreement with the observed diamagnetism[2] of the $[Re_2Cl_8]^{2-}$ ion. Furthermore, since there are four electron pairs occupying bonding orbitals, by the usual MO definition of bond order, the Re to Re bond is a quadruple bond.

Relation of Structure to Bonding

Although it is evidently the weakest of the Re to Re bonds, the δ bond is of great importance. The σ bond and the pair of π bonds have strengths which are independent of the angle of internal rotation between the two ReX_4 units, but the δ bond is quite sensitive to this angle. The experimental observation of an eclipsed configuration would seem, at face value, surprising, since by means of a rotation through 45° to give a staggered configuration, as in ethane and its derivatives, the potential energy of the system would presumably be lowered. The presence of the δ bond provides the explanation for the occurrence of the the eclipsed configuration. In the staggered configuration the overlap of the δ atomic orbitals would be precisely zero and the δ bond therefore nonexistent. This will be true even in more thorough treatments because it follows from the nature of δ symmetry, irrespective of the particular form of the δ orbitals.

In view of the existing uncertainty as to the origin of barriers to internal rotation in ethane and its deriva-

(1) Supported by the U. S. Atomic Energy Commission.
(2) F. A. Cotton, N. F. Curtis, B. F. G. Johnson, and W. R. Robinson, *Inorg. Chem.*, **4**, 326 (1965).
(3) F. A. Cotton and C. B. Harris, *ibid.*, **4**, 330 (1965).
(4) F. A. Cotton and T. E. Haas, *ibid.*, **3**, 10 (1964). There is a typographical error in Figure 3 of this paper such that the lower one of the levels labeled T_{2g} (*xz, yz*) should be labeled T_{1g} (*xz, yz*).
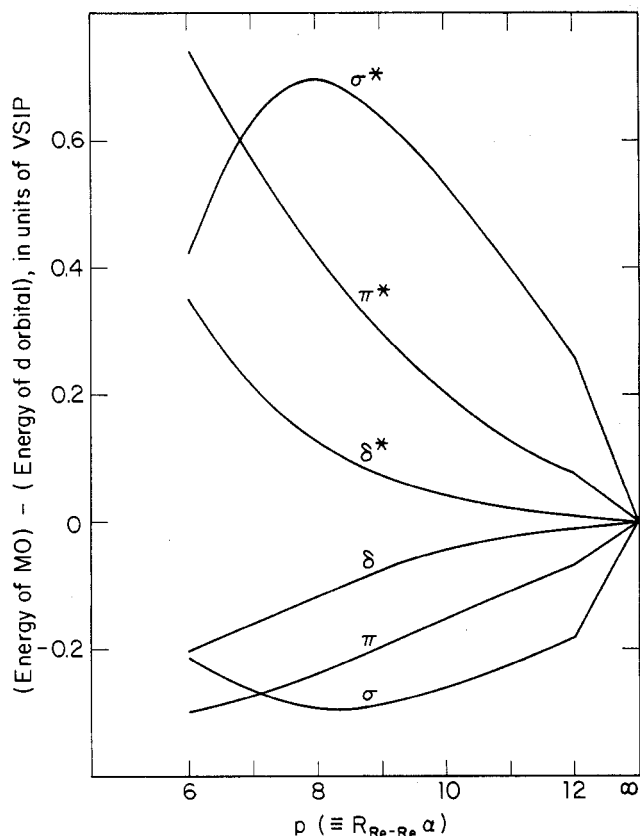(5) F. A. Cotton, *ibid.*, **3**, 1217 (1964).

(6) One of the approximations made in this type of treatment is to ignore the splittings between the σ, π, and δ d orbitals, which should be 2000–6000 cm.⁻¹ according to the calculations of Gray and Ballhausen.[7] Inclusion of these splittings would mean that instead of a common origin for all molecular orbitals there would be three separate origins, the distance between the highest and lowest being ~7000 cm.⁻¹. This spread would correspond to ~0.07 of the energy units used in Figure 1 and it is obvious that its inclusion will not change the order of levels nor will it alter the relative magnitudes of the separations between them to an extent which would be significant in the present discussion.
(7) H. B. Gray and C. J. Ballhausen, *J. Am. Chem. Soc.*, **85**, 260 (1963).

