

NYHOLM LECTURE*

Synergic Interplay of Experiment and Theory in Studying Metal–Metal Bonds of Various Orders

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1 Introduction

Chemistry, to my mind, is the most beautifully balanced of all the sciences with respect to the roles of theory and experiment, or, in different terms, with respect to there being both abstract and concrete aspects to the phenomena we deal with. We can predict enough to make the subject intellectually satisfying and yet there is also much scope (indeed absolute necessity) for experimental observation. There is also a soul-satisfying aesthetic side to chemistry, as well as an enormous practical side, but I shall not digress in those directions.

My lecture will focus on two aspects of the subject of multiple bonds between metal atoms¹ in which the constructive interplay between theory and experiment has been lively and fruitful. At one point a theoretical result would give the experimental programme a nudge in the right direction while at another point an experimental result would elicit an appropriate theoretical effort.

I shall be discussing, for the most part, triple and quadruple bonds between pairs of metal atoms, so I shall begin with the basic characteristics of these. They are formed primarily by the overlap of the *d* orbitals on the two metal atoms, as shown in Figure 1. How many of these five possible non-zero overlaps play a role, and what role they play in binding the metal atoms together depends on the number of electrons available and the number and types of ligands attached to the metal atoms.

The simplest case is that of Mo₂ where there are no ligands and six electron pairs. In this case the overlap of two *s* orbitals must also be considered and we obtain a total of six bonding two-centre MO's, all of which are occupied. A sextuple bond is thus formed, consisting of two non-degenerate σ , two degenerate π , and two degenerate δ components. As a result of this highly multiple bonding Mo₂ has the shortest Mo—Mo distance known,² 193 pm, which may be compared

* Delivered at University College, London, October 14, 1982 and also at Cambridge, Leicester, Edinburgh, Liverpool, and Bristol Universities and University College, Swansea in October, 1982.

¹ F. A. Cotton and R. A. Walton, 'Multiple Bonds Between Metal Atoms,' John Wiley and Sons, New York, 1982.

² Y. M. Efremov, A. N. Samoilova, V. B. Kozhukhovskiy, and L. V. Gurvich, *J. Mol. Spectrosc.*, 1978, 73, 430.

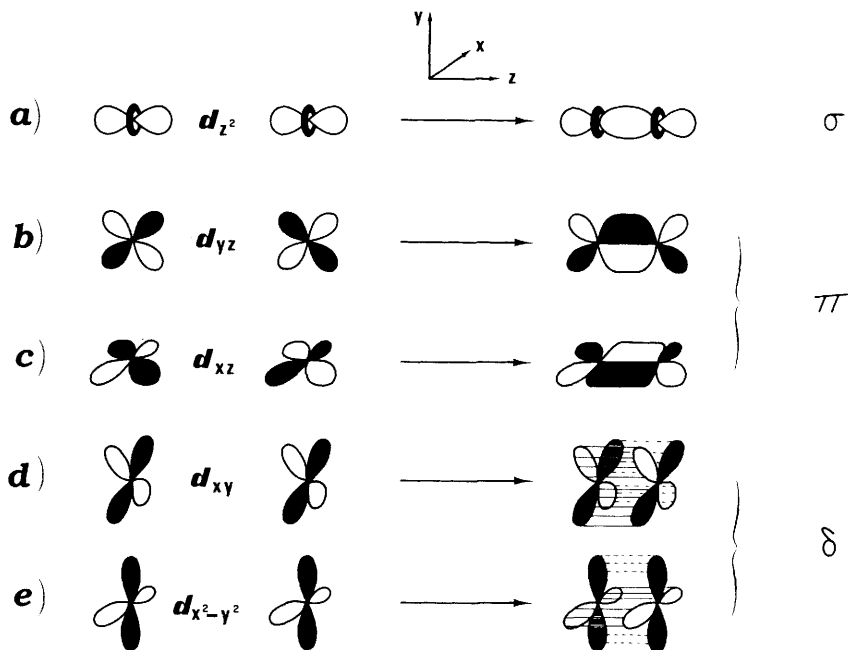


Figure 1 The positive (bonding) σ , π , and δ overlaps of d orbitals on a pair of metal atoms. There is a related set of negative (antibonding) overlaps (Reproduced by permission from *Advanced Inorganic Chemistry*, 4th Edn., by F. A. Cotton and G. Wilkinson, John Wiley & Sons, New York, 1980)

to that in the metal, 276 pm. Calculations by either the SCF- $X\alpha$ -SW or Hartree-Fock-CI methods³ support (but considerably amplify) this simple bonding picture. In the case of Cr_2 a similar qualitative bonding picture should obtain and in fact the internuclear distance⁴ in this molecule has the astonishing value of 168 pm [cf. 255 pm in Cr(s)]. In this case, however, quantitative theory has yet to catch up with experiment.⁵

When some electrons are removed from Mo_2 and ligands are added, several changes occur in the electronic structure. First, with increase in the oxidation number the role of the s orbitals becomes less important (actually, negligible for +2 and +3); second, there are fewer electrons; third, the ligands make some demand for the d orbitals to form metal–ligand bonds. In practice, two principal classes of compounds result, Figure 2: those based on a trigonal structure (a) and those based on a tetragonal structure (b).

³ B. E. Bursten, F. A. Cotton, and M. B. Hall, *J. Am. Chem. Soc.*, 1980, **102**, 6348; P. M. Atha, I. H. Hillier, and M. F. Guest, *Chem. Phys. Lett.*, 1980, **75**, 84.

⁴ D. L. Michalopoulos, M. E. Geusic, S. G. Hansen, D. E. Powers, and R. E. Smalley, *J. Phys. Chem.*, 1982, **86**, 3914.

⁵ M. M. Goodgame and W. A. Goddard, *J. Phys. Chem.*, 1981, **85**, 215.

