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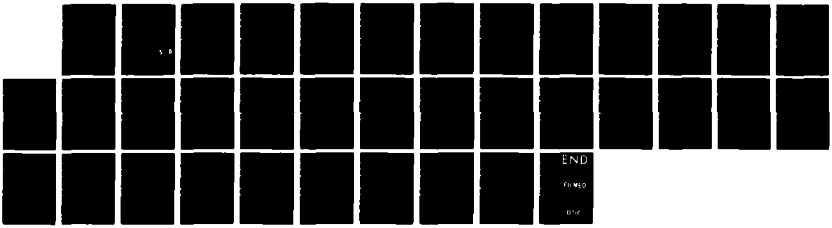

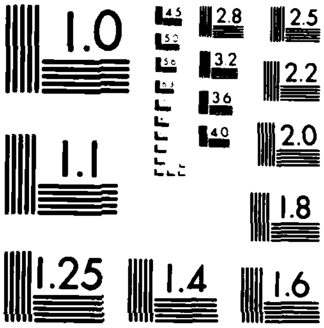

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COMPARATIVE STUDIES ON THE ELECTRONIC STRUCTURES OF $W_2(O_2CH)_4$ AND $W_2(O_2CH)_4(CH_3)_2$ BY THE RELATIVISTIC Xα-SW METHOD: A d^3-d^3 METAL DIMER WITH A QUADRUPLE METAL-METAL BOND?

by

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The bonding in $W_2(O_2CR)_4$ and in the recently characterized $W_2(O_2CR)_4R'_2$ molecules are compared via Xα-SW calculations with quasi-relativistic corrections on the model system $W_2(O_2CH)_4$ (I) and $W_2(O_2CH)_4(CH_3)_2$ (II). Several questions concerning the electronic structure of II have been addressed; in particular, the apparently strong W-W bond in the presence of strong W-C bonds was of interest. It has been found that II is best considered as a $W_2(O_2CH)_4$ fragment interacting with two CH_3 radicals, a description consistent with the photochemical decomposition of $W_2(O_2CEt)_4(CH_2Ph)_2$. The resulting W-W bond still retains the essential components of the quadruple bond in I. The W-W bonding remains strong in spite of strong axial ligation because of involvement of a higher-lying s-s σ bonding orbital, an orbital whose contribution is more important in II than in I. It is the presence of this orbital, which is lower-lying for third-row metals than for first, which is believed to account for the structural difference between $Cr_2(O_2CR)_4L_2$ and the $W_2(O_2CR)_4R'_2$ systems.

COMPARATIVE STUDIES ON THE ELECTRONIC STRUCTURES OF $W_2(O_2CH)_4$ AND $W_2(O_2CH)_4(CH_3)_2$ BY THE RELATIVISTIC Xα-SW METHOD: A d^3-d^3 METAL DIMER WITH A QUADRUPLE METAL-METAL BOND ?

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ABSTRACT

The bonding in $W_2(O_2CR)_4$ and in the recently characterized $W_2(O_2CR)_4R'_2$ molecules are compared via Xα-SW calculations with quasi-relativistic corrections on the model system $W_2(O_2CH)_4$ (I) and $W_2(O_2CH)_4(CH_3)_2$ (II). Several questions concerning the electronic structure of II have been addressed; in particular, the apparently strong W-W bond in the presence of strong W-C bonds was of interest. It has been found that II is best considered as a $W_2(O_2CH)_4$ fragment interacting with two CH_3 radicals, a description consistent with the photochemical decomposition of $W_2(O_2CEt)_4(CH_2Ph)_2$. The resulting W-W bond still retains the essential components of the quadruple bond in I. The W-W bonding remains strong in spite of strong axial ligation because of involvement of a higher-lying s-s σ bonding orbital, an orbital whose contribution is more important in II than in I. It is the presence of this orbital, which is lower-lying for third-row metals than for first, which is believed to account for the structural difference between $Cr_2(O_2CR)_4L_2$ and the $W_2(O_2CR)_4R_2$ systems.

INTRODUCTION

The rapid growth in the synthetic and structural chemistry of dinuclear transition metal complexes containing strong metal-metal bonds has provided a wealth of information about the nature of metal-ligand and metal-metal interactions.[2] The elegant story of the Cr-Cr quadruple bond as told by Cotton and Walton [3] beautifully emphasizes this point. The general conclusion gained through the structural studies of these Cr compounds is that it is not the electronic properties of the chelating ligands that determines the Cr-Cr bond lengths, but rather the presence or absence of axial ligands. Indeed, the unfailing occurrence of axial ligation in the dichromium tetracarboxylates and the enormous range of Cr-Cr distances has posed exceptional challenges to the theory of the electronic structure of these compounds. Numerous electronic structural calculations have appeared in the literature[3-10] over the past decade and both SCF-HF-CI and SCF-Xα-SW calculations have arrived at satisfactory descriptions of the Cr-Cr quadruple bond. For axial ligands, SCF-Xα-SW calculations[10] present the description that weak M-M σ bonding in the dichromium system results in a very low lying M-M σ^* orbital. Axial ligand donation into the σ^* orbital, as well as destabilization of the M-M σ orbital weakens and lengthens the Cr-Cr bond. It thus appears to be a general result that axial ligation weakens and lengthens the Cr-Cr quadruple bond. However, it is not safe to assume that axial ligation weakens and lengthens metal-metal bonds in general. The dirhodium tetracarboxylates have strong metal-metal bonds *and* axial ligation. We are in need of new structural data in order to gain better insight into the problem.

The recent addition of the ditungsten (II) tetracarboxylates[11-15] is not only of historical interest, but contributes structural data and new challenges with which to test and expand our theories about axial ligation. One of the most fascinating new structural developments in this area is the recent report by Chisholm and coworkers of a new class of d^3-d^3 dimer where strong axial ligation is observed to a ditungsten tetracarboxylate center, and results in extremely short W-W distances.[16] These new compounds, bis(alkyl) tetra(carboxylato) ditungsten (III), $W_2R_2(O_2CR')_4$ (R = CH_2Ph or CH_2Bu^t, and R' = Et) are well characterized in the solid state as having the centrosymmetric structure depicted in Figure 1.

The striking structural feature of these compounds is that the W-W distance of 2.19 Å and the parameters of the central $W_2(O_2CEt)_4$ core are essentially identical to those seen in $W_2(O_2CEt)_4$ ($W\overset{=}{-}W$).[15] The obvious question raised by this data is how (or why) does this molecule exist with strong metal-metal bonding, and strong metal-ligand bonding (W-C = 2.19 Å) in the axial position

In the initial report,[16] extended-Huckel calculations predicted a $\pi^4\delta^2$ electronic configuration for these compounds which did not provide a satisfactory explanation for the shortness of the W-W bond. It was suggested that s, p_z and d_{z^2} mixing could lead to a $\pi^4\sigma^2$ configuration more in accord with the shortness of the observed bond length.[17] It is apparent, however, that for any molecule containing atoms of such high atomic number as tungsten, valence corrections for relativistic effects, which can amount to an electron volt, are likely to be important towards gaining a satisfactory model for the electronic structure of such compounds.

In response to the situation just described we have carried out, and report here, the results of comparative, relativistic SCF-Xα-SW calculations on $W_2(O_2CH)_4$ and $W_2(O_2CH)_4(CH_3)_2$. The details of performing a calculation on a species of low symmetry (C_{2h}) will be presented, and the effect of relativistic corrections will be discussed and demonstrated to play an important role in the description of the electronic structure of these compounds. It will further be shown that the results are consistent with strong W-W bonding in the presence of the strongly σ-donating CH_3 groups in the axial positions. Finally, we will comment on the relationship of our calculations to those previously reported for other $M_2(O_2CH)_4$ and $M_2(O_2CH)_4L_2$ systems and try to formulate some general conclusions about axial ligation.