Figure 1.—An energy level diagram for the metal–metal bonding in $[\text{Re}_2\text{X}_8]^{2-}$ species.

Figure 2.—A plot of metal–metal distances *vs.* calculated bond orders for halo metal atom cluster systems. From upper left to lower right, circles represent $[\text{Re}_2\text{X}_8]^{2-}$, Re_3X_9, $\text{Mo}_6\text{X}_8^{4+}$, and the $[\text{M}_6\text{X}_{12}]^{2+}$ (M = Nb, Ta) systems.

tives,[8] an estimate of the energy differences between the staggered and eclipsed configurations of a non-δ-bonded $[\text{Re}_2\text{X}_8]^{2-}$ cannot be made in any *a priori* way. However, it seems safe to say that the fourfold barrier here would not be any greater than the threefold barrier[9] in C_2Cl_6, which is $\geqslant 7$ kcal./mole. Alternatively, if one chooses to attribute the energy difference solely to differences in $\text{Cl}\cdots\text{Cl}$ repulsions in the two configurations, a barrier of about this same magnitude can be calculated.[9] It is not at all unreasonable to believe that the energy of the δ bond is in excess of this small value, which is all that is required to stabilize the eclipsed configuration. It will be shown below that the δ bond energy is in fact very likely to be greatly in excess of this critical value.

It may also be noted here that the importance of the δ bond in stabilizing the staggered configuration of $[\text{Re}_2\text{X}_8]^{2-}$ provides an indirect argument for this formula as opposed to the formula[2] $[\text{Re}_2\text{X}_8\text{H}_2]^{2-}$. In $[\text{Re}_2\text{X}_8\text{H}_2]^{2-}$, one electron from each Re would be used to bond the hydrogen atoms, presumably one hydrogen atom on each end of the molecule, using d_{z^2}–p_z hybrid orbitals. These electrons would then be unavailable for δ bonding and the $[\text{Re}_2\text{X}_8\text{H}_2]^{2-}$ ion should be staggered.

Spectra of $[\text{Re}_2\text{X}_8]^{2-}$ Species

The visible spectra of the $[\text{Re}_2\text{Cl}_8]^{2-}$ and $[\text{Re}_2\text{Br}_8]^{2-}$ ions have been reported,[2] but only for the former are

(8) E. B. Wilson, Jr., *Advan. Chem. Phys.*, **2**, 367 (1959).
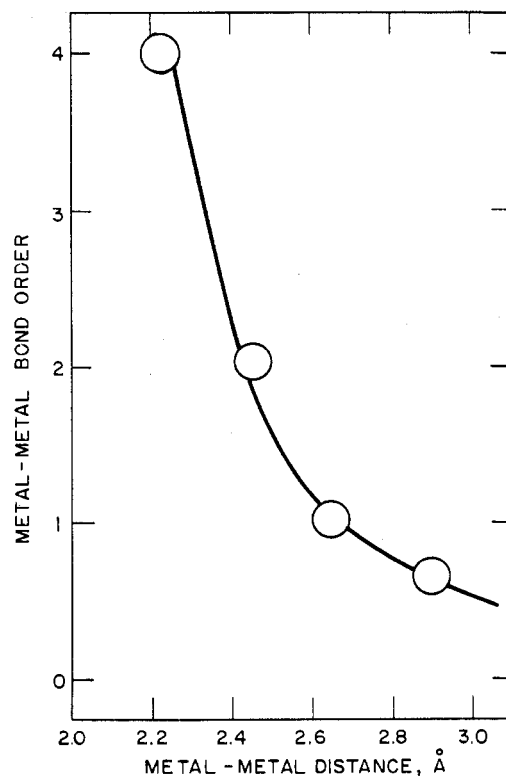(9) E. A. Mason and M. M. Kreevoy, *J. Am. Chem. Soc.*, **77**, 5808 (1955).