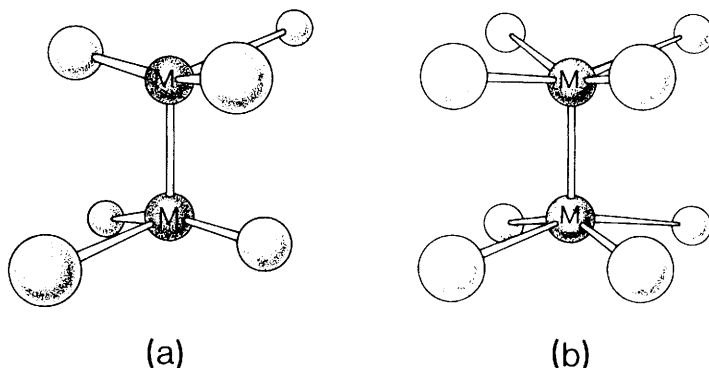


Figure 2 The most common general structures for dinuclear compounds with $M-M$ multiple bonds: (a) trigonal, D_{3d} ; (b) tetragonal, D_{4h}

In compounds with the trigonal structure we are usually dealing with M^{3+} atoms and the $M-M$ bond order is 3. All of the δ orbitals of the M_2 unit become involved in the $M-L$ bonding and we are left only with the σ and π overlaps for $M-M$ bonding. Thus, we expect, on the simple d orbital overlap picture, to have a σ bond and a π bond in which six electrons supplied by the metal atoms are used. Quantitative calculations by the SCF- $X\alpha$ -SW method verify this and photoelectron spectra confirm the validity of the calculations.⁶

However, it is with the molecules or ions of tetragonal symmetry that we shall be chiefly concerned in this lecture. In this case, one of the two sets of δ orbitals becomes primarily engaged in metal-ligand bonding, thus leaving σ , two π , and the other δ orbital available for $M-M$ bonding. On the basis of simple overlap considerations, we expect the σ bonding orbital to be very stable, the π bonding orbitals to be moderately stable and the δ orbital to be the least strongly bonding. In the event the M_2^{n+} unit concerned has a total of eight electrons, we have the qualitative picture shown in Figure 3.

This simple d -orbital overlap picture does, in fact, embody the essence of the $M-M$ bonding. If we look at the results of both $X\alpha$ and Hartree-Fock calculations we see qualitative verification. The δ , π , and σ orbitals do in fact lie highest, in that order, and have largely ($>70\%$) d character.⁷

Two final points are to be noted in this introduction. First, the δ and δ^* orbitals are close in energy and the $\delta \rightarrow \delta^*$ transition of an electron is orbitally allowed. This means that it is characteristic of all quadruply bonded systems to have such a transition in the visible region of the spectrum. Moreover, in nearly all cases, this allowed transition displays a progression in that totally symmetric vibrational frequency that is essentially ν_{MM} . A typical example is provided by

⁶ Ref. 1, pages 382–389, 415–417.

⁷ Ref. 1, pages 356–364.

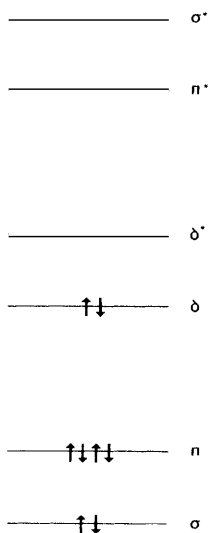


Figure 3 A qualitative picture of the M–M bonding orbitals for a tetragonal M_2X_8 unit having eight electrons available for M–M bonding

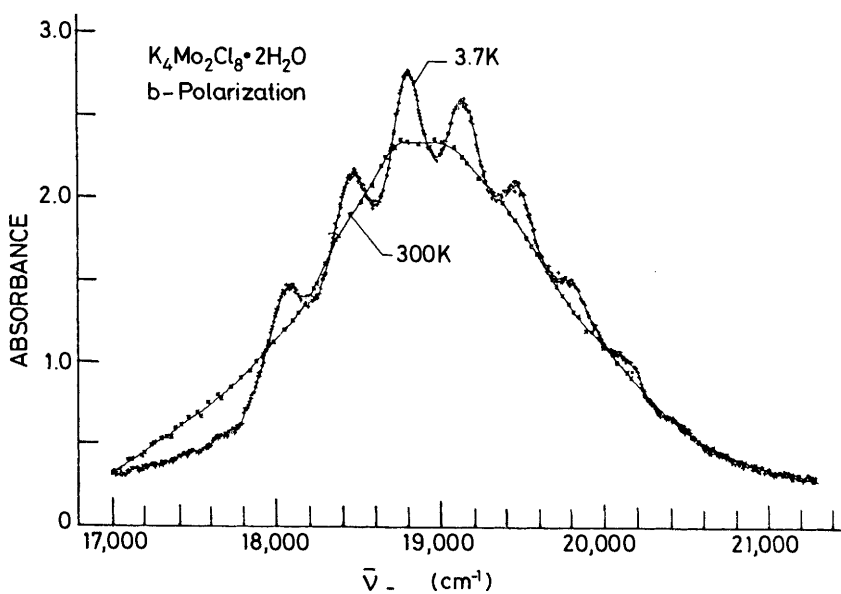


Figure 4 The $\delta \rightarrow \delta^*$ absorption band of the $[Mo_2Cl_8]^{4-}$ ion (Reproduced by permission from P. E. Fanwick, D. S. Martin, F. A. Cotton, and T. R. Webb, *Inorg. Chem.*, 1977, 16, 2103)