COMPUTATIONAL PROCEDURES

Initial Parameters

The W-W and W-C bond lengths used in the calculation of the electronic structure of $W_2(O_2CH)_4(CH_3)_2$ were taken from the crystal structure of $W_2(O_2CEt)_4(CH_2Bu^t)_2$.[16] The $W_2(O_2CH)_4$ fragment was idealized to D_{4h} point symmetry while the entire molecule was idealized to C_{2h} point symmetry with the two CH_3 groups oriented in an axially staggered geometry. The bond lengths and angles of the $W_2(O_2CH)_4$ fragment are within the ranges of structural parameters generally found in ditungsten tetracarboxylato compounds.[11-15] The bond lengths and angles used in the calculation are summarized in Table I.

An initial molecular charge density and potential were constructed from a superposition of Herman-Skillman[18] neutral charge densities for W, O, C and H. The α exchange parameters were taken from Schwarz[19] with the tungsten α value extrapolated to 0.69319. A valence-electron weighted average of atomic α values was used for the inter- and outer-sphere regions. Overlapping atomic sphere radii were taken to be 89% of the atomic number radii in accordance with the nonempirical procedure of Norman.[20] The outer sphere was made tangential to the outermost atomic spheres. The sphere radii and α parameters used are summarized in Table I.

The symmetry adapted linear combinations of atomic orbitals for all calculations (D_{4h} and C_{2h}) included s, p, d and f type spherical harmonics on the tungsten atoms, s and p on C and O atoms, s on H atoms, and spherical harmonics through $l = 9$ on the outer sphere. Core energy levels were never frozen; in each iteration they were calculated explicitly using only the surrounding atomic-sphere potential for the atom in question.

The iteration to self-consistency on $W_2(O_2CH)_4$ was started nonrelativistically using a 5% mixing of the new potential into the old to generate the starting potential for the next iteration. This mixing was gradually increased to a maximum value of 15% as the calculation neared convergence, which was assumed when the maximum shift in the potential from one iteration to the next was less than 0.0010 Ry. The virial ratio (-2T/V) at convergence was 1.00011.

The converged nonrelativistic potential of $W_2(O_2CH)_4$ was used as a starting potential for the relativistic calculation. The formalism of Wood and Boring [21] was used to incorporate the relativistic effects. The core levels of all atoms and the valence levels of tungsten explicitly included these effects which were slowly mixed into the potential over 10 iterations. The virial ratio at convergence increased to 1.0447 as a consequence of the relativistic formalism. This converged relativistic potential was used as a starting potential for the $W_2(O_2CH)_4$ fragment in $W_2(O_2CH)_4(CH_3)_2$. Likewise, an $X\alpha$ calculation was performed on "elongated" ethane using the same outer sphere radii, spherical harmonics and outer sphere α value as was used in $W_2(O_2CH)_4$. This amounted to having two CH_3 fragments in a staggered D_{3d} geometry with the same C-C distance as in the $W_2(O_2CH)_4(CH_3)_2$ molecule. This calculation was converged nonrelativistically and the converged potential was used as a starting potential for the $(CH_3)_2$ fragment in $W_2(O_2CH)_4(CH_3)_2$.

Executing the calculation in this manner is not only convenient, but very important in terms of establishing a one-to-one correspondence of the energy levels of $W_2(O_2CH)_4$ from higher to lower symmetry. This minimizes the possibility of "missing" an energy level in the energy search, a pervasive problem in Xα-SW calculations on low-symmetry systems.

RESULTS AND DISCUSSION

$W_2(O_2CH)_4$

The results of our nonrelativistic and relativistic calculations are compared in Figure 2 and Table II for the occupied valence and lowest virtual orbitals of $W_2(O_2CH)_4$. The bonding characteristics of the molecular orbitals of $W_2(O_2CH)_4$ are essentially the same as for $Mo_2(O_2CH)_4$ and have been discussed at length by Norman, et al.[22] We will focus our discussion on those orbitals primarily responsible for metal-metal σ bonding. Xα-SW calculations of $M_2(O_2CH)_4$ systems in general yield two components of the metal-metal σ bond, the $4a_{1g}$ and $5a_{1g}$ molecular orbitals. One can envision the formation of these orbitals as being derived from interaction of the nearly pure d_{z^2} σ_g orbital of a W_2^{4+} fragment with the lone pairs of the four formate ligands. This results in the formation of the $4a_{1g}$ and $5a_{1g}$ molecular orbitals of $W_2(O_2CH)_4$ which are W-O bonding and antibonding respectively (c.f. Figures 3 and 4 and Figure 3 of ref. 22). It should be noted that to a first approximation, since both the $4a_{1g}$ and $5a_{1g}$ molecular orbitals are occupied, this interaction will have no effect on the metal-metal σ bond. However, there is a second process occurring in these a_{1g} interactions which can contribute to a net stabilization of the W-W and W-L bonding, namely the involvement of virtual W 6s orbitals. In the relativistic calculations the $5a_{1g}$ orbital has 69% W character of which 38% is W s. This mixing of virtual W s character into the $5a_{1g}$ orbital has several important ramifications. First, it mitigates the W-O antibonding character of the orbital; and second it adds to the net W-W σ bonding, an effect which increases in importance when relativistic corrections are applied, as will be discussed below.

We believe that this additional s character, in conjunction with better W–L overlap due to the greater orbital extension of the 5d than either the 4d or 3d orbitals, leads to the conclusion that the M–L bonding in the W complex should be stronger and more covalent than either the Mo or Cr systems. The W–O bond lengths of 2.085 Å are shorter than the oberved Mo–O distances of 2.11 Å, consistent with this view. The $4a_{1g}$ molecular orbital is 51% W in character of which 93% is W d. We feel that it is this $4a_{1g}$ component that makes the major contribution to the W–W σ bond (see Figure 3, and Figure 2 of ref. 22). Qualitatively we have the expected metal–metal quadruple bond of electronic configuration $\sigma^2\pi^4\delta^2$, although it must be emphasized that discussing the configuration in this manner is somewhat of an oversimplification.

Relativistic Corrections on $W_2(O_2CH)_4$

The relativistic corrections cause large energy shifts in the tungsten core levels and similar shifts in valence orbitals containing significant tungsten character, while, as expected, the primarily O–, C–, and H–based molecular orbitals are scarcely effected. The observed differential shifts are similar in magnitude to those observed in previous molecular calculations using this relativistic formalism.[23-25]

The changes induced in the bonding picture upon the inclusion of relativistic effects are consistent with the expected influence of mass–velocity corrections on the W atomic orbitals.[26] The inner s–orbitals, having the highest classical velocities, are the most profoundly effected orbitals. The relativistic mass increase results in a contraction of all of the s–orbitals with a concomitant decrease in their orbital energies. This effect is mimicked by the p–orbitals although both the contraction and stabilization of these are less pronounced than for the the s-orbitals. The metal d- and f electrons, which have a much smaller probability of attaining a classical velocity close to c, are primarily influenced by the contraction of the s- and p-orbitals. The contraction of these latter orbitals results in an expansion and rise in energy of the d and f orbitals, i.e. the reverse of the effect seen for the s-orbitals.

In Figure 2, it is seen that the relativistic shifts in the orbital energy are in the expected direction. The valence levels containing significant W 5d character rise in energy with the exception of the $5a_{1g}$ orbital; without relativistic corrections this orbital has 17% W s and 38% W d character, and the substantial s character in this orbital causes it to drop in energy upon the inclusion of relativistic effects. A similar result has been observed in a recent Dirac scattered-wave (DSW) treatment of $W_2Cl_8^{4-}$ in which the relativistic effects are treated more properly using four-component spinors.[27] We find it encouraging that the quasi-relativistic corrections employed here mimic the effects on the orbital energies which are found under a more complete treatment.

Upon stabilization, the $5a_{1g}$ orbital acquires significantly more W s character (26%) and somewhat less W d character (36%). The s orbital contribution to this orbital represents a mixing of the 6s-6s σ bonding orbital, normally unoccupied, with the 5d-5d σ bonding orbital. This s-s σ bonding orbital is important in explaining the extremely short bond distances found for naked metal diatomics such as Mo_2[28,29] and we believe it serves a major role in the shortness of the W-W bond in the $W_2(O_2CR)_4)R_2$ systems.

