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Discovering and Understanding Multiple Metal-to-Metal Bonds

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Until the early 1960s the science of chemistry was devoid of the notion, much less the reality, of discrete multiple bonds between transition metal atoms,¹ and, of course, totally devoid of the concept of *quadruple* bonds between any atoms whatever. Then, in a very short space of time the existence of Re-Re double bonds,^{3a} triple bonds,^{3b} and quadruple bonds,⁴ the first double and triple bonds between transition metal atoms and the first quadruple bonds of any kind, was demonstrated. Since then, and especially in the last few years, this wholly new phase of transition-metal chemistry has developed very rapidly, as Figure 1 shows.

With respect to quadruple bonds, a statement^{2b} made by Pauling in 1960 is interesting:

It is customary to describe molecules not only in terms of single bonds, each involving a pair of electrons held jointly by two atoms, but also in terms of double bonds and triple bonds (*no one has as yet found evidence justifying the assignment to any molecule of a structure involving a quadruple bond between a pair of atoms*).

This statement was entirely accurate at that time, and remained so for approximately 4 more years when the author of this Account found, for the first time, "evidence justifying the assignment . . . of a structure involving a quadruple bond between a pair of atoms". Prior to that event in 1964, no less than 20 papers⁵⁻²⁴ in the literature dealt with, or at least mentioned, compounds that are now realized to contain quadruple bonds. Remarkably, some of them carry statements explicitly proclaiming the absence of *any* sort of metal-to-metal bond.

The story of how quadruple bonds were recognized to exist⁴ and of the development of the chemistry of compounds containing them and other multiple metal-metal bonds, up to about mid-1974, has been told elsewhere.²⁵ Actually, a great deal more of that chemistry has since been discovered; the number of papers in this area since 1974 exceeds the number before.

F. A. Cotton began graduate research with Geoffrey Wilkinson at Harvard in late 1951 just before the deluge of new chemistry keyed by the discovery of ferrocene began. These circumstances helped to foster the view that basic research at its best consists in discovering new natural phenomena not previously known to exist. His entire research career has been spent at MIT (1955-1971) and the Texas A&M University where he is the Robert A. Welch Distinguished Professor of Chemistry.

The rapid advances since 1974 have resulted from vigorous activity in the preparation and structural characterization of new compounds, from the application of sophisticated theoretical methods, and from the use of many spectroscopic tools, especially electronic absorption spectroscopy of single crystals, but also EPR and photoelectron spectroscopy. In this Account, we emphasize the preparative and structural advances and the theoretical work, with only a few remarks concerning spectroscopy. In the following Account, Trogler and Gray review the spectroscopic aspect in detail.²⁶

(1) In Pauling's discussion of the W-W interaction in the triply bridged $[\text{Cl}_3\text{W}(\mu\text{-Cl})_3\text{WCl}_3]^{3-}$ ion^{2a} the canonical structures $\text{W}=\text{W}$ and $\text{W}=\text{W}=\text{W}$ were introduced as part of a resonance hybrid description. Also Pauling noted^{2a} that in the dioxides MoO_2 and WO_2 the distortions relative to the ideal rutile structure could be attributed to M-M bonds of order >1 (specifically, he proposed 1.47). However, the presence of bridging atoms makes it impossible to specify unambiguously or quantitatively the character of the metal-metal bonds.

(2) L. Pauling, "The Nature of the Chemical Bond", 3rd ed., Cornell University Press, Ithaca, N.Y., 1960: (a) p 437; (b) p 64; (c) p 403.

(3) (a) J. A. Bertrand, F. A. Cotton, and W. A. Dollase, *J. Am. Chem. Soc.*, **85**, 1349 (1963); (b) M. J. Bennett, F. A. Cotton, and R. A. Walton, *J. Am. Chem. Soc.*, **88**, 3866 (1966); *Proc. R. Soc. London, Ser. A*, **303**, 175 (1968).

(4) F. A. Cotton, *Inorg. Chem.*, **4**, 334 (1965); see also F. A. Cotton et al., *Science*, **145**, 1305 (1964).

(5) V. G. Tronev and S. M. Bondin, *Dokl. Akad. Nauk, SSSR*, **86**, 87 (1952).

(6) V. G. Tronev and S. M. Bondin, "Chemistry of Rare Elements", No. 1, Akad. Nauk SSSR, 1954.

(7) A. S. Kotel'nikova and V. G. Tronev, *Zh. Neorg. Khim.*, **3**, 1008 (1958).

(8) G. K. Babeshkina and V. G. Tronev, *Zh. Neorg. Khim.*, **7**, 215 (1962).

(9) A. S. Kotel'nikova and G. A. Vinogradova, *Dokl. Akad. Nauk SSSR*, **152**, 621 (1963).

(10) A. S. Kotel'nikova and G. A. Vinogradova, *Zh. Neorg. Khim.*, **9**, 307 (1964).

(11) V. G. Kuznetsov and P. A. Koz'min, *Zh. Strukt. Khim.*, **4**, 55 (1963).

(12) F. Taha and G. Wilkinson, *J. Chem. Soc.*, 5406 (1963).

(13) E. W. Abel, Apar Singh, and G. Wilkinson, *J. Chem. Soc.*, 3097 (1959).

(14) E. Bannister and G. Wilkinson, *Chem. Ind. (London)*, 319 (1960).

(15) T. A. Stephenson, E. Bannister, and G. Wilkinson, *J. Chem. Soc.*, 2538 (1964).

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(17) E. Peligot, *C. R. Hebd. Seances Acad. Sci.*, **19**, 609 (1844).

(18) E. Peligot, *Ann. Chim. Phys.*, **12**, 528 (1844).

(19) W. R. King and C. S. Garner, *J. Chem. Phys.*, **18**, 689 (1950).

(20) J. N. van Niekerk, F. R. L. Schoening, and F. J. de Wet, *Acta Crystallogr.*, **6**, 501 (1953).

(21) B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, 3837 (1956).

(22) A. Earnshaw, L. F. Larkworthy, and K. S. Patel, *Proc. Chem. Soc., London*, 281 (1963).

(23) S. Herzog and W. Kalies, *Z. Chem.*, **4**, 183 (1964).

(24) S. Herzog and W. Kalies, *Z. Anorg. Allg. Chem.*, **329**, 83 (1964).

(25) F. A. Cotton, *Chem. Soc. Rev.*, **4**, 27 (1975).

(26) W. C. Trogler and H. B. Gray, *Acc. Chem. Res.*, **11**, following paper in this issue.

