

NMR (CDCl₃) δ 5.60 (m, 2 H, bridgehead); exact mass calcd for C₆H₁₀O₃ 130.0630, found 130.0627.

- (6) A. D. Bain, J. C. Bünzli, D. C. Frost, and L. Weiler, *J. Am. Chem. Soc.*, **95**, 291 (1973).
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- (9) Identified as such by the vibrational spacing in the ion state, $\nu^+ = 0.12$ eV. The peroxide unit should exhibit both a bonding and antibonding combination of the oxygen lone pairs (n_o^+ and n_o^-), but only the latter is easily identifiable in all known cases: R. S. Brown, *Can. J. Chem.*, **53**, 3439 (1975).
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- (11) In this case within the framework of Koopmans' theorem (T. Koopmans, *Physica*, **1**, 104 (1934)), an increase in IP constitutes a stabilization of the orbital giving rise to that ionization.
- (12) We assume that replacement of the methylene unit by an oxygen in changing from 1,2-dioxacyclopentane to 1 does not cause major distortions in the ring which would alter the n_o^- IP. Implicit in this argument is also the idea that changes in interaction of n_o and n_o^- with low lying σ orbitals in passing from tetrahydrofuran, and 1,2-dioxacyclopentane, to 1 are negligible (see ref 6).
- (13) Based on experimental IP's for 2,3-dioxabicyclo[2.2.1]heptane (8.99 eV), 2,3-dioxabicyclo[2.2.2]nonane (8.82 eV), 6,7-dioxabicyclo[3.2.2]nonane (8.97 eV), and 7,8-dioxabicyclo[4.2.2]decane (9.05 eV): D. J. Coughlin, R. S. Brown, and R. G. Salomon, unpublished work.
- (14) (a) D. A. Sweigart and D. W. Turner, *J. Am. Chem. Soc.*, **94**, 5599 (1972); (b) quoted value in R. Hoffmann, P. D. Mollère, and E. Heilbronner, *ibid.*, **95**, 4860 (1973).
- (15) Molecular models of 2 and 3 suggest that the ether n_o orbital is appropriately aligned to interact with a like symmetry "ribbon orbital" ^{14b} which could lead to the observed effect.

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An Exceedingly Short Quadruple Bond Involving Tungsten and the Enigma of Heteronuclear Metal-Metal Bonds with Multiple Bond Character

Sir:

In recent years there has been considerable interest in developing and understanding the chemistry of compounds with metal-metal bonds of multiple bond character. Especially compounds of Mo¹ and W,² having metal-metal triple bonds, and of Cr,³ Mo,^{4,5} Tc,^{4,6} and Re,^{4,7} having metal-metal quadruple bonds, have been intensely investigated. An important question raised by recent results concerns the ability of tungsten to participate in quadruple bonds, even though it is now well established that, like molybdenum, the tungsten atom can easily form stable triply bonded compounds.² Whereas a plethora of quadruply bonded molybdenum compounds have now been prepared and structurally characterized,^{4,5} only one compound providing unequivocal structural evidence of the W-W quadruple bond has been reported. In this case, Li₄W₂(CH₃)_{8-*x*} Cl_{*x*}·4THF,⁸ the W-W bond distance, 2.261 (2) Å, proved to be quite long compared with the bond distance of the closely related Mo₂(CH₃)₈⁴⁻, for which $d(\text{Mo-Mo}) = 2.147$ (2) Å.⁹ This comparison implies that the W-W quadruple bond should be much weaker than the corresponding Mo-Mo bond.

By contrast, our previous report¹⁰ of the Mo-W bond distance in [MoW[O₂CC(CH₃)₃]₄] I·CH₃CN, 2.194 (2) Å, with formal bond order 3.5, suggested that tungsten may enter into such bonds as strongly as molybdenum. This result, however, is somewhat indecisive since the bond order differs from 4.0 and the comparatively tight binding of the axial ligands, I and CH₃CN, exert an undetermined influence on the metal-metal bonding. We have now completed the structure determination of MoW[O₂CC(CH₃)₃]₄ in order to gain more definitive information.