$W_2(O_2CH)_4(CH_3)_2$

The correlation of the molecular orbitals of $W_2(O_2CH)_4(CH_3)_2$ with those of its component fragments $W_2(O_2CH)_4$ and $(CH_3)_2$ are shown in Figure 5. The energy levels of $W_2(O_2CH)_4$ and $(CH_3)_2$ do not represent the self consistent levels of these two neutral fragments. Rather, we have obtained orbital energies appropriate for direct comparison to those in the $W_2(O_2CH)_4(CH_3)_2$ complex in the following manner: Following the convergence of the relativistic potential of $W_2(O_2CH)_4(CH_3)_2$, the $W_2(O_2CH)_4$ and $(CH_3)_2$ portions of the potential were searched separately for energy levels under C_{2h} symmetry. The resulting energy levels, shown in Figure 5, represent the levels of the $W_2(O_2CH)_4$ and $(CH_3)_2$ fragments in the same potential as the entire molecule and is thus a method for constructing a molecular orbital correlation diagram using the Xα method.

The first feature evident in Figure 5 is that the M-M π, δ, δ^* and π^* levels, as well as the M-L and formate levels in $W_2(O_2CH)_4(CH_3)_2$ are essentially unperturbed by interaction of $W_2(O_2CH)_4$ with axial ligands. Secondly, the six C-H bonding levels in $(CH_3)_2$ $(2a_g + a_u + b_g + 2b_u)$ were found to be entirely noninteracting with the rest of the molecule. Therefore, we shall concentrate our discussion on the $W-CH_3$ σ interaction and its effect on M-M σ bonding. The $W-CH_3$ interaction manifests itself in two parts, an a_g and b_u interaction.

The $(CH_3)_2$ a_g orbital interacts most strongly with the $5a_{1g}$ orbital of the $W_2(O_2CH)_4$ molecule, this interaction being both energetically and spatially favored over that with the $4a_{1g}$ orbital. This interaction results in formation of the W-C σ bonding $13a_g$ and σ antibonding $16a_g$ molecular orbitals of $W_2(O_2CH)_4(CH_3)_2$ which are occupied and unoccupied, respectively. That the $13a_g$ and $16a_g$ molecular orbitals are derived from interaction with the $5a_{1g}$ orbital of $W_2(O_2CH)_4$ is readily seen by the comparison shown in Figure 4. The filled $13a_g$ orbital has 35% W character (Table III) of which 63% is W s. As was the case for its $5a_{1g}$ precursor, the W s character adds to M-M σ bonding although the M-M overlap is much less than was observed in the $5a_{1g}$ orbital of $W_2(O_2CH)_4$. Perhaps the single most important observation in the overall a_g interaction is that the $4a_{1g}$ molecular orbital of $W_2(O_2CH)_4$ is actually stabilized by the interaction and picks up 10% more W character (66% W, 90% d) to give the $10a_g$ molecular orbital of $W_2(O_2CH)_4(CH_3)_2$. Other than that, the $4a_{1g}$ orbital is essentially unperturbed by the axial a_g interaction and can be described as both M-M σ and M-L σ bonding. Comparison of these orbitals in Figure 3 illustrates this point rather nicely. It is important to recall that the $4a_{1g}$ molecular orbital is the major contributor to M-M σ bonding in $W_2(O_2CH)_4$. The fact that this orbital is actually stabilized by the a_g interaction means that the $W_2(O_2CH)_4(CH_3)_2$ system actually has a filled molecular orbital involved in strong M-M σ bonding.

The $(CH_3)_2$ b_u orbital interacts with the $5a_{2u}$ M-M σ^* orbital of $W_2(O_2CH)_4$ generating the W-C σ bonding and antibonding orbitals which are occupied and unoccupied respectively (Figure 6 and Table III). The filled $15b_u$ orbital is 49% C and 23% W of which, this small amount of W character is allocated between s, p and d angular contributions. This orbital is primarily M-L σ bonding but has some M-M σ^* character as well.

For $W_2(O_2CH)_4(CH_3)_2$ we are presented with the rather peculiar result of strong M-M bonding in consort with strong M-L bonding in the axial position. This result is perhaps counterintuitive in light of the chemistry of Cr-Cr quadruple bonds, wherein the bonding of axial ligands both weakens and lengthens the M-M bond. The strong W-W and W-C bonding in $W_2(O_2CH)_4(CH_3)_2$ is the result of several factors. 1) The first important M-M bond weakening upon axial ligation results from ligand donation into the M-M σ^* orbital. For the present calculation, the magnitude of this donation can be gauged by the amount of M-M σ^* character found in occupied orbitals of b_u symmetry. Figure 6 and Table III suggest that the amount of M-M σ^* character in the $15b_u$ orbital is rather small, and thus the M-M bond is not significantly weakened by the interaction. 2) The $4a_{1g}$ orbital of $W_2(O_2CH)_4$, which comprises the major component of the 5d-5d σ bond, is scarcely affected by the axial ligation and thus remains a strong, occupied component of W-W σ bonding in $W_2(O_2CH)_4(CH_3)_2$. 3) The major interaction of the a_g orbital of $(CH_3)_2$ is with the $5a_{1g}$ orbital of $W_2(O_2CH)_4$, resulting in a significant contribution of the W 6s orbitals in both the W-W and W-C σ bonding.

The importance of these last two points needs some amplification. If the s-s σ bonding orbital is unimportant, as it most certainly is in Cr-Cr quadruply bonded complexes, the interactions of both the symmetric and antisymmetric $(L)_2$ orbitals with a M-M quadruple bond must necessarily weaken the M-M bond. The antisymmetric combination donates into the M-M σ^* orbital, an interaction which obviously will weaken the M-M σ bond. The symmetric combination will participate in a "filled-filled" interaction with the M-M σ bond, resulting in M-L bonding and antibonding orbitals which are occupied and unoccupied, respectively. Thus a portion of the M-M σ bond is found in unoccupied orbitals, again weakening the M-M interaction. The importance of the s-s σ bonding orbital in tungsten systems, which is due in large part to the relativistic stabilization of the W 6s orbitals, is that it provides another mechanism by which the symmetric $(L)_2$ orbital can interact with the dimetal core. As is apparent in the character of the $13a_g$ orbital of $W_2(O_2CH)_4(CH_3)_2$, the s-s σ bond is the principal M-M contribution in the interaction with the symmetric (a_g) $(CH_3)_2$ orbital, and that the participation of the s-s σ bonding orbital interaction is greater in $W_2(O_2CH)_4(CH_3)_2$ than in $W_2(O_2CH)_4$. Thus, the M-M weakening "filled-filled" interaction described above is effectively replaced by a "filled-empty" interaction which actually increases the amount of σ bonding between the metal centers.

In view of the above factors, it becomes increasingly difficult to describe the bonding in terms of a simple electronic configuration. It was shown, for example, that in $M_2(O_2CH)_4$ systems the M-M σ bonding character is really allocated among two orbitals, and for W, appreciable s character becomes mixed in. This makes description of the electronic configuration in terms such as $\sigma^2\pi^4\delta^2$ an oversimplification. The description of the electronic configuration of $W_2(O_2CH)_4(CH_3)_2$ in these terms is really not possible. Formally the molecule might be considered as having a W_2^{6+} core, thus a d^3-d^3 dimer. Yet this description is not adequate since the molecule clearly has occupied molecular orbitals of M-M σ, π and δ symmetry; effectively, the CH_3 groups are not behaving as anionic ligands but rather appear to be axial one-electron donors. Thus, we offer the following alternative description. The bonding is consistent with a neutral $W_2(O_2CR)_4$ moiety interacting with two alkyl radicals. The major W-C interaction occurs via CH_3 donation into the M-M σ^* and empty s-s σ orbitals of $W_2(O_2CH)_4$, and thus, to a first approximation, the M-M bond order is still four. This description is consistent with the observed insensitivity of the W-

W bond length and also with the experimental observation[16] that $W_2(CH_2Ph)_2(O_2CEt)_4$ upon photolysis in hydrocarbon solvents, yields $W_2(O_2CEt)_4$ and dibenzyl by homolytic cleavage of a W-C bond.