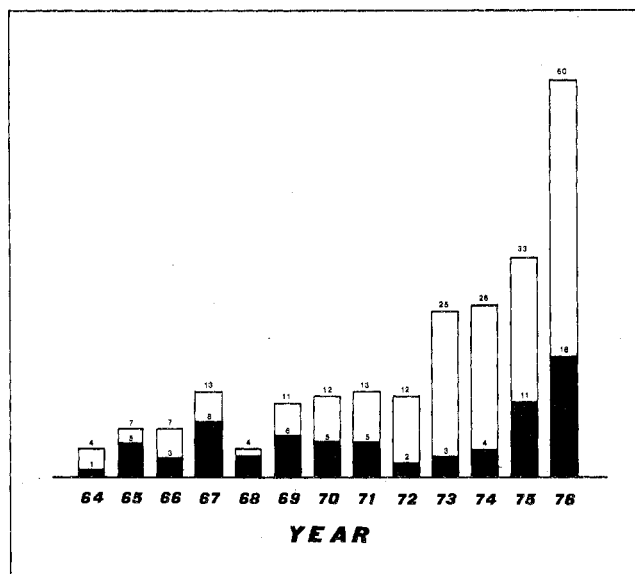
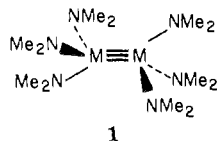


Figure 1. Growth of the literature on metal-to-metal bonds of orders 3 to 4. Black portions give papers from the author's laboratory.

Introductory, qualitative accounts of the nature of quadruple bonds are available in earlier reviews²⁵ and in textbooks. Briefly, a quadruple bond consists of a σ component (d_{z^2} - d_{z^2} overlap), a pair of equivalent π components (d_{xz} - d_{xz} and d_{yz} - d_{yz} overlaps) and a δ component (d_{xy} - d_{xy} overlap), where the d orbitals are defined with respect to a z axis coinciding with the M-M line.

Newer Preparative and Structural Advances

Compounds with Triple Bonds. The first metal-metal triple bond, unequivocal, and without bridges, in $\text{Re}_2\text{Cl}_5(\text{MeSCH}_2\text{CH}_2\text{SMe})_2$, was reported in 1966,^{3b} but this one did not lead directly to the eventual development of the field, nor did the later discovery of $\text{Mo}_2(\text{CH}_2\text{SiMe}_3)_6$.^{27,28} Systematic development began in 1974 with the description^{29,30} of the $\text{Mo}_2(\text{NMe}_2)_6$ and $\text{W}_2(\text{NMe}_2)_6$ molecules, 1. A large number of M_2X_6 (M



= Mo, W) compounds and derivatives thereof have now been prepared. Table I lists all those that are structurally characterized.

Work to date on these compounds has, naturally enough, emphasized preparative methods and definitive physical and structural characterization. All the evi-

(27) F. Huq, W. Mowat, A. Shortland, A. C. Skapski, and G. Wilkinson, *Chem. Commun.*, 1079 (1971).

(28) In other compounds with M-M triple bonds, besides those discussed here, there are bridging groups which introduce some ambiguity in assigning bond orders. None of these other compounds appear to be representative of any large class. Besides those mentioned in ref 25 there are $[(\text{PPh}_3)_4\text{H}_2\text{Ir}_2(\mu\text{-H})_3]\text{PF}_6$ (R. H. Crabtree et al., *J. Organometal. Chem.*, 113, C7 (1976)) and $(\text{PEt}_2\text{Ph})_4\text{H}_4\text{Re}_2(\mu\text{-H})_4$ (R. Bau et al., *J. Am. Chem. Soc.*, 99, 3872 (1977)). There are also the three $(\eta^5\text{-C}_5\text{H}_5)_2\text{M}_2(\text{CO})_4$ (M = Cr, Mo, W) compounds which have quite long triple bonds. They are not discussed here; a separate review of their chemistry (M. Chisholm and F. A. Cotton) has been accepted for publication in a future issue.

(29) M. H. Chisholm, F. A. Cotton, B. A. Freng, W. W. Reichert, L. W. Shive, and B. R. Stults, *J. Am. Chem. Soc.*, 98, 4469 (1976).

(30) M. H. Chisholm, F. A. Cotton, M. W. Extine, and B. R. Stults, *J. Am. Chem. Soc.*, 98, 4477 (1976).

Table I
Triple Bond Lengths (Å)^a

V≡V	
$\text{V}_2(2,6\text{-dimethoxyphenyl})_4$ ³⁹	2.200 (2)
Mo≡Mo	
$\text{Mo}_2(\text{CH}_2\text{SiMe}_3)_6$ ²⁷	2.167 (?)
$\text{Mo}_2(\text{NMe}_2)_6$ ²⁹	2.214 (2)
$\text{Mo}_2(\text{NMe}_2)_4\text{Cl}_2$ ⁴⁵	2.201 (2)
$\text{Mo}_2(\text{NMe}_2)_4\text{Me}_2$ ⁴⁶	2.201 (1)
$\text{Mo}_2(\text{OCH}_2\text{CMe}_3)_6$ ⁴¹	2.222 (2)
$\text{Mo}_2(\text{OSiMe}_3)_6(\text{NHMe}_2)_2$ ³⁵	2.242 (1)
W≡W	
$\text{W}_2(\text{CH}_2\text{SiMe}_3)_6$ ⁴²	2.254 (2)
$\text{W}_2(\text{NMe}_2)_6$ ³⁰	2.293 (2)
$\text{W}_2(\text{NMe}_2)_4\text{Cl}_2$ ⁴⁵	2.285 (2)
$\text{W}_2(\text{NET}_2)_4\text{Cl}_2$ ⁴⁴	2.301 (1)
$\text{W}_2(\text{NET}_2)_4\text{Br}_2$ ⁴⁰	2.301 (2)
$\text{W}_2(\text{NET}_2)_4\text{I}_2$ ⁴⁰	2.300 (2)
$\text{W}_2(\text{NET}_2)_4(\text{CH}_3)_2$ ⁴³	2.291 (1)
$\text{W}_2(\text{O}_2\text{CNMe}_2)_6$ ³¹	2.279 (1)
$\text{W}_2(\text{O}_2\text{CNEt}_2)_4(\text{CH}_3)_2$ ³¹	2.272 (1)
Re≡Re	
$\text{Cl}_4\text{ReRe}(\text{MeSCH}_2\text{CH}_2\text{SMe})_2\text{Cl}$ ^{3b}	2.293 (2)
O_4ReReO_4 (in $\text{La}_4(\text{Re}_2)\text{O}_{10}$) ³³	2.262 (1)
$\text{Re}_2\text{Cl}_4(\text{PET}_3)_4$ ³⁶	2.232 (5)

^a Figures in parentheses, here and elsewhere, are estimated standard deviations in the last digit.