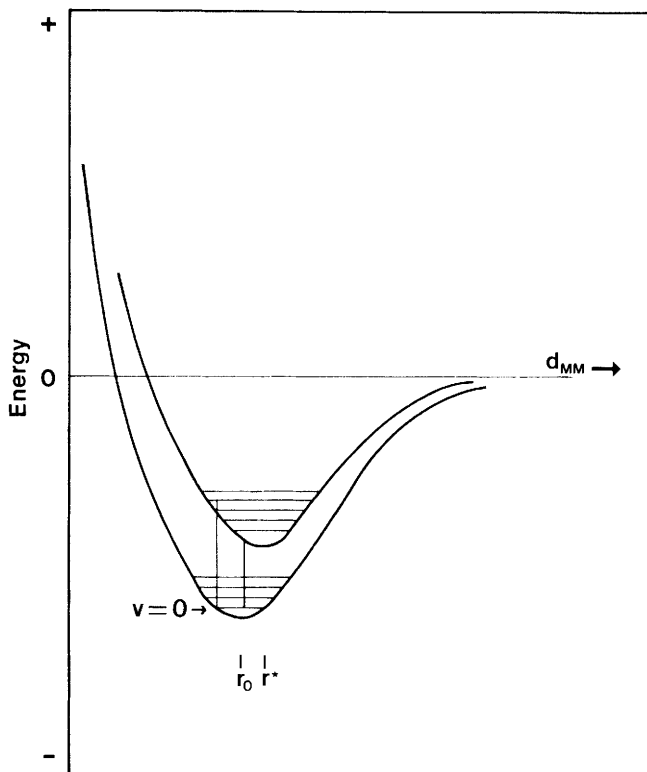


Figure 5 A schematic representation of the basis for the appearance of a progression in the ν_{MM} vibration in the $\delta \rightarrow \delta^*$ excited state

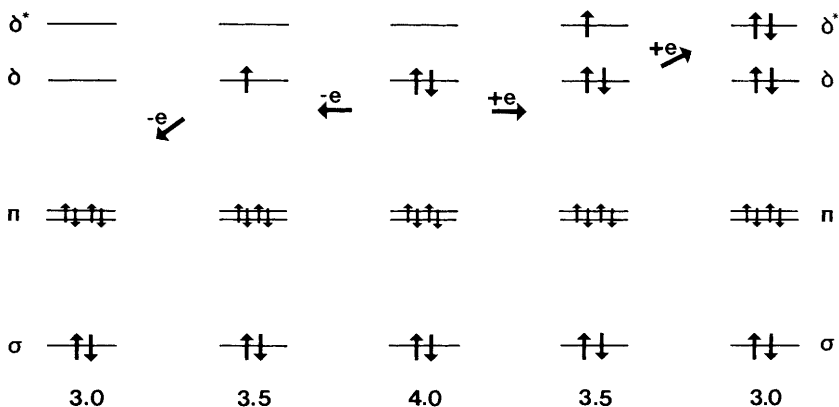
the $[\text{Mo}_2\text{Cl}_8]^{4-}$ ion, Figure 4. The reason for the appearance of such a progression is that the potential energy curve for the excited state is displaced along the d_{M-M} co-ordinate, and thus transitions from the zero-ith vibrational level of the electronic ground-state strike several of the upper vibrational levels of the electronic excited-state, as shown in Figure 5. We shall later make use of this phenomenon.

Finally, because of the fact that the δ orbital is only weakly bonding and the δ^* orbital is only weakly antibonding, a $\sigma^2\pi^4\delta^2$ quadruple bond is readily subjected to either electron loss or electron gain, as shown in Figure 6. Thus, an entire range of bond orders, 3.0, 3.5, 4.0, 3.5 and again 3.0 is accessible.

2 Bond Length versus Bond Order: Not Always What One Expects

It is one of the truisms of valence theory that the higher the bond order (other things being equal) the shorter the bond. Examples in support of this 'rule' are legion. There is, for example, the series from O_2^+ to O_2^{2-} in which there

Synergic Interplay of Experiment and Theory in Studying Metal–Metal Bonds



Bond Orders

Figure 6 A schematic representation of how changes in the occupation of the δ and δ^* orbitals change the M–M bond order

is a steady decrease of bond order as π^* electrons are added, and the bond length increases from 112 pm to 149 pm.

	O—O distance/pm	Bond Order
O_2^+	112	2.5
O_2	121	2.0
O_2^-	133	1.5
O_2^{2-}	149	1.0

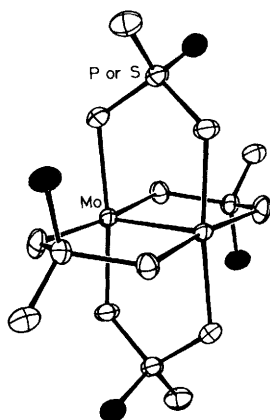


Figure 7 The essential structural features of the $[Mo_2(SO_4)_4]^{n-}$ or $[Mo_2(HPO_4)_4]^{n-}$ ions

Relatively early in the study of M—M multiple bonds there emerged what seemed to be an equally satisfactory example of the same phenomenon in the following series of ions,⁸ all of which are effectively isostructural (*cf.* Figure 7) in all other respects:

	Bond Length/pm	Electronic Configuration	Bond Order
$[\text{Mo}_2(\text{SO}_4)_4]^{4-}$	211.1(1)	$\sigma^2\pi^4\delta^2$	4.0
$[\text{Mo}_2(\text{SO}_4)_4]^{3-}$	216.7(1)	$\sigma^2\pi^4\delta$	3.5
$[\text{Mo}_2(\text{HPO}_4)_4]^{2-}$	222.3(2)	$\sigma^2\pi^4$	3.0

Two further examples^{9,10} from work in other laboratories are:

	Bond Length/pm	Electronic Configuration	Bond Order
Ru_2L_2^a	237.9(1)	$\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$	2.0
$[\text{Ru}_2\text{L}_2]^+$	226.7(3)	$\sigma^2\pi^4\delta^2\delta^{*2}\pi^*$	2.5
$[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2]$	238.6(1)	$\sigma^2\pi^4\delta^2\pi^{*4}\delta^{*2}$	1.0
$[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2]^+$	231.6(2)	$\sigma^2\pi^4\delta^2\pi^{*4}\delta^*$	1.5