An intriguing possibility suggested by our calculations relates to the bonding in $W_2(O_2CR)_4L_2$ systems where L is a neutral two-electron donor ligand such as PPh_3 or an oxygen donor ligand such as THF. If the ligand-metal interactions are similar to those of CH_3 with W, a possibility which seems likely for a strong donor ligand such as a phosphine, the resulting electronic configuration would be $\sigma^2\pi^4\delta^2\delta^{*2}$, i.e. a W-W triple bond bearing a striking electronic similarity to d^5-d^5 triple bonds such as those based on the Re_2^{4+} core.[3]

It is important to emphasize that the types of interactions seen here between axial ligands and an $M_2(O_2CR)_4$ framework have been observed previously for $M_2(O_2CR)_4L_2$ systems.[10,30-32] The magnitude of the interactions are apparently quite variable, however, as exemplified by previous Xα-SW calculations on $Rh_2(O_2CH)_4$,[32] $Rh_2(O_2CH)_4(H_2O)_2$,[32] and $Rh_2(O_2CH)_4(PH_3)_2$.[30] In these systems, the dominant Rh-L interaction is ligand donation into the Rh-Rh σ^* orbital. We find this interaction to be less important in the tungsten system, a result which is doubtless dependent on the accessability of the s-s σ bonding orbital. It is the contribution of this orbital which we believe will be largely responsible for the electronic structural differences between first-row and third-row multiply metal-metal bonded systems.

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REFERENCES

1. a) Ohio State University; b) Indiana University; c) 1983/84 Indiana University SOHIO fellow.
2. Cotton, F.A. *Acc. Chem. Res.*, **1978**, 11, 225.
3. Cotton, F.A.; Walton, R.A. "Multiple Bonds Between Metal Atoms", Chapter 4, John Wiley and Sons, New York, 1982.
4. Benard, M. *J. Am. Chem. Soc.*, **1978**, 100, 2354.
5. Benard M.; Veillard, A. *Nouv. J. Chim.*, **1977**, 1, 97.
6. Garner, C.D.; Hillier, I.H.; Guest, M.F.; Green, J.C.; Coleman, A.W. *Chem. Phys. Lett.*, **1976**, 41, 91.
7. Cotton, F.A.; Stanley, G.G. *Inorg. Chem.*, **1977**, 16, 2668.
8. Guest, M.F.; Hillier, I.H.; Garner, C.D. *Chem. Phys. Lett.*, **1977**, 48, 587.
9. Benard, M. *J. Chem. Phys.*, **1979**, 71, 2546.
10. Bursten, B.E.; Cotton, F.A.; Stanley, G.G., results to be published.
11. Sattelberger, A.P.; McLaughlin, K.W.; Huffman, J.C. *J. Am. Chem. Soc.*, **1981**, 103, 2880.
12. Santure, D.J.; McLaughlin, K.W.; Huffman, J.C.; Sattelberger, A.P. *Inorg. Chem.*, **1983**, 22, 1877.
13. Santure, D.J.; Huffman, J.C.; Sattelberger, A.P. *Inorg. Chem.*, **1984**, 23, 938.
14. a) Cotton, F.A.; Wang, W. *Inorg. Chem.*, **1982**, 21, 3859.
    b) ibid, **1984**, 23, 1604.
15. Chisholm, M.H.; Chiu, H.T.; Huffman, J.C. *Polyhedron*, **1984**, 3(6), 759.

16. Chisholm, M.H.; Hoffman, D.M.; Huffman, J.C.; Van Der Sluys, W.G.; Russo, S. *J. Am. Chem. Soc.*, **1984**, *106*, 5386.

17. It is well established that the δ component adds little to the strength of a M-M quadruple bond. See for example, Cotton, F.A. *Chem. Soc. Rev.*, **1983**, *12*, 35.

18. Herman, F.; Skillman, S. "Atomic Structure Calculations," Prentice-Hall: Englewood Cliffs, N.J., 1963.

19. Schwarz, K. *Phys. Rev. B*, **1972**, *5*, 2466.

20. Norman, J.G.,Jr.; *Chem. Phys.*, **1974**, *61*, 4630.

21. Wood, J.H.; Boring, M.A. *Phys. Rev. B*, **1978**, *18*, 2701.

22. Norman, J.G., Jr; Kolari, H.J. *J. Am. Chem. Soc.*, **1978**, *100*, 791.

23. Bursten, B.E.; Cotton, F.A.; Fanwick, P.E.; Stanley, G.G. *J. Am. Chem. Soc.*, **1983**, *105*, 3082.

24. Bursten, B.E.; Cotton, F.A.; Green, J.C.; Seddon, E.A.; Stanley, G.G. *J. Am. Chem. Soc.*, **1980**, *102*, 955.

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

26. Many excellent reviews exist, see for example a) Pitzer, K.S. *Acc. Chem. Res.*, **1979**, *12*, 271; b) Pyykko, P.; Desclaux, J. *Acc. Chem. Res.*, **1979**, *12*, 276; c) Snijders, J.G.; Pyykko, P. *Chem. Phys. Lett.*, **1980**, *75*, 5; d) Ziegler, T.; Snijders, J.G.; Baerends, E.J. *Chem. Phys. Lett.*, **1980**, *75*, 1.

27. Arratia-Perez, R.; Case, D.A. *Inorg. Chem.*, **1984**, *23*, 3271.

28. Bursten, B.E.; Cotton, F.A. *Symp. Faraday Soc.*, **1980**, *14*, 180.

29. Bursten, B.E.; Cotton, F.A.; Hall, M.B. *J. Am. Chem. Soc.*, **1980**, *102*, 6348.

30. Bursten , B.E.; Cotton, F.A. *Inorg. Chem.*, **1981**, *20*, 3042.

31. Norman, J.G., Jr.; Renzoni, G.E.; Case, D.A. *J. Am. Chem. Soc.*, **1979**, *101*, 5256.

32. Norman, J.G., Jr.; Kolari, H.J. *J. Am. Chem. Soc.*, **1978**, *100*, 791.

Table 1: Bond Lengths and Angles, Atomic Sphere Radii, and Statistical Exchange Parameters for $W_2(O_2CH)_4(CH_3)_2$.

Atoms	Length, Å	Atoms	Angle, degree
W-W	2.186	W-W-O	90.5
W-C	2.190	W-O-C	118.6
W-O	2.085	O-C-H	119.2
O-C	1.270	W-W-C	180.0
C-H[a]	1.090	W-C-H	113.2
C-H[b]	1.090	H-C-H	109.0

Atom	sphere radius, bohr	α
Outer Sphere	8.4988	0.74519
W	2.4710	0.69319
O	1.6876	0.74447
C[a]	1.5787	0.75923
H[a]	1.2963	0.77725
C[b]	1.8143	0.75923
H[b]	1.2895	0.77725

[a] formate

[b] alkyl

Table 2: Upper Valence Molecular Orbitals of $W_2(O_2CH)_4$

level[a]	Energy eV	% Contributions[b]				W Angular Contributions[c]			
		W_2	$(O_2CH)_4$	INT	OUT	s	p	d	f
A. Nonrelativistic Calculation									
$5a_{2u}$	-1.5526	41	5	37	16		5	92	3
$4a_{2u}$	-3.4673	24	3	64	8	5	18	74	3
$5e_g$	-4.3453	81	4	15	0		1	97	2
$2b_{1u}$	-5.1993	78	12	9	0			100	
$2b_{2g}$	-6.6775	73	10	16	0			100	
$6e_u$	-8.6564	74	15	10	0			98	2
$5a_{1g}$	-9.7335	59	35	6	0	29	6	63	2
$1a_u$	-10.1293	0	84	15	0				
$4e_g$	-10.2099	4	81	14	0				
$5e_u$	-10.2436	15	72	12	1		24	72	4
$3e_g$	-10.5364	1	81	18	0				
$3a_{2u}$	-10.7882	7	77	15	0				
$3b_{2u}$	-11.1002	12	76	12	0			99	1
$1b_{1u}$	-11.4074	10	68	22	0			100	
$4b_{1g}$	-11.7065	21	67	11	1			99	1
$4a_{1g}$	-11.9946	54	42	3	0		3	94	3