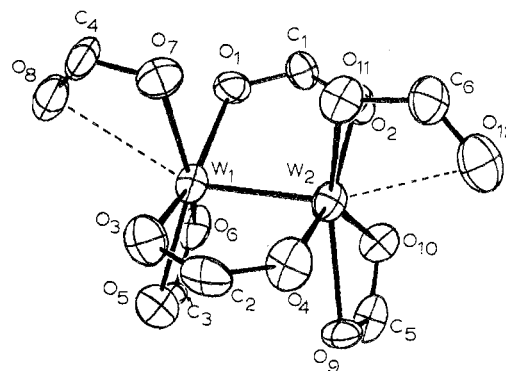
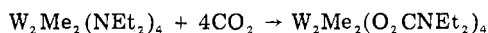
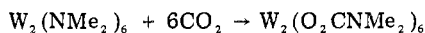
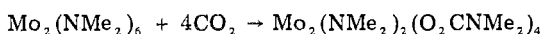


Figure 2. The inner portion of the $\text{W}_2(\text{O}_2\text{CNMe}_2)_6$ molecule. The NMe_2 groups have been omitted for clarity.

dence points to a simple qualitative picture of the M-M bonding with a bond order of 3 consisting of a σ bond, formed mainly by overlap of metal d_{z^2} orbitals, and a pair of orthogonal π bonds, formed mainly by overlap of metal d_{xz} and d_{yz} orbitals. In other words, the bonding situation is analogous to that in the quadruple bonds except that there is no δ component. Strong theoretical support for this picture will be cited later.

Much remains to be learned about the chemistry of this class of compounds, but already several interesting observations have been made. For example, they react with CO_2 to give products with the CO_2 inserted in some or all of the metal-ligand bonds. In the case of tungsten compounds,³¹ CO_2 insertion occurs in all W-N bonds, converting all NR_2 groups to carbamate, O_2CNR_2 , ligands. With some molybdenum compounds,³² only partial conversion occurs. Representative reactions are:



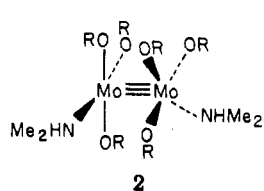
(31) M. H. Chisholm, F. A. Cotton, M. W. Extine, and B. R. Stults, *Inorg. Chem.*, 16, 603 (1977).

(32) M. H. Chisholm and W. W. Reichert, in press.

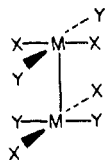
The structures³¹ of the products are complex, as shown by that of $W_2(O_2CNMe_2)_6$, Figure 2. The $W \equiv W$ bond is preserved, essentially unchanged in length, but the coordination number increases considerably. Two O_2CNR_2 groups are bidentate bridges, two are bidentate but chelating, and the other two form only one strong bond to the metal bond though they are also weakly bonded through the other oxygen atom. The $W_2Me_2(O_2CNET_2)_4$ structure³¹ is similar with Me groups replacing the essentially monodentate O_2CNR_2 ligands. Still more remarkable is the fluxionality of these molecules. The NMR spectrum of $W_2(O_2CNMe_2)_6$ at $-60^\circ C$ corresponds with the crystal structure, but by $77^\circ C$ all ligands are rapidly interchanging to give a single-line proton spectrum.

Besides the large class of $M \equiv M$ compounds just discussed, there are others in which the metal atoms have four rather than three ligand atoms. In the mixed metal oxide $La_4Re_2O_{10}$ ³³ the Re atoms occur as Re_2^{8+} units and the array of five cations (mono- or dinuclear) and ten oxide ions forms a tetragonally distorted fluorite structure, with each Re_2 unit in a square parallelipiped of eight oxygen atoms. Since we are dealing with Re(IV) there is only a triple bond between the rhenium atoms. This is the only known case in which D_{4h} geometry of the M_2X_8 unit persists in the absence of both δ bonding electrons, but clearly, it is the overall crystal packing that imposes the local structure.

An M_2X_8 unit with a triple M-M bond may also result from addition of two ligands to a triply bonded M_2X_6 unit. For example, $Mo_2(OSiMe_3)_6$ readily reacts with amines and other donors to form adducts³⁴ such as $Mo_2(OSiMe_3)_6(NHMe_2)_2$, which has the structure³⁵ 2. The rotational conformation is staggered, since there is no δ bond.



2
3a, X = Cl; Y = PEt_3 , M = Re
b, X = Y = Cl or Me; M = W



A triple bond in an M_2X_8 unit may also result from adding two electrons to the δ^* orbital of a quadruply bonded one, thus canceling (as opposed to abolishing) the δ bond. This happens in $Re_2Cl_4(PEt_3)_4$ and homologous compounds,³⁶ where, according to a recent SCF- $X\alpha$ -SW type MO calculation,³⁷ the configuration is $\sigma^2\pi^4\delta^2\delta^*2$. In this case the conformation remains eclipsed (3a) because of steric effects. In order for the four large PEt_3 groups to be staggered, which is the overriding steric requirement, the entire set of eight ligands must be eclipsed.

The "design principle" of the M_2X_6 species, namely, the use of formal oxidation number 3 for a group 6

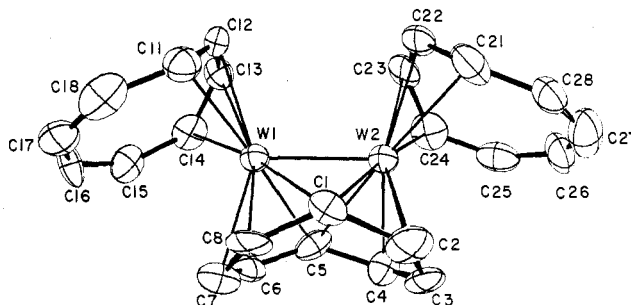
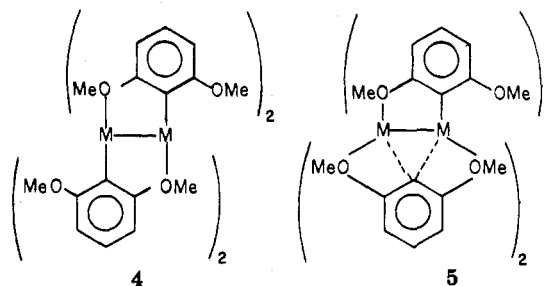


Figure 3. The $W_2(C_8H_8)_3$ molecule.

element, so as to have three electrons for use in forming the triple M-M bond, has not as yet born fruit in the first transition series; no triply bonded Cr_2X_6 type molecule has yet been identified. Recently, however, the analogous procedure of using formal oxidation number 2 for a group 5 element has been shown to give a triple V-V compound. An effort to prepare tris-(2,6-dimethoxyphenyl)vanadium, $V(DMP)_3$, led instead to the isolation of $V(DMP)_2$, a diamagnetic dimer for which a structure of type 4 was proposed.³⁸ The



structure is, in fact, that shown in 5, but the geometry and V-V distance, 2.200 (2) Å, are consistent with the occurrence of a V-V triple bond.³⁹

Tungsten-to-Tungsten Quadruple Bonds. The abundance of Mo-Mo and Re-Re quadruple bonds might seem to argue that quadruple W-W bonds ought to be easily obtainable. The existence of an extensive class of analogous Mo and W compounds containing triple bonds and a theoretical study⁴⁷ also encouraged this view. Yet, preparation and proof of existence of quadruple W-W bonds have been an extraordinarily difficult and frustrating task, only recently accomplished.^{48,49} Finally, in late 1976 the break came with

(33) K. Waltersson, *Acta Crystallogr., Sect. B*, 32, 1485 (1976).
 (34) M. H. Chisholm, F. A. Cotton, C. A. Murillo, and W. W. Reichert, *Inorg. Chem.*, 16, 8101 (1977).
 (35) M. H. Chisholm, F. A. Cotton, M. W. Extine, and W. W. Reichert, *J. Am. Chem. Soc.*, 100, 153 (1978).
 (36) (a) J. R. Ebner and R. A. Walton, *Inorg. Chem.*, 14, 1987 (1975);
 (b) F. A. Cotton, B. A. Frenz, J. R. Ebner, and R. A. Walton, *ibid.*, 15, 1630 (1976).
 (37) F. A. Cotton and G. G. Stanley, to be published.