^a L = C₂₂H₂₂N₄²⁻ a tetradentate macrocycle

Clearly, then, it was a simple matter to predict, confidently, that on oxidizing the $[\text{Tc}_2\text{Cl}_8]^{3-}$ ion with a configuration of $\sigma^2\pi^4\delta^2\delta^*$ to $[\text{Tc}_2\text{Cl}_8]^{2-}$ the bond length should decrease by 6—12 pm. The experimental results¹¹ are:

	Bond Length/pm	Bond Order	$\nu_{\text{Tc-Cl}}/\text{cm}^{-1}$
$[\text{Tc}_2\text{Cl}_8]^{3-}$	210.5(1); 211.7(2)	$\sigma^2\pi^4\delta^2\delta^*$	370
$[\text{Te}_2\text{Cl}_8]^{2-}$	215.1(1)	$\sigma^2\pi^4\delta^2$	307

There is no mistake in this tabulation: the species with the higher bond order has the longer bond. Moreover, this relationship is supported by the observed values of $\nu_{\text{Tc-Cl}}$. How do we explain this apparent contradiction of conventional wisdom?

The explanation is based on two observations: (1) The σ and π components of the quadruple bond are far more important in determining its total strength than the δ component; hence even a small percentage change in the σ and π bond strengths might be as important as a 50% change in the δ bond strength. (2) In all these comparisons there are changes in the extent of ionization of the metal atoms accompanying the changes in the number of δ or δ^* electrons; as the effective positive charge on the metal atoms increases, there will be some contraction in the d orbitals and this will reduce the overlap in all components of the bond, including the strong σ and π components.

⁸ A. Bino and F. A. Cotton, *Inorg. Chem.*, 1979, **18**, 3562, and earlier references therein cited.

⁹ L. F. Warren and V. L. Goedken, *J. Chem. Soc., Chem. Commun.*, 1978, 909.

¹⁰ J. J. Ziolkowski, M. Moszner, and T. Glowiak, *J. Chem. Soc., Chem. Commun.*, 1977, 760.

¹¹ F. A. Cotton, A. Davison, V. W. Day, M. F. Fredrich, C. Orvig, and R. Swanson, *Inorg. Chem.*, 1982, **21**, 1211.

Let us return now to the first series, the set of dimolybdenum compounds, in which the bond order decreases from 4.0 to 3.0. The formal state of ionization of the metal atoms also increases from +2 to +3. The increase in Mo–Mo bond length is the result of two factors, lower δ bond order and decreased σ and π overlaps, operating in the *same* direction. It is impossible, in the absence of some other source of information, to say how much of the total effect is due to each factor. Our earlier assumption that it could all be attributed to reduction in δ bond order was (pardonably, we hope) naive and unjustified.

The $[\text{Tc}_2\text{Cl}_8]^{3-}$ to $[\text{Tc}_2\text{Cl}_8]^{2-}$ transformation differs from the preceding example in that the δ bond order is *increasing* while the change in state of ionization is tending to *decrease* the strength of the σ and π components; the two factors are opposed in this case. The net increase of *ca.* 3.5 pm in the Tc–Tc bond length would then imply that in this case the latter factor is more effective than the former in determining the bond length.

If we look at other examples, we quickly see that there is no general rule as to which factor will predominate. In the Ru and Rh cases cited the two factors are opposed and each time the net effect shows the bond order change to be controlling. The rhodium example is not straightforward, however, because of near degeneracy of the δ^* and π^* orbitals and mixing of metal and ligand orbitals. In the Ru case, the bond order change is in the π bonding, which is much stronger than δ bonding and might thus have been expected to predominate.

In the case of the following series of rhenium compounds¹² we have data that further illustrate the subtlety of the problem:

	<i>Bond Length/pm</i>	<i>Electronic Configuration</i>	<i>Bond Order</i>
1. $\text{Re}_2\text{Cl}_6(\text{PEt}_3)_2$	222.2(3)	$\sigma^2\pi^4\delta^2$	4.0
2. $\text{Re}_2\text{Cl}_4(\text{PEt}_3)_4$	223.2(6)	$\sigma^2\pi^4\delta^2\delta^{*2}$	3.0
3. $\text{Re}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4$	224.1(1)	$\sigma^2\pi^4\delta^2\delta^{*2}$	3.0
4. $[\text{Re}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4]^+$	221.8(1)	$\sigma^2\pi^4\delta^2\delta^*$	3.5
5. $[\text{Re}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4]^{2+}$	221.5(2)	$\sigma^2\pi^4\delta^2$	4.0

Comparison of 2 and 3 indicates that differences of the order of 1 pm can arise from minor variations having nothing to do with changes in oxidation state or bond order. Several years ago, from a comparison of 1 and 2, it appeared that for the di-rhenium compounds the change from bond order 4 to 3 (which should increase the distance) accompanied by a decrease in ionization state of the metal atoms from +3 to +2 (which might decrease it) approximately offset each other. However, the change in composition, which could have a significant effect on internal repulsions, made this a less than ideal case.

We now have the results for compounds 3–5 in which composition is unchanged, and we also alter the electron configuration one step at a time. Here we see again (from the 5 to 4 comparison) an insensitivity of the Re–Re

¹² F. A. Cotton, K. R. Dunbar, L. R. Falvello, M. Tomas, and R. A. Walton, in course of publication.

distance to addition of the first δ^* electron. The addition of the second one, however, causes an increase of 2.3(1) pm, indicating that here the bond order effect is, by a slight amount, dominant.

In all the foregoing work, changes in bond order have been inextricably coupled with changes in the total number of electrons and, hence, with the charges on the metal atoms. It would obviously be desirable to have a way of changing the bond order without adding to or subtracting from the total electronic population, with the attendant charge effects.

There are, in fact, two ways in which the influence of δ bond order of M—M distance can be observed independently of charge effects. One depends on reduction of the δ bond order by internal rotation from the eclipsed towards the staggered conformation. The second depends on estimating bond lengths in electronically excited states.