Table 2 continued

B. Relativistic Calculation

$5a_{2u}$	-1.3865	40	4	38	17		6	91	3
$4a_{2u}$	-3.6441	22	3	67	8	13	23	61	3
$5e_g$	-3.8910	79	4	17	0		1	97	2
$2b_{1u}$	-4.7354	79	11	10	0			100	
$2b_{2g}$	-6.2695	72	10	17	0			100	
$6e_u$	-8.2742	78	11	11	0			100	
$1a_{1u}$	-10.1927	0	84	15	0				
$4e_g$	-10.3101	3	81	14	0				
$5e_u$	-10.3792	12	69	12	1		34	60	6
$3e_g$	-10.6111	1	81	18	0				
$5a_{1g}$	-10.9982	69	27	4	0	38	8	52	2
$3a_{2u}$	-10.9984	8	77	15	0				
$3b_{2u}$	-11.1035	11	76	12	0			99	1
$1b_{1u}$	-11.4174	9	69	22	0				
$4b_{1g}$	-11.6596	19	68	11	1			7	93
$4a_{1g}$	-11.8552	51	45	3	0		3	93	4

[a] HOMO is the $2b_{2g}$ orbital

[b] INT = intersphere and OUT = outersphere charge contributions

[c] Listed only for levels which have 10% or more W contribution

Table 3: Upper Valence Molecular Orbitals of $W_2(O_2CH)_4(CH_3)_2$ (Relativistic)

Level[a]	Energy eV	% Contributions[b]					W Angular Contributions[c]			
		W_2	$(O_2CH)_4$	$(CH_3)_2$	INT	OUT	s	p	d	f
$17a_g$	-3.337	83	3	3	12	0		1	97	2
$9b_g$	-3.338	83	3	3	12	0		1	97	2
$16a_g$	-3.978	31	1	51	12	4	1	49	39	11
$10a_u$	-4.488	78	12	0	10	0			100	
$8b_g$	-6.063	71	11	0	18	0			100	
$15b_u$	-6.854	23	1	54	19	3	14	25	55	6
$14b_u$	-7.886	76	10	5	10	0			97	3
$9a_u$	-7.888	76	10	5	10	0			97	3
$8a_u$	-9.969	0	84	0	15	0				
$15a_g$	-10.027	3	79	4	13	0				
$7b_g$	-10.041	3	79	4	13	0				
$13b_u$	-10.079	10	57	2	12	1	2		98	
$7a_u$	-10.093	10	57	2	12	1	2		98	
$6b_g$	-10.396	1	80	0	18	0				
$14a_g$	-10.409	1	80	0	18	0				
$12b_u$	-10.774	8	77	0	15	0				
$11b_u$	-10.864	11	76	0	13	0			99	1
$13a_g$	-11.050	35	45	7	11	1	63	6	30	1
$12a_g$	-11.165	2	4	88	4	2				
$5b_g$	-11.171	2	4	88	4	2				
$6a_u$	-11.175	5	22	61	9	1				

Table [illegible] continued

$10b_u$	-11.201	4	2	87	4	2				
$5a_u$	-11.265	7	47	26	17	1				
$11a_g$	-11.379	19	57	0	11	1			99	1
$10a_g$	-11.749	66	23	9	0	1	4	3	90	3

[a] HOMO is the $8b_g$ orbital

[b] INT = intersphere and OUT = outersphere charge contributions

[c] Listed only for levels which have 10% or more W contribution

CAPTIONS TO FIGURES

Figure 1: An ORTEP view of the centrosymmetric $W_2(CH_2Ph)_2(O_2CEt)_4$ molecule from reference 16.

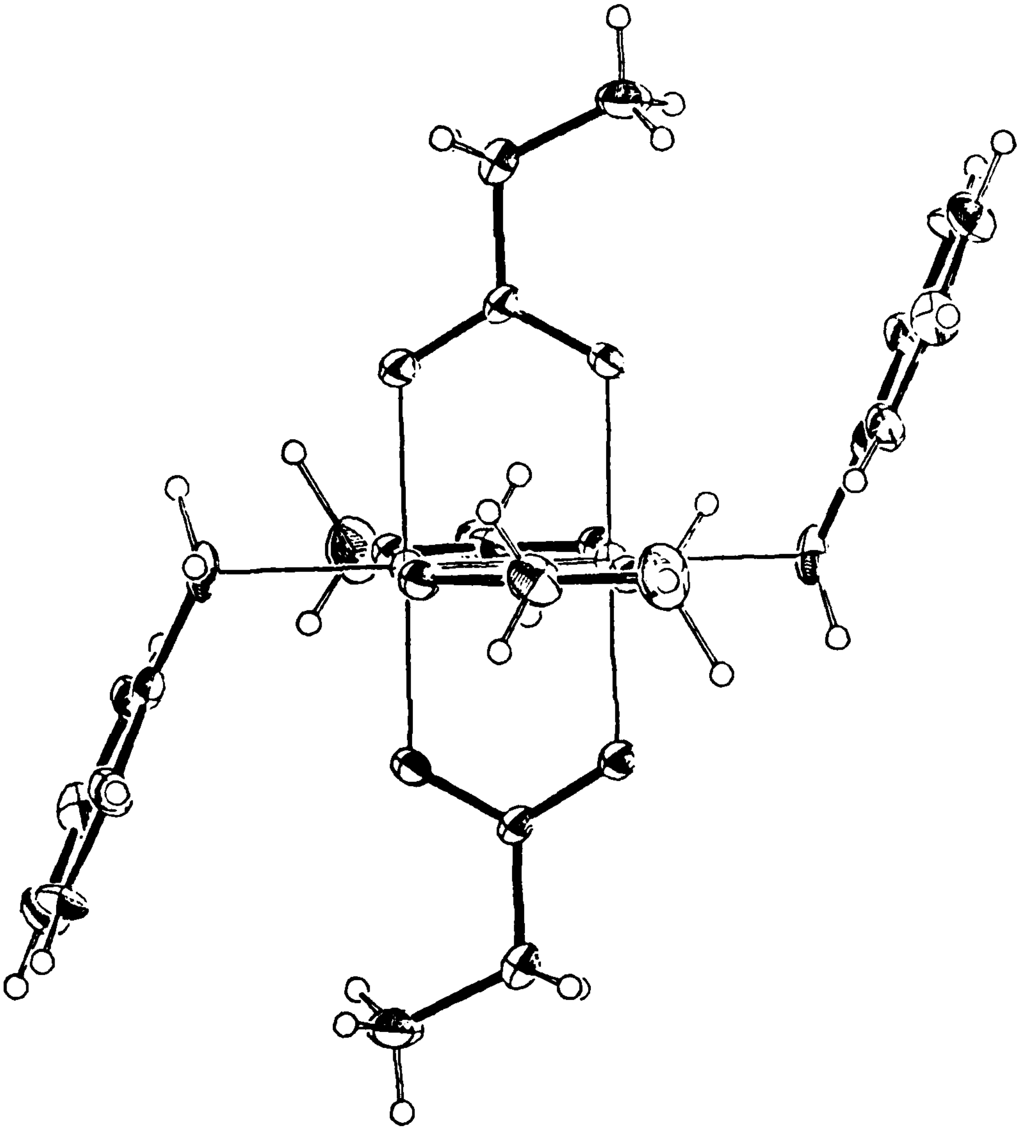
Figure 2: Nonrelativistic and relativistic converged $X\alpha$-SW eigen values for $W_2(O_2CH)_4$. Primarily W-based levels are in bold face along with their percentage of W contribution.