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 (39) F. A. Cotton and M. Millar, *J. Am. Chem. Soc.*, 99, 7886 (1977).
 (40) M. H. Chisholm, F. A. Cotton, M. W. Extine, M. Millar, and B. R. Stults, *Inorg. Chem.*, 16, 320 (1977).
 (41) M. H. Chisholm, F. A. Cotton, C. A. Murillo, and W. W. Reichert, *Inorg. Chem.*, 16, 8101 (1977).
 (42) M. H. Chisholm, F. A. Cotton, M. Extine, and B. R. Stults, *J. Am. Chem. Soc.*, 98, 4683 (1976).
 (43) M. H. Chisholm, F. A. Cotton, M. Extine, M. Millar, and B. R. Stults, *Inorg. Chem.*, 15, 2244 (1976).
 (44) M. H. Chisholm, F. A. Cotton, M. Extine, M. Millar, and B. R. Stults, *J. Am. Chem. Soc.*, 98, 4486 (1976).
 (45) M. Akiyama, M. H. Chisholm, F. A. Cotton, M. W. Extine, and C. A. Murillo, *Inorg. Chem.*, 16, 2407 (1977).
 (46) M. H. Chisholm, F. A. Cotton, M. W. Extine, and C. A. Murillo, *Inorg. Chem.*, in press.
 (47) F. A. Cotton and B. J. Kalbacher, *Inorg. Chem.*, 16, 2386 (1977).
 (48) D. M. Collins, F. A. Cotton, S. Koch, M. Millar, and C. A. Murillo, *J. Am. Chem. Soc.*, 99, 1259 (1977).
 (49) Several years ago a series of $W_2(O_2CR)_4$ compounds were prepared and their compositions firmly established, but, for reasons still unknown, these have resisted all attempts to crystallize them for X-ray characterization: F. A. Cotton and M. Jeremic, *Synth. Inorg. Metal-Org. Chem.*, 1, 265 (1971).

Table II
Newer Cr-Cr Quadruple Bond Structures

Compound	Cr-Cr, Å	Ref
$\text{Cr}_2(\text{O}_2\text{CCF}_3)_4(\text{Et}_2\text{O})_2$	2.541 (1)	53
$\text{Cr}_3(\text{O}_2\text{CH})_6(\text{H}_2\text{O})_2$	2.451 (1)	53
$\text{Cr}_2(\text{O}_2\text{CH})_6(\text{C}_5\text{H}_5\text{N})_2$	2.408 (1)	53
$\text{Cr}_2(\text{O}_2\text{CCMe}_3)_4$	2.388 (4)	53
$\text{Cr}_2(\text{O}_2\text{CPh})_4(\text{PhCO}_2\text{H})_2$	2.352 (3)	53
$\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$	2.288 (2)	54
$\text{Cr}_2(\text{O}_2\text{CC}_{14}\text{H}_9)_4(\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3)$	2.283 (2)	53
$\text{Cr}_2(\text{C}_8\text{H}_8)_3$	2.214 (1)	55
$\text{Cr}_2(\text{CH}_2\text{SiMe}_3)_2(\text{Me}_3\text{P})_2(\mu\text{-CH}_2\text{SiMe}_3)_2$	2.100 (1)	56
$\text{Cr}_2[2,6\text{-C}_6\text{H}_3(\text{OMe})_2]_4$	1.847 (1)	57

the preparation and structure determination⁴⁸ of the compound $\text{Li}_4\text{W}_2\text{Cl}_x\text{Me}_{8-x}\cdot 4\text{THF}$. This extremely air- and heat-sensitive compound had to be prepared and maintained throughout the course of all experimentation at or below -20°C . It was shown to contain an anion of charge -4 with structure **3b** in which Cl and CH_3 ligands, in a ratio typically $\sim 3/5$, appear to be randomly distributed over the eight available positions. The W-W distance, 2.261 Å, is scarcely shorter than the typical $\text{W}\equiv\text{W}$ distance, implying that the δ component contributes but weakly. Somewhat more thermally stable compounds containing the $\text{W}_2\text{Me}_8^{4-}$ ion can be prepared,⁵⁰ but these have so far failed to afford useable single crystals. Efforts to obtain a compound of $\text{W}_2\text{Cl}_8^{4-}$ have so far failed.

In view of this dismal record, the recent discovery of an air-stable compound containing quadruple W-W bonding is startling. A structural report on $\text{Cr}_2(\text{C}_8\text{H}_8)_3$ (see Table II) mentioned that Mo and W homologues were known, though no description of their preparation or properties had ever been published. We found that $\text{W}_2(\text{C}_8\text{H}_8)_3$ can be prepared easily from $\text{K}_2\text{C}_8\text{H}_8$ and WCl_4 as a stable green-black solid that readily forms large crystals. The crystal structure⁵¹ shows a molecule similar to the Cr analogue, Figure 3, with a W-W bond 2.375 (1) Å in length.

Chromium-to-Chromium Quadruple Bonds. As I have remarked before,²⁵ the first compound containing a quadruple bond was discovered in 1844, namely, $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$. But only in 1970 was the bond so formulated⁵² on the basis of the newly determined Cr-Cr distance at 2.36 Å. While quadruple Mo-Mo and Re-Re bonds are each restricted to a narrow range of lengths (~ 0.1 Å), quadruple Cr-Cr bonds cover an enormous range. A few years ago²⁵ the limits were ~ 1.97 Å for $\text{Cr}_2(\text{allyl})_4$ to 2.36 Å in the hydrated acetate. Now these limits have been extended, and many more intermediate values reported. A list of structures done since the last review,²⁵ in order of decreasing Cr-Cr distance, appears as Table II.⁵³⁻⁵⁷

(50) F. A. Cotton, S. Koch, K. Mertis, M. Millar, and G. Wilkinson, *J. Am. Chem. Soc.*, **99**, 4989 (1977).

(51) F. A. Cotton and S. Koch, *J. Am. Chem. Soc.*, **99**, 7371 (1977).

(52) F. A. Cotton, B. G. DeBoer, M. D. LaPrade, J. R. Pipal, and D. A. Ucko, *J. Am. Chem. Soc.*, **92**, 2926 (1970); *Acta Crystallogr., Sect. B*, **27**, 1664 (1971).