A. Internal Rotation.—Let us consider an eclipsed M_2X_8 species. As the angle of internal rotation, χ , changes from 0° (eclipsed conformation) to 45° (fully staggered conformation) the δ - δ overlap changes from its maximum value to zero according to the function $\cos 2\chi$.¹³

Since $X \cdots X$ repulsive forces would lessen with increasing χ , since the δ bond strength need not be strictly proportional to overlap, and since bond length need not be strictly proportional to bond strength, a strictly linear relationship between d_{MM} and $\cos 2\chi$ cannot necessarily be expected, but one might expect a relationship approximating to this.

Of course, the biggest problem is that the observation of d_{MM} as χ is changed in an otherwise invariant species $X_4M \equiv MX_4$ is not experimentally possible. There is, however, a feasible experimental approach that provides nearly the same information. We examine the structures of several $M_2X_4(LL)_2$ molecules in which the steric properties of the bridging bidentate ligand, LL, serve to change the torsion angle while keeping M, X, and the ligating atoms of L invariant, or virtually so. $Mo_2Cl_4(dmpe)_2$, Figure 8, is an example.¹⁴ Thus far, for the Mo_2^{4+} unit, three suitable systems have been found and studied. The results are presented in Figure 9, where it is seen that there is an essentially linear experimental relationship between $d(Mo-Mo)$ and $\cos 2\chi$. The phosphine ligands differ somewhat in basicity (and one contains As and P rather than two P atoms) but control experiments suggest that these changes alone have little effect on $d(Mo-Mo)$. It is also known that in general $d(Mo-Mo)$ is not sensitive to a change from Cl to Br in $M_2X_8^{n-}$ species. The total change in Mo—Mo distance (extrapolated) as χ goes from 0° to 45° is 6.4 pm. This should probably be regarded only as a lower limit on the change resulting from loss of the δ bond since the bridging diphosphine ligands probably tend to hold the metal atoms together.

¹³ F. A. Cotton, P. E. Fanwick, J. W. Fitch, H. D. Glicksman, and R. A. Walton, *J. Am. Chem. Soc.*, 1979, **100**, 1752.

¹⁴ F. A. Cotton and G. L. Powell, *Inorg. Chem.*, in press.

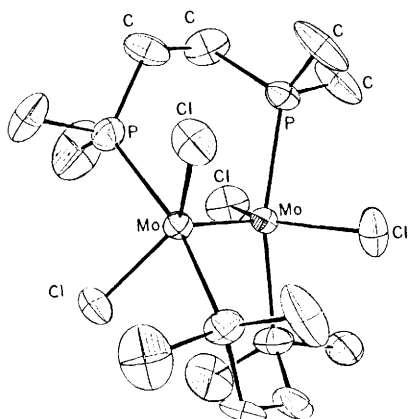


Figure 8 The structure of the $\text{Mo}_2\text{Cl}_4(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2$ molecule

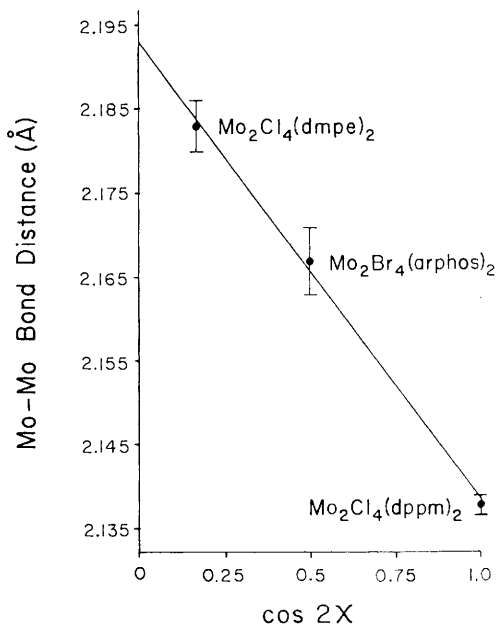


Figure 9 Mo–Mo bond distance vs. $\cos 2\chi$, where χ is the torsion angle. *dmpe* = $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$; *arphos* = $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{PPh}_2$; *dppm* = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$

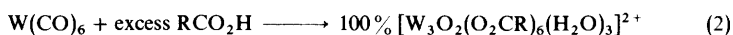
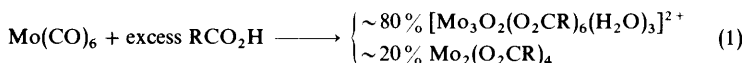
B. Electronic Excitation.—The excitation of an electron from the δ to the δ^* orbital has an effect formally equivalent to diminishing the δ bond order by one unit. For the ground state of the system the M—M bond length is known by direct X-ray crystallographic measurement. For the excited states the expected increase can be estimated from the Franck–Condon factors when a progression in ν_{M-M} is observed, as it usually is for the $\delta \rightarrow \delta^*$ transitions. Several such estimates have been made:¹⁵

$\text{Mo}_2(\text{O}_2\text{CMe})_4$	11(1) pm
$[\text{Mo}_2\text{Cl}_8]^{4-}$	11(1) pm
$[\text{Re}_2\text{Cl}_8]^{2-}$	7(1) pm
$[\text{Re}_2\text{Cl}_4(\text{PPr}_3)_4]^+$	6.5(5) pm

These magnitudes are consistent with the observations already discussed. However, the paucity of data of all kinds still leaves the subject in a quantitatively unsatisfactory state.

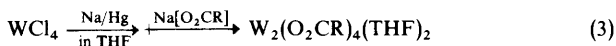
3 Why do Tungsten-to-tungsten Quadruple Bonds Differ so Greatly from those of Molybdenum?

From the initial discovery that $\text{Mo}(\text{CO})_6$ reacts with acetic acid and other carboxylic acids to give products of composition $\text{Mo}(\text{O}_2\text{CR})_2$ (and even before the true nature of these compounds was recognized) attempts to prepare homologous compounds of tungsten by similar methods have been unavailing. With respect to the reaction just mentioned, we now know that for both $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ the major product is the same, as shown in equations (1) and (2).^{16,17} The reaction with $\text{W}(\text{CO})_6$ simply fails to produce *any* W^{II} product.