The compound was prepared according to the previously reported procedure¹⁰ and crystals suitable for X-ray crystallographic examination were obtained after slow recrystalli-

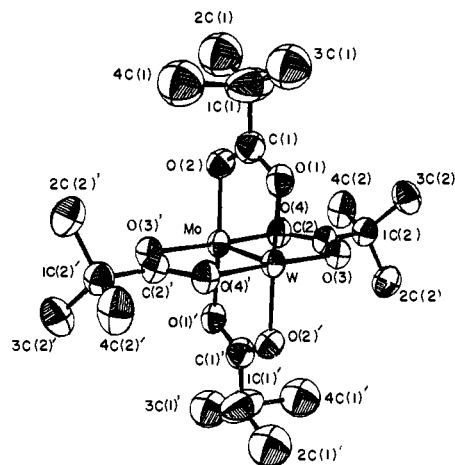


Figure 1. Structure and labeling scheme for the molecule MoW[O₂CC(CH₃)₃]₄. Thermal ellipsoids enclose 50% of the electron density. Metal positions are disordered and occupied with equal probability by either Mo or W.

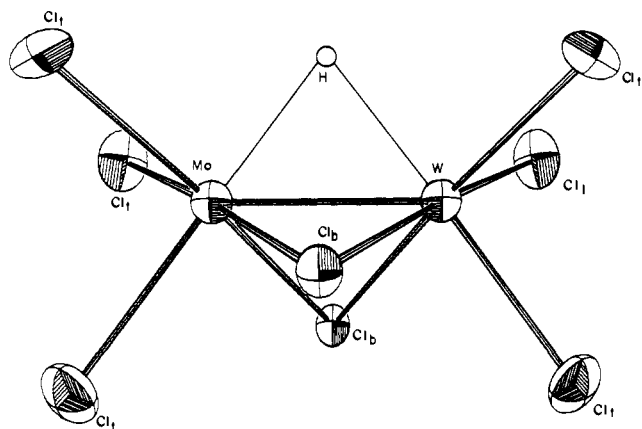


Figure 2. Structure of MoWCl₈H₃⁻ ion. Bridging Cl and H positions are statistically disordered in the real structure. Metal positions are occupied with equal probability by either Mo or W. Thermal ellipsoids enclose 50% of the electron density.

zation from acetonitrile. The crystal used for data collection provided the following unit cell information: triclinic; space group $P\bar{1}$; $Z = 1$; $a = 10.886$ (4), $b = 5.774$ (1), $c = 11.263$ (2) Å; $\alpha = 92.81$ (2), $\beta = 109.63$ (2), $\gamma = 89.61$ (2)°.

The molecular structure of MoW[O₂CC(CH₃)₃]₄ is shown in Figure 1.¹¹ Since the molecule occupies a site with inversion symmetry the metal positions are disordered and occupied with equal probability by either Mo or W. However previous work has shown that each molecule indeed contains one Mo and one W atom;¹⁰ so the disordering involves only statistical orientation of the molecules with respect to the direction of the Mo-W vector. Thus only average M-O distances can be obtained.¹²

The important and surprising result revealed by the structure determination is the remarkably short Mo-W bond distance of 2.080 (1) Å. This is 0.01 Å shorter than the average Mo-Mo distance of 2.092 ± 0.004 Å reported for several Mo₂(O₂CR)₄ derivatives, including Mo₂[O₂CC(CH₃)₃]₄.¹³ Only the Mo-Mo distance in Mo₂(DMP)₄,¹⁴ 2.064 (1) Å, is shorter. In terms of the "formal shortness" suggested by Cotton, Koch, and Millar,¹⁴ the Mo-W quadruple bond found here has the value 0.800 which is exceeded among metal-metal bonds only by Mo₂(DMP)₄ and Cr₂(DMP)₄ with values of 0.796 and 0.778, respectively. We conclude that tungsten can indeed form strong quadruple bonds and assert that other examples are likely to be found as work in this field continues.

Let one too quickly concludes that it is the heteronuclear

nature of the bond in the above case which leads to unusual bond strength we also offer the result of the structure analysis of $\text{Rb}_3\text{MoWCl}_8\text{H}$. The latter compound was prepared as described previously for $\text{Cs}_3\text{MoWCl}_8\text{H}^{15}$ and found to be isomorphous and isostructural with $\text{Rb}_3\text{Mo}_2\text{Cl}_8\text{H}^{16}$. Whereas the Mo-Mo triple bond in the latter compound has the distance 2.38 (1) Å, the Mo-W triple bond in the heteronuclear $\text{MoWCl}_8\text{H}^{3-}$ anion (Figure 2) has the distance 2.445 (3) Å.¹⁷ This result not only confuses the role of heteronuclearity in determining the net metal-metal bond strength but is doubly enigmatic because this distance is also greater than that in $\text{K}_3\text{W}_2\text{Cl}_9$, 2.41 Å.¹⁸ By contrast we see that, when one bridging H atom is substituted for Cl in $\text{Mo}_2\text{Cl}_9^{3-}$ to generate $\text{Mo}_2\text{Cl}_8\text{H}^{3-}$, there is a decrease from 2.66 to 2.38 Å in the Mo-Mo distance. Contraction of the metal-metal distance upon substitution of the smaller bridging H atom for the larger Cl atom is the expected result. To complete this comparison it would be desirable to obtain structural data for the presently unknown anions MoWCl_9^{3-} and $\text{W}_2\text{Cl}_8\text{H}^{3-}$. Attempts to prepare compounds containing the anions are underway in this laboratory.