(53) F. A. Cotton, M. Extine, and G. W. Rice, *Inorg. Chem.*, **17**, 176 (1978).

(54) F. A. Cotton, C. E. Rice, and G. W. Rice, *J. Am. Chem. Soc.*, **99**, 4704 (1977).

(55) D. J. Brauer and C. Krüger, *Inorg. Chem.*, **15**, 2511 (1976).

(56) R. B. Anderson, R. A. Jones, G. Wilkinson, M. B. Hursthouse, and K. M. A. Malik, *J. Chem. Soc., Chem. Commun.*, 283 (1977).

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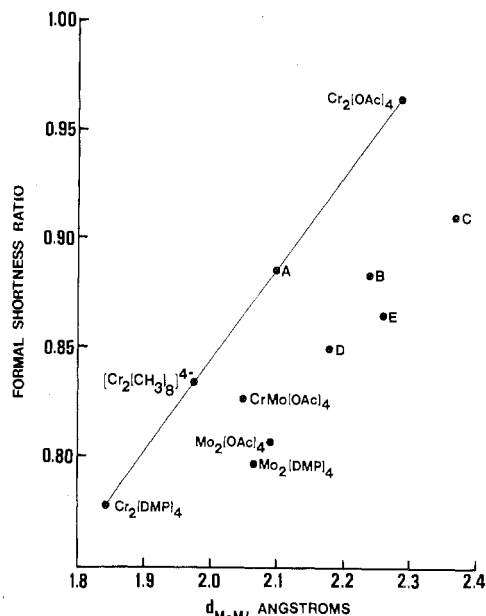


Figure 4. A plot of the "formal shortness" ratio vs. M-M bond lengths. Points not identified by formula are for (A) $\text{Cr}_2(\text{C}_8\text{H}_8)_3$, (B) $\text{Re}_2\text{Cl}_8^{2-}$, (C) $\text{W}_2(\text{C}_8\text{H}_8)_3$, (D) $\text{Re}_2\text{Me}_8^{2-}$, (E) $\text{W}_2(\text{CH}_2\text{SiMe}_3)_6$.

The first seven compounds all contain $\text{Cr}_2(\text{O}_2\text{CR})_4$ molecules, with a variety of R groups in the carboxylato ions and a considerable range of axial ligand to Cr (Cr-L_{ax}) distances. Even in the two cases where the formula does not explicitly indicate the presence of axial interactions, they exist because of intermolecular $\text{O}\cdots\text{Cr}$ contacts through which the molecules are linked in infinite chains. This wide range of Cr-Cr distances among the carboxylato compounds has not yet been fully interpreted. There is a rough correlation with the Cr-L_{ax} distance, the Cr-Cr distance showing a tendency to increase as Cr-L_{ax} decreases. This is not unexpected, since there is likely to be direct competition between Cr-Cr σ bonding and Cr-L_{ax} σ bonding for the d_{z^2} orbital on each Cr atom. The basis for insisting that the carboxylato compounds do indeed contain quadruple Cr-Cr bonds will be discussed later (see Theoretical Advances).

The shorter Cr-Cr bonds all occur in organometallic compounds, but these are of quite disparate types. The Cr-Cr distances in $\text{Cr}_2(\text{C}_8\text{H}_8)_3$ and $\text{Cr}_2(\text{CH}_2\text{SiMe}_3)_2(\text{Me}_3\text{P})_2(\mu\text{-CH}_2\text{SiMe}_3)_2$ are the first two between 1.98 and 2.28 Å, but are not otherwise remarkable. It is the compound containing the 2,6-dimethoxyphenyl, DMP, ligand that is truly remarkable. It has the type structure shown schematically as 4, and the Cr-Cr distance is by far the shortest M-M distance ever observed: more than 0.1 Å shorter than the previously recognized shortest M-M bond. The corresponding $\text{Mo}_2(\text{DMP})_4$ contains the shortest Mo-Mo quadruple bond ever observed. It is not yet known what characteristics of the DMP ligand are responsible for the encouragement of such tight M-M bonding.

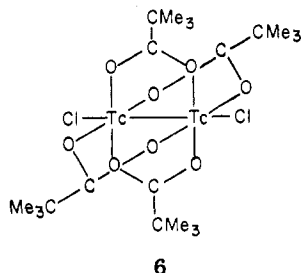
In order to convey a feeling for just how short the Cr-Cr bond in $\text{Cr}_2(\text{DMP})_4$ is compared to other relatively short bonds, a method for comparing bond lengths involving different atoms is needed. This can be done by scaling each M-M or other bond to the inherent size of the atoms composing it by using Pauling's single bond radii, R_1 , which are available for nearly all elements,^{2c} including the transition elements.

Each observed bond length is divided by the sum of the radii of the two atoms so as to obtain a "formal shortness" ratio. Figure 4 shows a plot of these ratios vs. actual internuclear distances. It is clear the quadruple Cr-Cr and Mo-Mo bonds in the $M_2(DMP)_4$ molecules are formally shorter than any other M-M bonds known. Note that while the Cr-Mo bond in $Mo_2(DMP)_4$ is longer than the Cr-Cr bond in $[Cr_2Me_8]^{4-}$, it is formally shorter, i.e., shorter relative to the inherently larger size of the atoms composing it.

The Cr-Cr bond in $Cr_2(DMP)_4$ is in fact the formally shortest homonuclear bond known. Even the strongest homonuclear bonds for which bond energies are known, $N\equiv N$ (946 kJ mol⁻¹), $C\equiv C$ (813 kJ mol⁻¹), and $P\equiv P$ (490 kJ mol⁻¹), are not quite as formally short (ratios of 0.786, 0.783, 0.860) as the Cr-Cr quadruple bond, with a ratio of 0.778.

Technetium Compounds. It is curious that the first Tc-Tc quadruply bonded compounds isoelectronic with their rhenium analogues were reported only in 1977, although compounds^{16,58-60} of the $Tc_2Cl_8^{3-}$ ion, with a $\sigma^2\pi^4\delta^2\delta^*$ configuration,^{47,61,62} had been thoroughly studied since 1965. It was shown⁶⁰ in 1975 that oxidation of $Tc_2Cl_8^{3-}$ to $Tc_2Cl_8^{2-}$ proceeds reversibly at 0.14 V vs. SCE and that the product is probably diamagnetic, with a lifetime in solution of at least 5 min. It was suggested that "a suitably designed effort to isolate (it) might be successful". Early in 1977 it was reported⁶³ that $[(C_4H_9)_4N]_2Tc_2Cl_8$, crystallographically isomorphous to its rhenium analogue, had been isolated; the isolation actually involved no exceptional precautions, and it is really rather odd that no one had isolated a $Tc_2Cl_8^{2-}$ compound earlier, if only inadvertently. The Tc-Tc bond length is not yet known.