The trinuclear species contain equilateral-triangular clusters with M—M single bonds and are quite interesting in their own right.

Gradually, over the past twenty years, methods have been found to prepare compounds with W—W quadruple bonds, and analogues of nearly all the principal types known for molybdenum have been made and studied. Almost always, the tungsten compounds are less stable and more reactive than their molybdenum analogues. The carboxylates themselves have been made by the following reactions: (3; R = CF_3 ,¹⁸ or Ph ¹⁹):



¹⁵ I am indebted to Professor P. E. Fanwick of the University of Kentucky for these estimates.

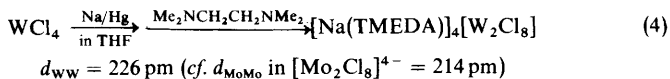
¹⁶ A. Bino, F. A. Cotton, Z. Dori, S. Koch, H. Küppers, M. Millar, and J. C. Sekutowski, *Inorg. Chem.*, 1978, 17, 3245.

¹⁷ A. Bino, F. A. Cotton, and Z. Dori, *J. Am. Chem. Soc.*, 1981, 103, 243.

¹⁸ A. P. Sattelberger, K. W. McLaughlin, and J. C. Huffman, *J. Am. Chem. Soc.*, 1981, 103, 2880.

¹⁹ F. A. Cotton and W. Wang, *Inorg. Chem.*, 1982, 21, 3859.

Recently, even a compound containing the $[\text{W}_2\text{Cl}_8]^{4-}$ ion has been isolated and structurally characterized (equation 4)²⁰



In contrast to the relative instability and inaccessibility of the quadruply bonded di-tungsten compounds, there is a great variety of triply bonded W_2X_6 compounds that are as easily made and as stable as their molybdenum analogues,²¹ e.g., $\text{W}_2(\text{NMe}_2)_6$.

Before searching for an explanation of these curious homologies and dishomologies, we may note that for both triple and quadruple bonds, the W–W distances are systematically about 10–12 pm greater than the Mo–Mo distances when molecules of the same stoichiometry are compared.

Our first step towards an explanation was the recognition that while the ordinary bond radii of Mo and W are approximately equal (with that of W actually being a few pm smaller!) the two atoms should behave quite differently at the extremely short internuclear distances found in the triple and quadruple bonds. This would be expected because of the markedly denser core of the W atom.²² At distances in the range of 205–235 pm core–core repulsions should be far more important between a pair of tungsten atoms than between a pair of molybdenum atoms. It is for this reason that for both triple and quadruple bonds, the W–W distances are 10–12 pm greater than Mo–Mo distances.

In the case of the triple bonds, where only σ and π overlaps contribute to the bonding, an increase of ca. 10 pm has only a minor effect on the strength or reactivity of the bond. This is because the magnitude of σ and π overlaps is not strongly distance-sensitive in the range we are dealing with. For the δ bond, however, the strength and the stability of the electrons might be expected to show considerable sensitivity to a 10 pm change in distance, when the qualitative character of the δ – δ overlap is considered. This qualitative idea has been tested quantitatively by SCF–X α –SW calculations and by photoelectron spectroscopy, as will now be explained.

With the aid of calculations we can assign the measured photoelectron spectra (PES) of $\text{Mo}_2\text{Cl}_4(\text{PH}_3)_4$ and its W analogue.²³ We chose these particular substances because they are the simplest type of compound formed by both Mo and W that are sufficiently stable and volatile to allow measurement of the PES. Figure 10 shows the HeI spectra of the Mo and W compounds. These spectra confirm our qualitative idea that while the electronic structures of quadruply bonded Mo_2^{4+} and W_2^{4+} compounds are overall very similar, there is a significant — indeed crucial — difference in the stability of the δ bonding

²⁰ F. A. Cotton, G. N. Mott, R. R. Schrock, and L. G. Sturgeooff, *J. Am. Chem. Soc.*, 1982, **104**, 6781.

²¹ M. H. Chisholm and F. A. Cotton, *Acc. Chem. Res.*, 1978, **11**, 356.

²² Ref. 1, page 350.

²³ F. A. Cotton, J. L. Hubbard, D. L. Lichtenberger, and I. Shim, *J. Am. Chem. Soc.*, 1982, **104**, 679.

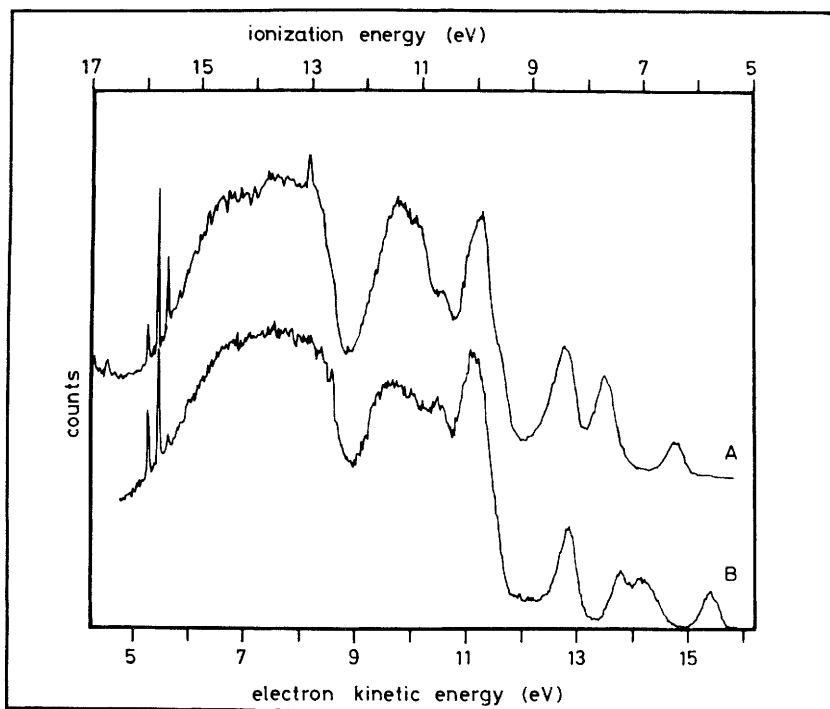
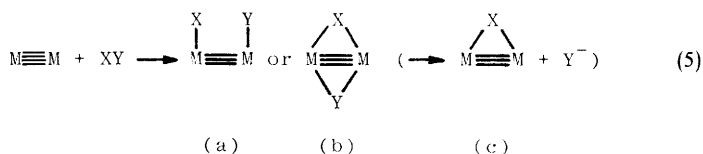