Figure 3: Comparison of contour plots of the $4a_{1g}$ molecular orbital of $W_2(O_2CH)_4$ and the $10a_g$ molecular orbital of $W_2(O_2CH)_4(CH_3)_2$. These plots and all subsequent plots are in the horizontal mirror plane containing the W atoms, two of the formate ligands, the axial C atoms, and two of the C-H bonds. Contour values for this and subsequent plots are ±1, ±2, ±3, ±4 = ±0.02, ±0.04, ±0.08, ±0.16 e/Å^3, respectively.

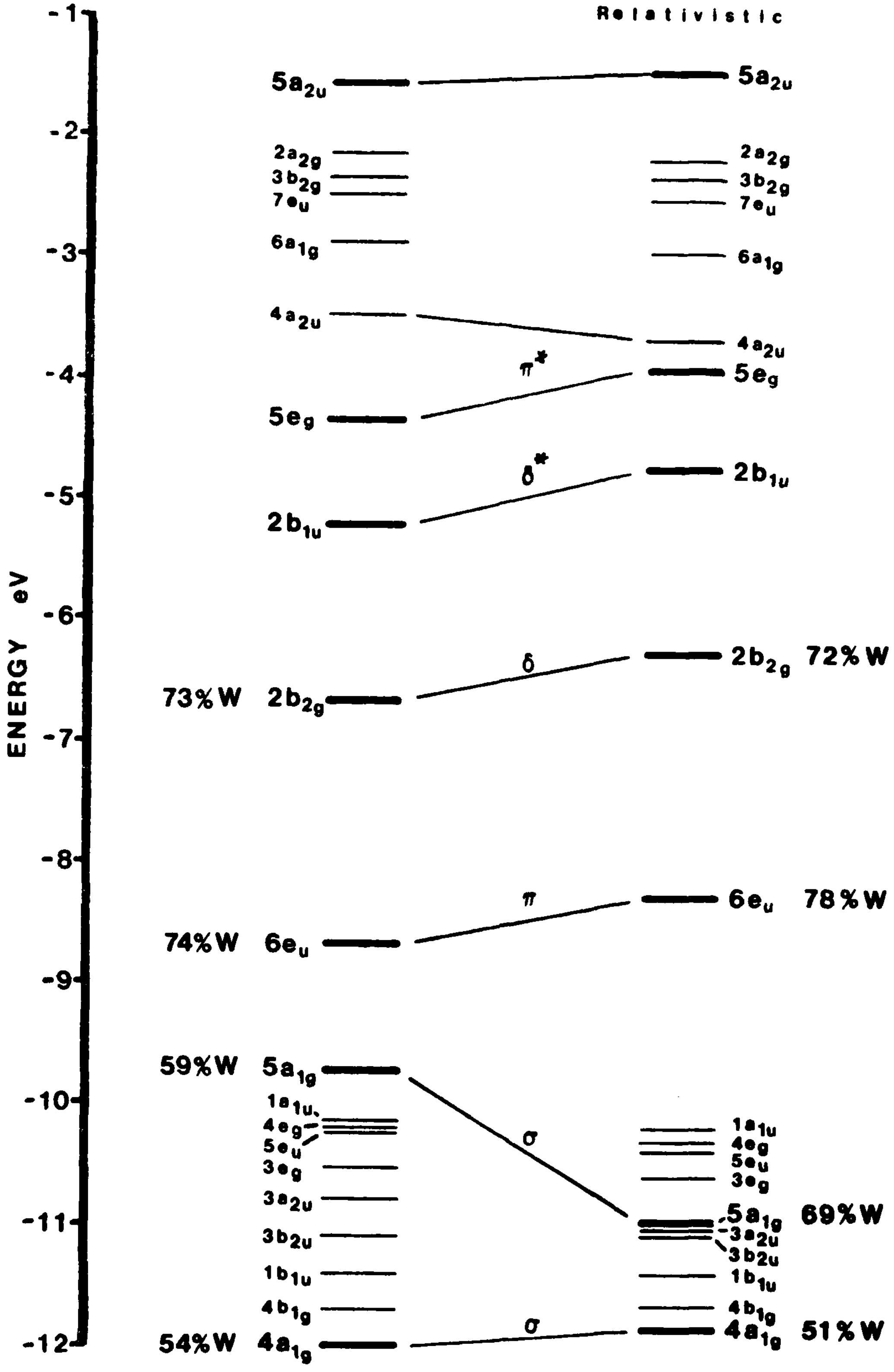
Figure 4: Contour plots of the $5a_{1g}$ orbital of $W_2(O_2CH)_4$ and the $13a_g$ and $16a_g$ orbials of $W_2(O_2CH)_4(CH_3)_2$.

Figure 5: Results of the relativistic SCF-Xα-SW calculations on $W_2(O_2CH)_4(CH_3)_2$. This diagram shows the correlation of the orbitals of $W_2(O_2CH)_4(CH_3)_2$ to those of $W_2(O_2CH)_4$ and $(CH_3)_2$. Only those levels involved in W-W bonding or antibonding are shown. The $8b_g$ orbital is the highest occupied orbital of $W_2(O_2CH)_4(CH_3)_2$.

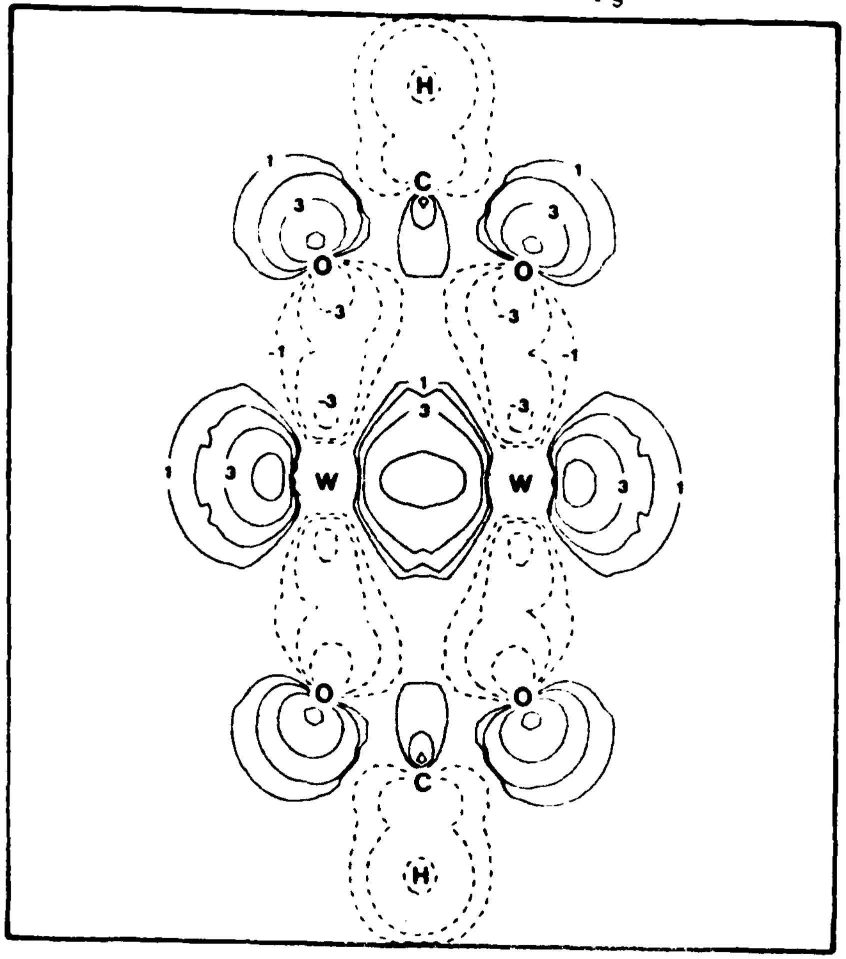
Figure 6: Contour plot of the $15b_u$ molecular orbital of $W_2(O_2CH)_4(CH_3)_2$.