It was simultaneously shown in my laboratory that reaction of pivalic acid with $(NH_4)_3Tc_2Cl_8$ produces the red, crystalline compound $Tc_2(O_2CCMe_3)_4Cl_2$, the first quadruply bonded Tc_2 compound to be structurally characterized.⁶⁴ Its structure, 6, is qualitatively as



6

expected, but has a surprisingly long Tc-Tc bond, 2.192 (2) Å. In $Tc_2Cl_8^{3-}$ the distance⁵⁹ is 2.117 (2) Å and in $Re_2(O_2CCMe_3)_4Cl_2$, which is isostructural, the Re-Re distance is 2.236 (1) Å. An explanation for this long Tc-Tc distance is seen in the very short Tc-Cl distance. It is clear from other studies that the strengths of M-M multiple bonds are inversely related to the strengths of the bonds from the M atoms to axial ligands. In

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Table III
Recently Reported Mo-Mo and Re-Re Quadruply Bonded Structures

	M-M, Å	Ref
Re ₂ Compounds		
$(NH_4)_2Re_2Cl_6(O_2CH)_2$	2.260 (5)	65
$Re_2Cl_4(PhNC(Ph)NPh)_2$	2.177 (2)	66
$Re_2Cl_4(PhNC(Ph)NPh)_2(THF)$	2.209 (1)	66
$[(C_4H_9)_4N]_2Re_2Cl_8$	2.222 (2)	67
$Re_2Cl_4[(Ph_2P)_2CH_2]_2$	2.263 (1)	68
$Li_2[Re_2Me_8] \cdot 2Et_2O$	2.178 (1)	69
$Cs_2Re_2Cl_8 \cdot H_2O$: $Re_2Cl_8^{2-}$	2.237 (2)	70
$[Re_2Cl_8(H_2O)_2]^{2-}$	2.252 (2)	70
$Re_2(O_2CCMe_3)_4Cl_2$	2.236 (1)	71
$Re_2(O_2CCMe_3)_4Br_2$	2.234 (1)	71
Mo ₂ Compounds		
$[Mo_2(O_2CCH_2NH_3)_4](SO_4)_2(H_2O)_4$	2.115 (1)	72
$Mo_2(O_2CH)_4$	2.091 (2)	73
$Mo_2[(C_3H_5N)_2]_2BEt_2(O_2CCH_3)_2$	2.129 (1)	74
$Mo_2[(C_3H_5N)_2]_2BH(O_2CCH_3)_2$	2.147 (3)	74
$Mo_2(O_2CPh)_4(diglyme)_2$	2.100 (1)	75
$(CH_3C_5H_4NH)_2[Mo_2Br_6(H_2O)_2]$	2.122 (2)	76
$Mo_2(O_2CPh)_2[(C_4H_9)_3P]_2Br_2$	2.091 (3)	77
$Mo_2(O_2CPh)_4$	2.096 (1)	78
$Mo_2(O_2CCMe_3)_4$	2.088 (1)	78
$Mo_2(6\text{-azaindolyl})_2(Et_3P)_2Br_2$	2.125 (1)	79
$Mo_2[2,6\text{-}C_6H_3(OMe)_2]_4$	2.065 (1)	57

$Tc_2Cl_8^{3-}$, there is essentially no axial interaction, whereas the cation, $Tc_2(O_2CCMe_3)_4^{2+}$, binds the axial Cl⁻ ions quite strongly and this leads to a weakening and lengthening of the Tc-Tc quadruple bond itself.

Other New Compounds with Bond Orders of 3.5 to 4.0. In addition to the highlights just mentioned, there has been continued development along more conventional lines leading to the preparation and structural characterization of large numbers of new compounds with $\sigma^2\pi^4\delta^2$, $\sigma^2\pi^4\delta$, and $\sigma^2\pi^4\delta^2\delta^*$ configurations, especially those formed by molybdenum and rhenium. In Table III^{57,65-79} are listed, along with the M-M distances, all those for which structures have been reported since my last review.²⁵

Among the newly characterized quadruply bonded Re-Re compounds are those setting new records for the shortest (2.18 Å) and the longest (2.26 Å) such bonds. The majority, however, like those previously known, fall in the narrower range of 2.22 to 2.24 Å. For the Mo-Mo quadruple bond, the tetrakis(2,6-dimethoxyphenyl)

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compound has the shortest distance ever reported, 2.065 (1) Å. Its structure is of type 4.

Theoretical Advances

In 1964 I proposed an essentially qualitative, symmetry-based description of the quadruple bond.⁴ It was argued that the metal d orbitals would play such a dominant role that it would be a reasonable approximation to assign them the entire responsibility for M–M bonding. For bonds between rhenium atoms, and even molybdenum or technetium atoms, there was then no practical way to do rigorous calculations, but in the early 70s this situation began to change.

In mid-1971, the late John C. Slater visited me, as he had occasionally done over the years, and told me how he and a young colleague, Keith Johnson, had developed certain ideas implicit in the previous decades of pioneering work by the Slater group on the electronic structure of metals and alloys into a new method for molecular electronic structure calculations.⁸⁰ It had occurred to him that this method, about which he and Johnson had not yet published much, was admirably suited to deal with the metal atom clusters and strong metal–metal bonds that I had previously discussed with him. He gave me a brief account of how the method worked and quickly had me in a mood of high enthusiasm. However, I had just decided to heed Horace Greely's admonition (Go west, young man!), and the complexities of decamping for Texas, with research group, family, horses, etc., etc., the following winter effectively rendered me hors de combat for the next year or so. Fortunately, I had an excellent graduate student, Joe G. Norman, Jr., now Associate Professor of Chemistry at the University of Washington, who had been doing experimental work on quadruple bonds, who had a NSF predoctoral fellowship to support him in my absence during the spring of 1972, and who had the aptitude to do theoretical work. It was, therefore, arranged that he spend the spring of 1972 working with Keith Johnson to learn the SCF–X α –SW method, with the ultimate objective of applying it to strong metal–metal bonds. Thus it was that shortly after he joined the faculty at Washington Joe Norman was able to report⁸¹ that an SCF–X α –SW calculation on Mo₂Cl₈⁴⁻ gives a picture of the quadruple bond in almost perfect accord with my original proposal. This work initiated a continuing effort^{47,82–85} to elucidate the nature of M–M multiple bonds by means of SCF–X α –SW calculations.