Figure 10 The HeI photoelectron spectra of $\text{Mo}_2\text{Cl}_4(\text{PMe}_3)_4$ (A) and $\text{W}_2\text{Cl}_4(\text{PMe}_3)_4$ (B) (Reproduced by permission from Ref. 23)

electrons. Armed with this result, we can now discuss and explain the chemical differences between the molybdenum and tungsten compounds.

In general, the W_2^{4+} compounds tend to be more reactive because of the higher energy of the electrons in the HOMO — the δ -bonding orbital. This could account for reactivity of many kinds being more rapid for the tungsten compounds. We shall examine one mode of reaction that seems to be especially important, oxidative addition, as represented schematically in equation (5).



Actually, a few oxidative addition reactions are known to occur with Mo_2^{4+} compounds, but they are favoured only under strenuous conditions and are generally reversible. Thus, the preparation of $[\text{Mo}_2\text{Cl}_8]^{4-}$ from $\text{Mo}_2(\text{O}_2\text{CMe})_4$

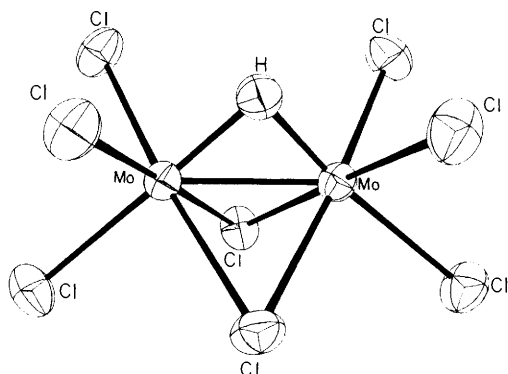


Figure 11 The structure of the $[\text{Mo}_2\text{Cl}_8\text{H}]^{3-}$ ion resulting from oxidative addition of HCl (or H^+) to $[\text{Mo}_2\text{Cl}_8]^{4-}$ at higher temperatures

is carried out in 12 M-HCl at about 0 °C. If the temperature is raised to about 60 °C one obtains instead the $[\text{Mo}_2\text{Cl}_8\text{H}]^{3-}$ ion,²⁴ which can be considered to arise by oxidative addition of HCl to $[\text{Mo}_2\text{Cl}_8]^{4-}$ followed by loss of Cl^- or simply by protonation of the δ bond [i.e., it is a product of type (c) in the above equation]. The structure of this hydrido-bridged anion is shown in Figure 11. This ion undergoes many of the same reactions as the $[\text{Mo}_2\text{Cl}_8]^{4-}$ ion because

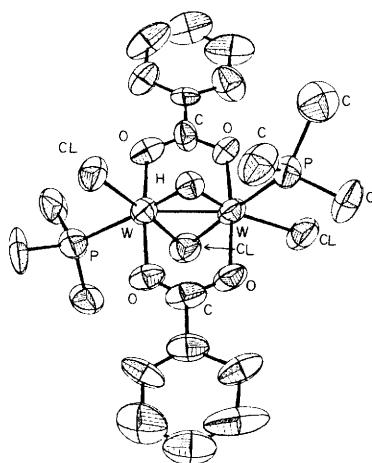
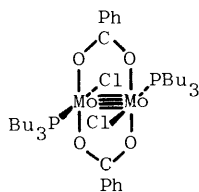


Figure 12 The structure of the $\text{W}_2\text{Cl}_2(\text{PBu}_3)_2(\text{O}_2\text{CPh})_2(\mu\text{-H})(\mu\text{-Cl})$ molecule

²⁴ A. Bino, B. E. Bursten, F. A. Cotton, and A. Fang, *Inorg. Chem.*, 1982, **21**, 3755, and earlier references therein cited.

reversal of the protonation or oxidative addition reaction readily occurs.²⁵ With tungsten compounds the oxidative addition occurs even under very mild acidic conditions and generally appears to continue through further irreversible steps leading to end products in higher oxidation states, such as the $[\text{W}_3\text{O}_2(\text{O}_2\text{CMe})_6(\text{H}_2\text{O})_3]^{2+}$ clusters obtained when $\text{W}(\text{CO})_6$ reacts with acetic acid. Direct proof for an initial oxidative addition has thus far been lacking.²⁶

Recently we were fortunate enough to find a system in which the product of oxidative addition can be intercepted and structurally characterized. Several years ago, San Filippo and co-workers demonstrated²⁷ that $\text{Mo}_2\text{X}_4(\text{PR}_3)_4$ compounds react with benzoic acid to afford $\text{Mo}_2\text{X}_2(\text{PR}_3)_2(\text{O}_2\text{CPh})_2$ species,



(1)

of the type shown in (1). On attempting the same reaction with $\text{W}_2\text{Cl}_4(\text{PBU}^n)_4$ we obtained instead the oxidative addition product resulting, presumably, from reaction of the initially formed $\text{W}_2\text{Cl}_2(\text{PBU}^n)_2(\text{O}_2\text{CPh})_2$ with the HCl generated.²⁸ The structure of this molecule is shown in Figure 12. The bridging hydrogen atom was found and refined (actually twice, since there are two independent molecules in the crystal), but lest there be those who doubt the reliability of such a result, the n.m.r. evidence summarized in Figure 13 unequivocally supports its presence.