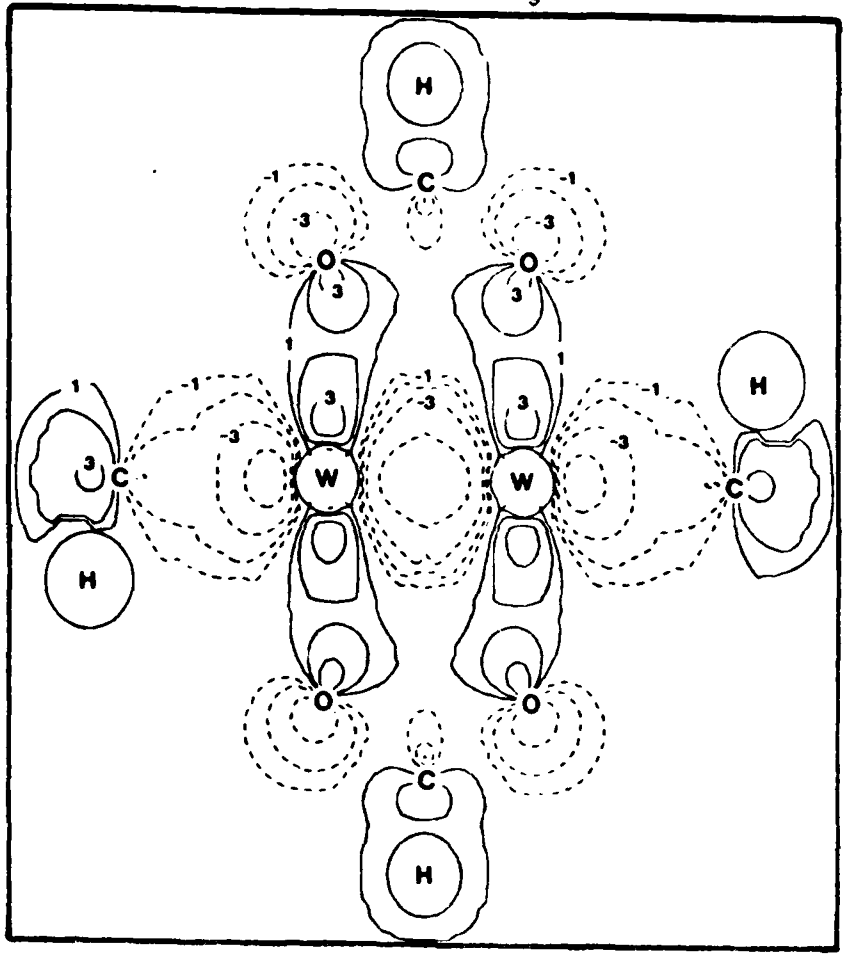
$W_2(O_2CH)_4$


ENERGY eV
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
-12
Relativistic
5a2u
2a2g
3b2g
7eu
6a1g
4a2u
5eg
π*
δ*
2b1u
δ
73%W 2b2g
72%W
π
74%W 6eu
78%W
59%W 5a1g
1a1u
4eg
5eu
3eg
3a2u
3b2u
1b1u
4b1g
σ
69%W
54%W 4a1g
51%W