Several of the more recent calculations have shown that clean-cut attribution of quadruple bonding to just three discrete σ , π , and δ orbitals is not always possible. The situation conforms most closely to such a simple description for the Mo₂Cl₈⁴⁻ and W₂Cl₈⁴⁻ cases where the metals are in a low formal oxidation state and the

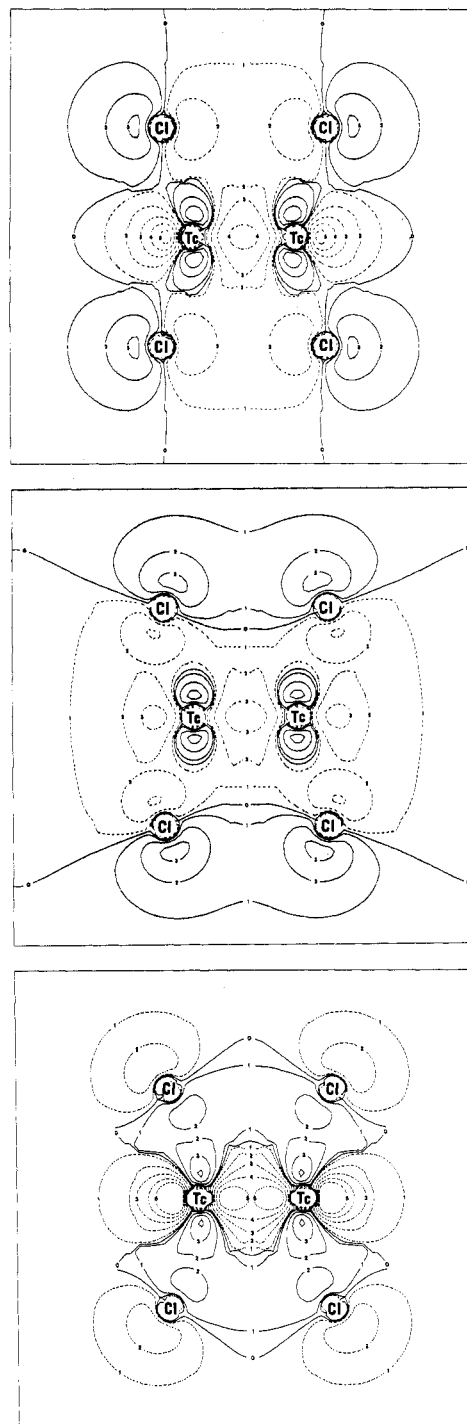


Figure 5. Contours of the $2a_{1g}$ (bottom), $3a_{1g}$ (middle), and $4a_{1g}$ (top) orbitals of $Tc_2Cl_8^{3-}$.

ligands are rather simple. An increase in the oxidation state of the metal atoms, not unexpectedly, leads to more complicated patterns of orbital mixing, and more complex ligands, e.g., RCO₂⁻ groups, also become involved more intimately with the metal d orbitals so that in many cases the M–M bonding interactions are distributed over more than one MO of the appropriate symmetry type.

The δ orbitals are least affected by these added complications; they retain high d character ($\geq 90\%$), and one can nearly always speak of "the" δ -bonding orbital. For the π bonding, the highest filled e_g orbital continues to carry much of the bonding interaction, but there is a steady decrease with increasing metal oxidation

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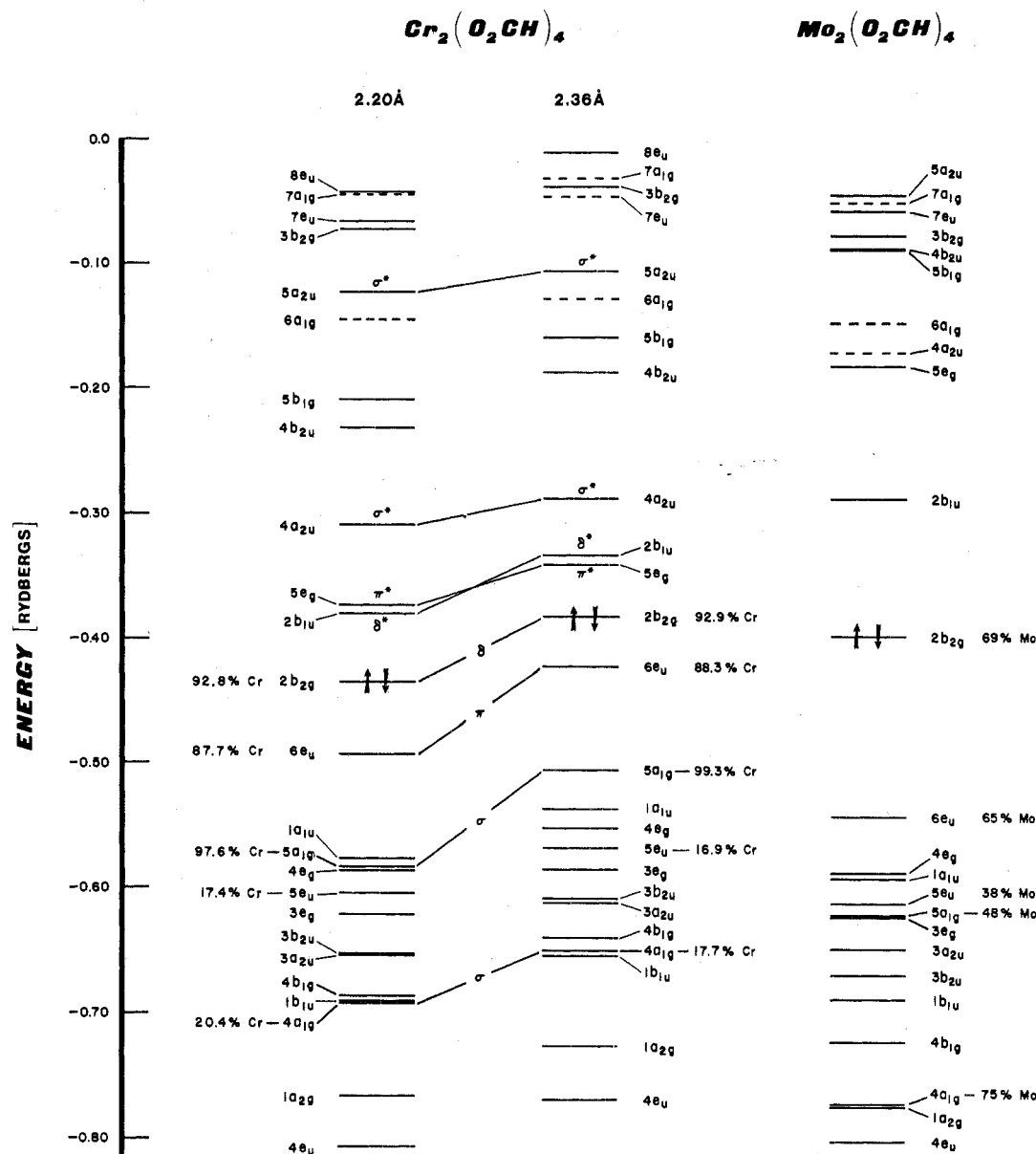


Figure 6. Energy levels calculated for $\text{Cr}_2(\text{O}_2\text{CH})_4$ at two Cr-Cr distances and, for comparison, Norman and Kolari's results for $\text{Mo}_2(\text{O}_2\text{CH})_4$.

number as shown by the following⁴⁷ percentages of metal character: $\text{Mo}_2\text{Cl}_8^{4-}$ (76%), $\text{Tc}_2\text{Cl}_8^{3-}$ (52%), $\text{Re}_2\text{Cl}_8^{2-}$ (47%). In $\text{Tc}_2\text{Cl}_8^{3-}$ the second-highest filled e_u orbital has nearly as much metal character (46%) as the highest, although contour diagrams show that it is not nearly so much M-M as M-Cl in nature.