the data fairly complete. Both species have a band around 14,000 cm.$^{-1}$ with an oscillator strength of ~ 0.03. In addition, the $[\text{Re}_2\text{Cl}_8]^{2-}$ ion has strong bands at $\sim 32,000$ and $\sim 40,000$ cm.$^{-1}$ with oscillator strengths of ~ 0.4 and ~ 0.7, respectively. In order to obtain some measure of the strength of the δ bond, it would be useful to determine whether any of these bands can be assigned to the δ–δ^* transition. For the 14,000 cm.$^{-1}$ band this assignment can be definitely ruled out. The δ–δ^* transition is an allowed one, of the type Mulliken calls an N $\rightarrow$ V transition and for which he has described a simple method[10] of computing the oscillator strength. Such a calculation leads to the result that the oscillator strength must be close to unity, whereas the experimental value is only about 10^{-2}. Since the calculation was performed so as to take into account the effect of overlap between the d_{xy} orbitals and the π electrons of the X atoms, the calculated value is not subject to any corrections or adjustments which could possibly lower it by a factor of 10^{-2}. The δ–δ^* assignment is thereby eliminated for the 14,000 cm.$^{-1}$ bands.

The following assignment is suggested. Denoting the nonbonding, empty d_{z^2}–p_z orbitals of σ symmetry on each Re as σ_n, the transition can be denoted $\delta \rightarrow \sigma_\text{n}$. These σ_n orbitals should be grouped into an a_{1g} combination, $\sigma_\text{n} + \sigma_\text{n}'$, and an a_{2u} combination, $\sigma_\text{n} - \sigma_\text{n}'$; the δ orbital has b_{2g} symmetry. Neither a $b_{2g} \rightarrow a_{1g}$ nor a $b_{2g} \rightarrow a_{2u}$ transition is electric-dipole-allowed. The observed intensity which is only 10^{-2} times

(10) R. S. Mulliken and C. A. Rieke, *Rept. Progr. Phys.*, **8**, 240 (1941).

that for an allowed transition, can probably be attributed mainly to vibronic coupling and/or vibronically induced intensity borrowing from the strong absorptions in the ultraviolet.

In connection with this proposed assignment, it is interesting to compare the $[Re_2X_8]^{2-}$ species with the $[Re(RCOO)_2X]_2$ molecules recently reported by Taha and Wilkinson.[11] For the latter, a RCOO-bridged structure, analogous to the structure of the Cu(II) alkanoate complexes, has been proposed.[11] While it is true, as stated by Taha and Wilkinson, that the diamagnetism of these compounds does not *necessarily* demonstrate that there is Re to Re bonding, we believe that strong Re to Re bonding probably occurs.[12] If it does, the $[Re(RCOO)_2X]_2$ compounds are isoelectronic with the $[Re_2X_8]^{2-}$ species, *except* that the σ_n orbitals are here used in bonding the X atoms. Therefore there should be no $\delta \rightarrow \sigma_n$ absorption band, and, in fact, these compounds are yellow to orange, which shows that they do not have absorption bands at the red end of the visible region.

On the basis of the above assignment of the visible absorption bands of $[Re_2X_8]^{2-}$ species, a rough estimate can be made of the strength of the δ bond. Using Figure 1, in which the energy of the σ_n orbitals would be zero, the δ orbital can be placed at $\sim -15,000$ cm.$^{-1}$ and the energy of a two-electron δ bond therefore estimated to be 30,000 cm.$^{-1}$, or about 3.7 e.v.