To close, I should like to tell you of some recent observations by Malcolm Chisholm and his co-workers²⁹ that beautifully complement those just discussed. The proposition that $\text{W}-\text{W}$ quadruple bonds far more readily undergo oxidative addition than their $\text{Mo}-\text{Mo}$ analogues implies the following 'conjugate' proposition: $\text{Mo}-\text{Mo}$ triple bonds will far more readily undergo reductive elimination (to generate quadruple bonds) than their $\text{W}-\text{W}$ analogues. Chisholm has reported reactions (6)—(9) that fully support this proposition.

²⁵ J. San Filippo, Jr., H. J. Sniadoch, and R. L. Grayson, *Inorg. Chem.*, 1974, **13**, 2121.

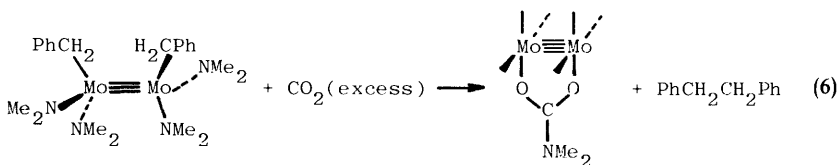
²⁶ Sattelberger and co-workers (ref. 18) have reported observations leading them to the tentative conclusion that reaction of $\text{W}_2(\text{O}_2\text{CCF}_3)_4$ with aqueous HCl at -10°C may give $[\text{W}_2\text{Cl}_8\text{H}]^{3-}$ in addition to $[\text{W}_2\text{Cl}_6]^{3-}$.

²⁷ J. San Filippo, Jr. and H. J. Sniadoch, *Inorg. Chem.*, 1976, **15**, 2209; J. A. Potenza, R. J. Johnson, and J. San Filippo, Jr., *ibid.*, 1976, **15**, 2215.

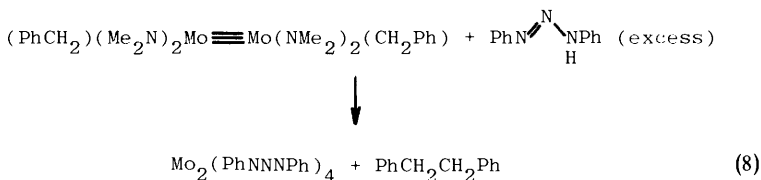
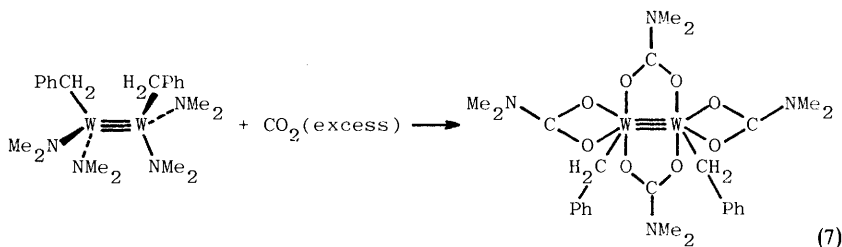
²⁸ F. A. Cotton and G. N. Mott, *J. Am. Chem. Soc.*, 1982, **104**, 5978.

²⁹ M. J. Chetcuti, M. H. Chisholm, K. Folting, J. C. Huffman, and J. Janos, *J. Am. Chem. Soc.*, 1982, **104**, 4684.

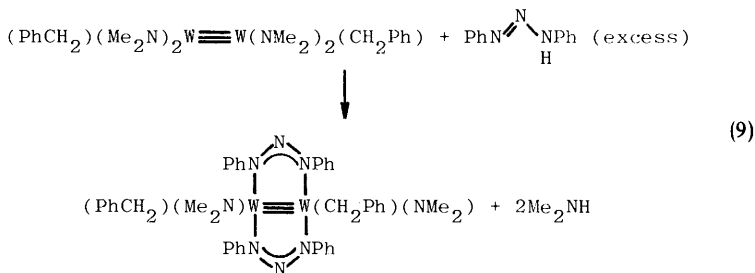
Synergic Interplay of Experiment and Theory in Studying Metal–Metal Bonds

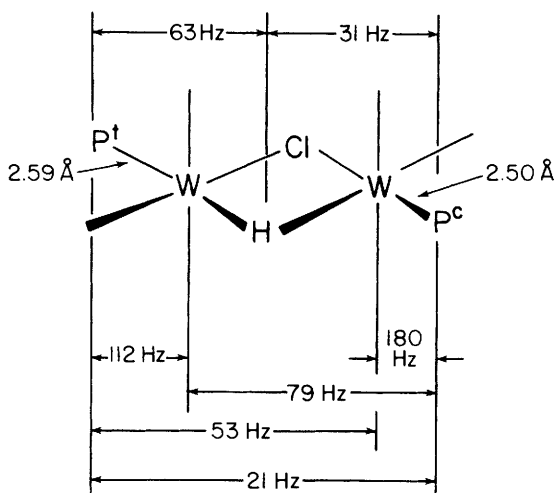


but



but





$$\begin{aligned} \delta(\text{H}) &= 1.92 \text{ vs. TMS} \\ \delta(\text{P}^c) &= 12.0 \\ \delta(\text{P}^t) &= -8.0 \end{aligned} \left. \vphantom{\begin{aligned} \delta(\text{H}) \\ \delta(\text{P}^c) \\ \delta(\text{P}^t) \end{aligned}} \right\} \text{ vs. H}_3\text{PO}_4$$

Figure 13 A diagrammatic summary of the n.m.r. evidence for the presence of the μ -H atom in $\text{W}_2\text{Cl}_2(\text{PBu}^t_3)_2(\text{O}_2\text{CC}_6\text{H}_5)_2$. Coupling constants are given in Hz (For details see Ref. 28)

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