For the M-M σ bonding there is often partial participation by several a_{1g} orbitals, and their relative contributions vary considerably from case to case. For $\text{Mo}_2\text{Cl}_8^{4-}$ the highest occupied a_{1g} orbital, $4a_{1g}$, is almost the sole contributor to M-M σ bonding, but in $\text{Tc}_2\text{Cl}_8^{3-}$ both $4a_{1g}$ and $2a_{1g}$, as shown in Figure 5, make important contributions, and $2a_{1g}$ actually makes the more important one. It should be kept in mind that these are contours of Ψ and that the relative electron densities are proportional to Ψ^2 ; thus the ratio of maximum internuclear σ -electron densities in the $2a_{1g}$ and $4a_{1g}$ orbitals is roughly $5^2/4.2^2 = 1.4$. The $3a_{1g}$ orbital, though intermediate in energy, is essentially a lone-pair orbital on the chlorine atoms, as can be seen. Figure 5 affords a very good illustration of how the contour diagrams are instrumental in allowing us to infer the

roles played by the individual MOs in the various bond types.

Another significant example⁸⁵ of how enlightening the SCF-X α -SW calculations can be is provided by comparison of the energy level diagrams for $\text{Cr}_2(\text{O}_2\text{CH})_4$ and $\text{Mo}_2(\text{O}_2\text{CH})_4$ (Figure 6). As noted earlier, a conspicuous difference between quadruple Mo-Mo and Cr-Cr bonds is the resistance of the former to bind axial ligands with concomitant weakening of the Mo-Mo bond, whereas the dichromium species readily form strong bonds to axial ligands while lengthening considerably the Cr-Cr distance. The interrelationship between M-L_{ax} and M-M bonding can be regarded, at least predominantly, as based on competition for the d_z orbitals, which are the key components of both types of σ bonds.

It can be seen in Figure 6 that for $\text{Cr}_2(\text{O}_2\text{CH})_4$ the highest (i.e., least stable) a_{1g} orbital, $5a_{1g}$, is the predominant contributor while the more stable $4a_{1g}$ orbital contributes little to M-M σ bonding. In $\text{Mo}_2(\text{O}_2\text{CH})_4$, however, $4a_{1g}$ lies at even lower energy relative to $5a_{1g}$, and is largely responsible for Mo-Mo σ bonding. The

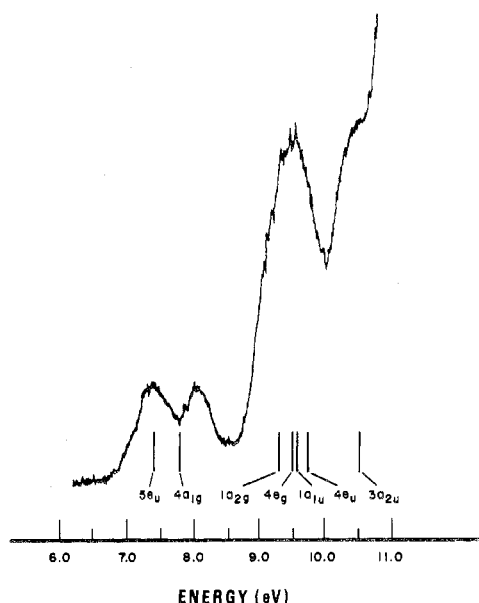


Figure 7. The observed and calculated PES for $\text{Mo}_2(\text{OCH}_2\text{CMe}_3)_6$. The energy scale is for the experimental spectrum and the calculated values are arbitrarily shifted to match the lowest calculated ionization energy to the first observed maximum.

very different tendencies of the two systems to sacrifice M–M σ bonding, which is the strongest component of the entire quadruple bond, in favor of M–L_{ax} σ bonding are clearly implied by these results.

The calculation⁸⁵ for $\text{Cr}_2(\text{O}_2\text{CH})_4$ clearly shows the presence of a quadruple bond, in which the δ and π ($2b_{2g}$, $6e_u$) orbitals are close in energy. This feature and, indeed, all other key features of the calculated level pattern for a Cr–Cr distance of ca. 2.30 Å are in excellent accord with the observed PES⁸⁶ for gaseous $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$, and this close agreement provides powerful evidence that the calculation is reliable and

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that there are indeed quadruple Cr–Cr bonds in the $\text{Cr}_2(\text{O}_2\text{CR})_4$ compounds.

Finally, in this extremely brief and selective sampling of theoretical results, we draw attention to the way in which SCF–X α –SW calculations have confirmed and quantified the simple qualitative picture of the triple Mo–Mo and W–W bonds in M_2X_6 species. Figure 7 shows the UV photoelectron spectrum of $\text{Mo}_2(\text{OCH}_2\text{CMe}_3)_6$ together with the calculated ionization energies for the seven highest energy levels. The fit, though not impeccable, is very satisfactory overall. The $5e_u$ orbital is the M–M π bonding orbital and the $4a_{1g}$ is the M–M σ bonding level, exactly as expected from the qualitative picture discussed earlier.

The first attempts to employ Hartree–Fock (so-called *ab initio*) methods for these multiple bonds have recently been reported.^{86,87a} For $\text{Cr}_2(\text{O}_2\text{CH})_4$ it is clear^{87a} that unless configuration interaction is included, erroneous results are obtained; this, of course, adds greatly to the expense of an already expensive calculation. For several second-row compounds, single configuration calculations have afforded results that are essentially in accord with SCF–X α –SW calculations as far as the qualitative order of levels is concerned.^{87b} No Hartree–Fock calculation has yet been tested in terms of its ability to account for electronic absorption or photoelectron spectra. In at least one case, $\text{Tc}_2\text{Cl}_8^{3-}$, an SCF–X α –SW calculation has been shown to give a virtually quantitative fit to the observed absorption spectrum,⁶² although it must be admitted that in other cases the agreement has not been as good.

Work in my own laboratory in this field has been supported by the National Science Foundation during the period covered. I am grateful to many talented co-workers, whose names may be found in the reference list, for their contributions to this work. It has been a privilege to collaborate with Professor D. S. Martin, Jr., of Iowa State University, Ames, and Professor Malcolm H. Chisholm of Princeton University in several phases of the work.

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Electronic Spectra and Photochemistry of Complexes Containing Quadruple Metal–Metal Bonds

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Study of the nature of metal–metal interactions in cluster complexes has been an active area of research in our laboratory for 10 years. Our initial investigations involved $\text{Mn}_2(\text{CO})_{10}$ and related complexes containing

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single metal–metal bonds.^{1,2} We established that the electronic spectra of such binuclear complexes feature a relatively low-lying, intense absorption band that is not present in reference mononuclear systems. In the spectrum of $\text{Mn}_2(\text{CO})_{10}$, this band peaks at 29400 cm^{-1} ($\epsilon\ 2 \times 10^4$).²

Simple theoretical considerations taken together with the experimental finding that the absorption in

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