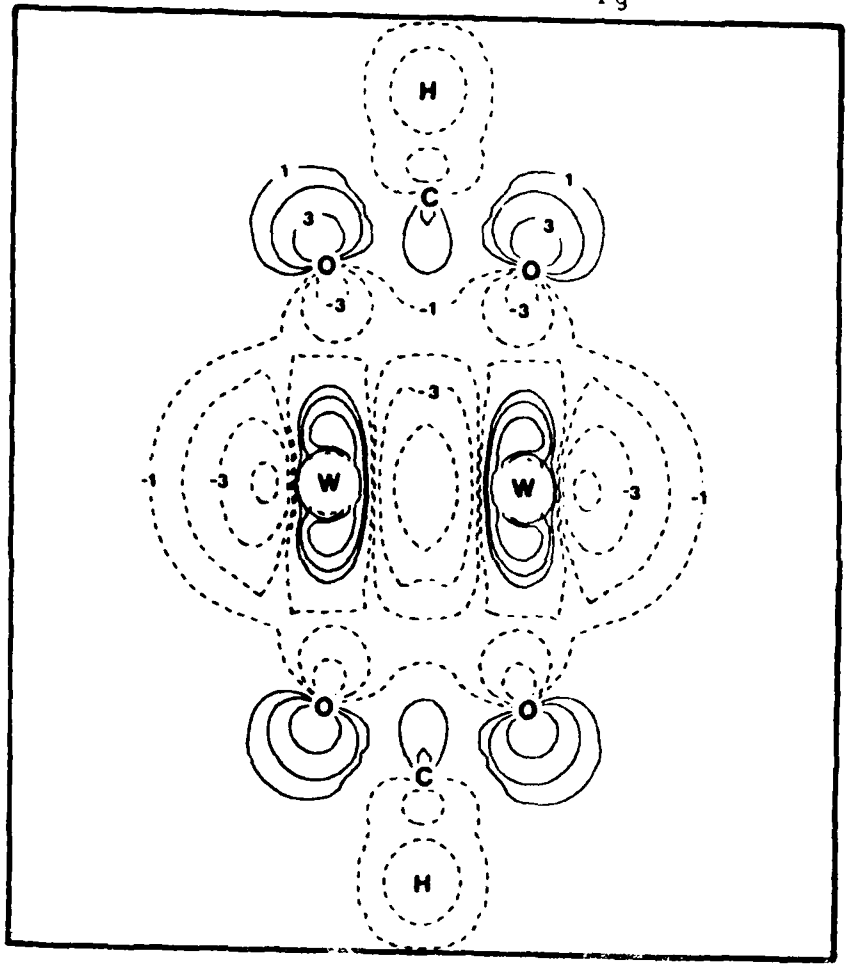
$W_2(O_2CH)_4$ **** $4a_{1g}$ ****



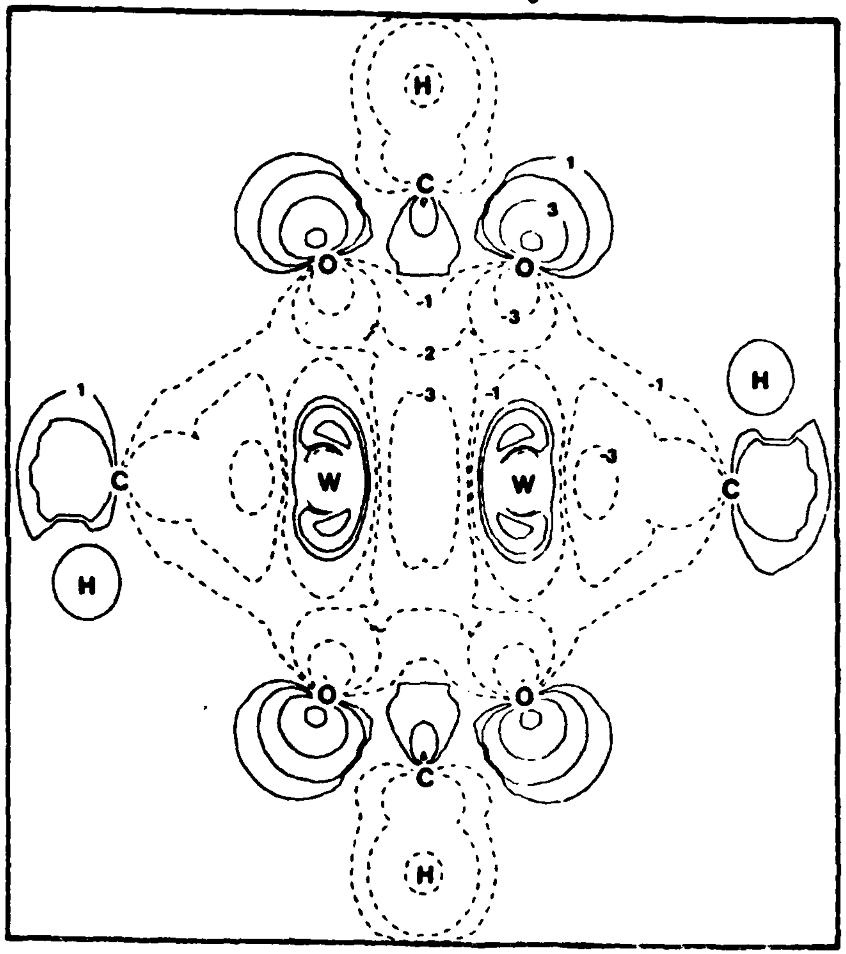
$W_2(O_2CH)_4(CH_3)_2$ $10a_g$

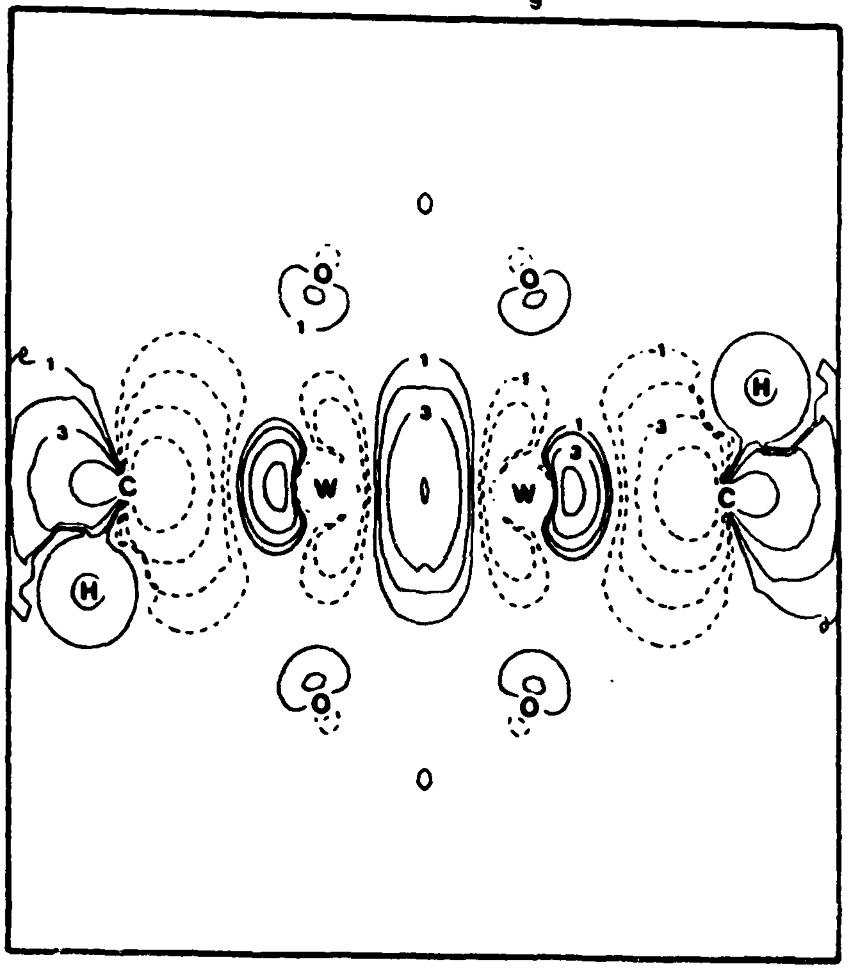


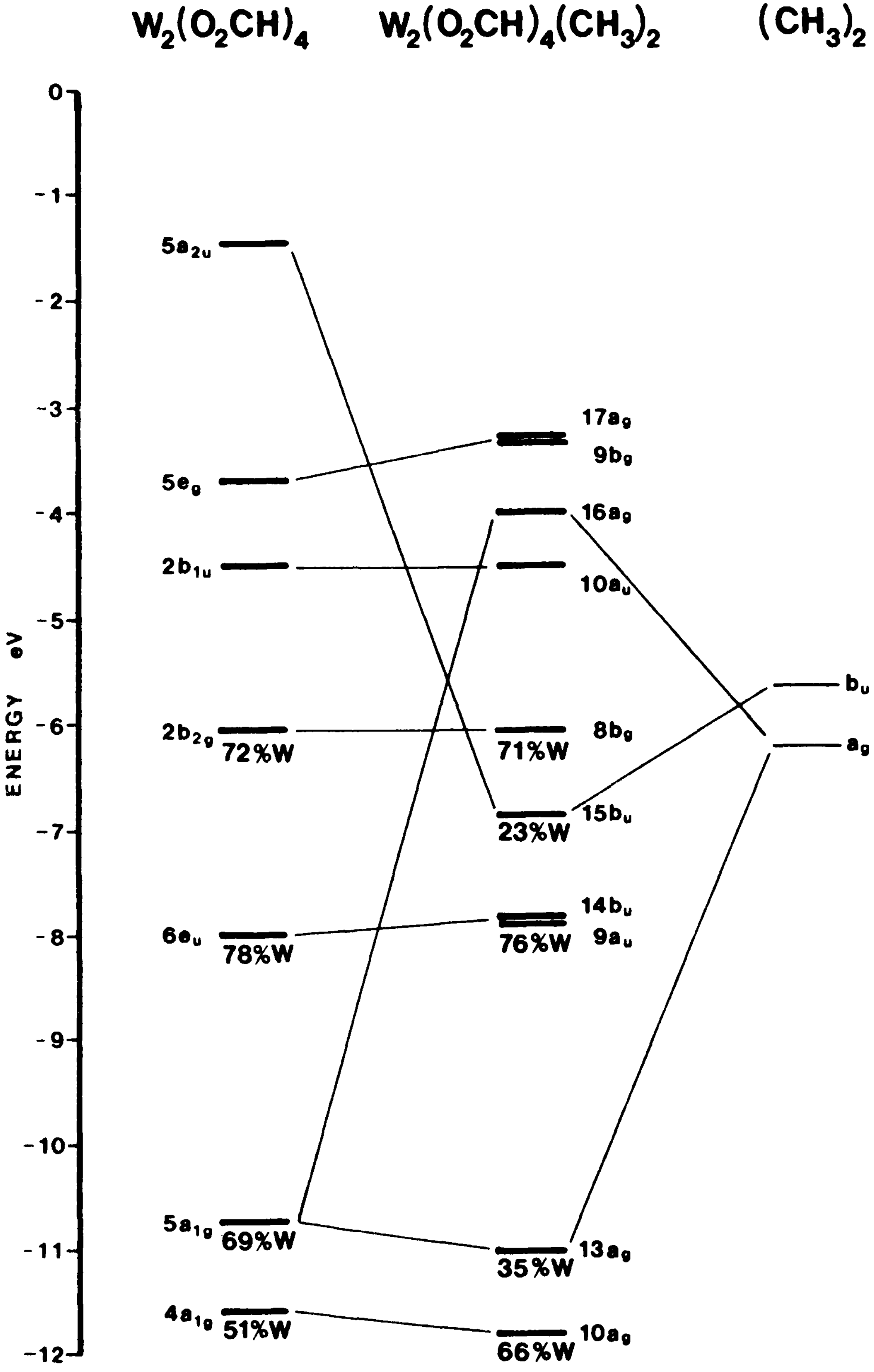
$W_2(O_2CH)_4$ **** $5a_{1g}$ ****



$W_2(O_2CH)_4(CH_3)_2$ $13a_g$




$W_2(O_2CH)_4(CH_3)_2$ 16a_g


$W_2(O_2CH)_4$
$W_2(O_2CH)_4(CH_3)_2$
$(CH_3)_2$
ENERGY eV
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
-12
$5a_{2u}$
$5e_g$
$2b_{1u}$
$2b_{2g}$
72%W
$6e_u$
78%W
$5a_{1g}$
69%W
$4a_{1g}$
51%W
$17a_g$
$9b_g$
$16a_g$
$10a_u$
$8b_g$
71%W
$15b_u$
23%W
$14b_u$
$9a_u$
76%W
$13a_g$
35%W
$10a_g$
66%W
b_u
a_g

$W_2(O_2CH)_4(CH_3)_2$ $15b_u$