Since the two bands in the near-ultraviolet have oscillator strengths approaching unity, either of these could be due to the $\delta \rightarrow \delta^*$ transition, the other then being most likely due to a Cl→Re charge-transfer band. From a δ–δ^* separation of 32,000–40,000 cm.$^{-1}$, one would estimate the strength of the two-electron δ bond, using Figure 1, to be 32,000–40,000 cm.$^{-1}$ or 4–5 e.v. Thus from the preceding discussion of the weak, visible band and the above assignment of the $\delta \rightarrow \delta^*$ band to the near-ultraviolet, we estimate, consistently, that the δ bond has a strength in the neighborhood of 4 e.v.

This estimate is, of course, of a very tentative nature and could be out by a factor of perhaps 2. However, even if it is lowered by that much it is consistent with the requirement that the δ bond be strong enough to hold the molecule in the eclipsed configuration. The chief reasons for considering the estimate to be a very crude one are (1) neglect of d_{z^2}–p_z hybridization in the σ_n orbitals, and (2) neglect of the d-orbital splittings caused by the chlorine atoms.

The relative simplicity of the $[Re_2X_8]^{2-}$ systems, com-

pared to other metal atom cluster compounds, and the encouraging results already obtained[7] for the still simpler MX_4 systems strongly suggest that more complete LCAO–MO calculations for $[Re_2X_8]^{2-}$ ions would be useful and might rectify the above shortcomings. Such calculations are being carried out, along with more detailed studies of the spectra, and further discussion of the spectra and bonding will therefore be deferred until a later time.

Relation of Bond Orders to Bond Lengths in Metal Atom Cluster Compounds

The various metal atom cluster compounds which have now been investigated cover a very wide range of metal-to-metal distances, and there appears to be an excellent correlation between metal-to-metal distances and bond orders, as the latter are obtained from the molecular orbital calculations.[4] Thus, in the $[Nb_6X_{12}]^{2+}$ and $[Ta_6Cl_{12}]^{2+}$ clusters, there are 16 bonding electrons per 12 nearest neighbor pairs of metal atoms, making the mean bond order $\sim^2/_3$; the distances are ~2.9 Å. In $[Mo_6Cl_8]^{4+}$, there are 24 bonding electrons per 12 shortest metal–metal distances, making the bond orders ~1.0; the distance is ~2.65 Å. In the Re_3Cl_9 clusters, there are 12 bonding electrons per 3 metal–metal pairs, making the bond order ~2.0; the distance is 2.48 Å. Finally, in $[Re_2Cl_8]^{2-}$, where we have estimated (*vide supra*) that the Re–Re bond is quadruple, the bond distance is only 2.24 Å.

For bonds of various orders between a given pair of atoms, it is well known that a plot of bond orders *vs.* bond lengths gives a smooth curve which is concave upward. Since the inherent size differences between the various atoms with which we are here concerned, *viz.*, Re, Ta, Mo, Nb, should not be large (<0.1 Å.) compared to the great range of distances (~0.7 Å.), such a curve should be given by the various bond orders and bond lengths cited above if the bond orders obtained from our MO calculations are really meaningful. Such a plot is shown in Figure 2, and it can be seen that a curve of the proper shape (approaching the bond length axis asymptotically as bond order goes to zero) does fit the points. Thus, the simple MO treatments[13] seem to produce realistic and internally consistent results, and the curve can perhaps be taken as a nomograph for estimating bond orders from bond lengths (and *vice versa*) in other metal atom cluster compounds, at least those not too dissimilar to the ones used in constructing it.

(11) F. Taha and G. Wilkinson, *J. Chem. Soc.*, 5406 (1963).
(12) The ready interconvertibility² of the $[Re(RCO_2)_2Cl]_2$ and $[ReCl_8]^{2-}$ species supports this.

(13) Acronyms for this method might be CHEAT (Cotton–Haas Easy Approximate Treatment) or CHARM (Cotton–Haas Anything-but Rigorous Method), depending on one's tolerance for the sort of ruthless approximation which has played a long and prominent, if not always honored, role in chemical theory.