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Supplementary Material Available: Positional and thermal parameters and structure factors for $\text{MoW}[\text{O}_2\text{CC}(\text{CH}_3)_4]_4$ and $\text{Rb}_3\text{MoWCl}_8\text{H}$ (13 pages). Ordering information is given on any current masthead page.

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- (12) Intramolecular M-O bond distances of 2.090 (7), 2.092 (6), 2.091 (7) and 2.106 (6) Å were obtained for the four crystallographically independent O atoms. The nearest intermolecular M-O distance of 3.05 (1) Å indicates extremely weak axial interactions of the type discussed recently by Cotton et al.¹³
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- (17) Crystals of $\text{Rb}_3\text{MoWCl}_8\text{H}$ are hexagonal: $a = 7.226$ (2), $c = 16.695$ (3) Å; space group $P6_2c$. Intensity data for reflections, 2θ (maximum) = 45° , were averaged providing 354 independent data with $l > 3\sigma(l)$. Since $\mu = 203.9 \text{ cm}^{-1}$, an absorption correction was applied. Using the initial positions of atoms in $\text{Rb}_3\text{Mo}_2\text{Cl}_8\text{H}$, refinement of the structure was initiated. Subsequent steps in the refinement cycles showed that the bridging Cl atoms were disordered as in $\text{Rb}_3\text{Mo}_2\text{Cl}_8\text{H}$ with the average weighting of $2/3$ Cl atom in each of the three bridging sites. Also the metal positions were found to be statistically occupied with equal probability by either Mo or W. Refinement converged with anisotropic thermal parameters for all atoms (H not included) to the final conventional discrepancy factors of $R = 0.071$ and $R_w = 0.081$. The following bond distances were found: $d(\text{Mo-W})$, 2.445 (3); $d(\text{M-Cl}_b)$, 2.492 (6); and $d(\text{M-Cl}_l)$, 2.397 (5) Å.
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Book Reviews

Gas Chromatography of Polymers. By V. G. BEREZKIN, V. R. ALISHOYEV, and I. B. NEMIROVSKAYA (Institute of Petrochemical Synthesis, Academy of Sciences of the U.S.S.R.). Elsevier North-Holland, Inc., New York, N.Y. 1977. xiii + 225 pp. \$41.95.

Both gas chromatography and polymer science are comparatively recent additions to the field of chemistry, and both have had major impacts on the subject. This book brings them together in a generally well-balanced and highly readable account. Extensive references are presented, particularly to the Russian literature, with some as recent as 1975.

The last two chapters, dealing with pyrolysis and inverse chromatography, respectively, are the high points of this book. Pyrolysis has long been recognized as a valuable technique for the identification of polymers. This discussion goes well beyond that aspect to include such applications as determining polymer crystallinity, degree of cross-linking, tacticity, and other topics.

Inverse chromatography is the technique in which the sample (a polymer) is used as the stationary phase in the column. Its structure is then examined by the manner in which various "probe" molecules are retained. An enormous amount of information can be obtained by this technique, and the authors present a wide-ranging account of many investigations in which it has been used.

Anyone involved in the study of polymer structure and reactions will find a great deal of thought-provoking material in this book. The discussion of any given technique is necessarily brief, but the reader is constantly confronted by ingenious applications and adaptations of the chromatographic separation process.

I feel that I must include one warning, however. Chapter 1, "Basic Principles of Gas Chromatography", should be carefully avoided. It is filled with factual errors, omissions, misleading statements, and inconsistencies. Several of the figures are mislabeled. This chapter has all the traits of something written hastily, edited poorly, and inserted at the last moment. It is of a totally different nature from the rest of the book and should not deter the reader from reading the remaining chapters, which are of very high quality.

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Thermal Analysis of Minerals. By DUMITRU N. TODOR. Translated by SERGIU MARCUS. Abacus Press, Tunbridge Wells, Kent, England (distributed by ISBS, Inc., Forest Grove, Ore.). 1976. 256 pp. \$32.50.

This book is a translation of the Romanian language edition which was first published in 1972. The first four chapters survey in about 100 pages the basic principles of thermal analysis, pertinent experi-